EDITORIAL

The Middle–Lower Yangtze Metallogenic Belt

We dedicate this special issue to Professor Yinfo Chang in appreciation of his lifetime contribution to the study of economic geology in China and in celebration of his 80th birthday. Professor Chang started his geological prospecting work in 1952 and discovered a series of skarn Cu–Au–Pb–Zn deposits in the Middle–Lower Yangtze Metallogenic Belt (MLYMB). He was appointed the Chief Engineer of the Bureau of Geology and Mineral Resources, Anhui Province, in the early 1980s, leading the National Project, 'Iron and Copper Metallogenic Belt along the Middle-Lower Yangtze Metallogenic Belt'. He postulated the strata-bound model for the formation of skarn deposits in the MLYMB, which has proven effective in regional ore exploration. Due to this special contribution in geological research and ore exploration, his research group was awarded the top prize of National Science and Technology of China in 1987. The publication of his research entitled 'The copper-iron belt of the middle and lower reaches of the Changjiang River' (Geological Publishing House, Beijing, 379 p. eds. Chang et al. 1991) became a guidebook for scientific research in the MLYMB. Due to his great contribution, Professor Chang was elected to the Chinese Academy of Sciences and to the Chinese Academy of Engineering in 1991 and 1994, respectively.

Although occupying a very high position, Professor Chang has shown considerable care for the progress of young generations of geoscientists. During the very hard times in the Geological Department in the 1990s, he proposed that the government provide more funding for geological research, especially for young geologists, guiding them to do good research, waiting for scientific opportunities and economic growth. In this way, a number of young geologists have been trained.

The MLYMB is one of the most important metallogenic provinces in China, with more than 200 polymetallic Cu–Fe–Au, Mo, Zn, Pb, and Ag deposits, mostly associated with Early Cretaceous igneous rocks. The igneous rocks can be grouped into two associations: the Fe-related group and the Cu-related group. Because of the great economic value and scientific significance of the MLYMB, geologists have intensively studied its tectonic processes, magmatic evolutions, and metallogenic processes for more than a century.

This region is also a cradle for the training of geologists in China. According to statistics, over 10 famous Chinese geologists, now academicians of the Chinese Academy of Sciences and the Chinese Academy of Engineering, did their most fundamental research in this district. Hundreds of geologists have selected targets in this region, training dozens of new PhD students.

Although increasing amounts of research data have been obtained, the basic scientific problems remain unsolved. For example, what is the mechanism responsible for the observed large-scale magmatic eruption and polymetal formation in a very short period of
time (140–130 Ma)? Did palaeo-Pacific plate subduction control the magmatism? During the past decade, the Chinese government has increased funding for both research and ore exploration in the MLYMB. To our joy, more young experts have joined the research, and we believe that this special issue will help them to better understand the background and complicated geological history in the MLYMB.

This special issue has attracted great interest from geologists in China, who have generously contributed their excellent research. A total of 23 manuscripts were reviewed, with 15 included in this special issue due to space limitations. These contributions are classified into two parts. The first part, containing 11 papers, covers magmatism and ore deposits and focuses on regional magmatism and formation of ore deposits along the MLYMB and adjacent regions; the second part, containing 4 papers, involves ore genesis models and reviews, providing a broad perspective on the mechanism generating the massive Yanshanian magmatism and formation of the ore deposits. These studies will considerably improve both metallogeny and ore exploration in the MLYMB.

The contributors are affiliated with the best-known universities and institutes undertaking advanced research on the MLYMB. All manuscripts received constructive review comments from dozens of experts, which substantially improved the quality of this issue. We would especially thank the review experts Professors/Drs Xianwu Bi, David R. Cooke, Yanjing Chen, Hongrui Fan, Jun Gao, Jianwei Li, Guangpin Li, Xiaofeng Li, Kye-Hun Park, Young-Rok Park, Franco Pirajno, Kezhang Qin, Zhanli Ren, Chaowen Su, Xiaoming Sun, Christina Yan Wang, Qiang Wang, Guiqing Xie, Chunji Xue, Xiaochun Xu, Wanming Yuan, Jianxin Zhang, Zhaocong Zhang, Qingdong Zeng, Guochun Zhao, and of course, W.G. Ernst, Editor-in-Chief of International Geology Review.

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Tectonic-magmatic-metallogenic system, Tongling ore cluster region, Anhui Province, China

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The Tongling ore district of the Middle-Lower Yangtze metallogenic belt is a famous Cu-Au-Fe-S polymetal region, and its tectonic deformation, magmatic evolution, and metallogenic processes have been studied for decades. In this article, we propose a comprehensive tectonic-magmatic-metallogenic model of the ore-forming mechanism constrained by magmatism and regional deformation. In the Tongling district, the tectonic regime underwent two transitions. (1) In the Middle Triassic, the tectonic regime transitioned from quiescence to intense compression. During contraction, the lithosphere thickened and a series of NE-trending folds developed in the cover sequence; because of the multi-layered structure of this caprock, bedding faults, typically cut by steeply dipping faults, developed widely. (2) From 134 to 150 Ma, the tectonic regime changed from compression to extension. During this transition, mantle–crust interaction was prominent; ore-bearing magma was generated by the mixing of crust-derived and mantle-derived melts triggered by delamination of the thickened lithosphere. Meanwhile, detachment faults developed along the interfaces, for example between the lower and upper crust, serving as emplacement sites for several magma chambers. Ore-bearing magma dikes containing large amounts of volatiles derived from a shallow chamber at about –10 km depth migrated into the cover sequence along the pre-existing steeply dipping faults. Melt injection reworked the structural framework, facilitating further development of steeply dipping faults, as well as the vertical transport of ore-bearing fluids. Hydrothermal fluids derived from the emplaced magmas not only formed a range of deposits, including skarns, porphyries, and cryptobreccias around the intrusions but also widely replaced carbonates along bedding-parallel faults and formed so-called stratabound skarn ore bodies, as well as superimposing synsedimentary orebodies developed in the quiescence stage to form several large polymetallic hydrothermal ore deposits. Various types of ore deposits at different depths are clustered in a single orefield, composing a multi-layered mineralization network. In the network, skarn deposits dominate and are characterized by fluid immiscibility processes and diverse element enrichments. The intense mineralization in the Tongling region was caused by the abundance of metals derived from the mantle, favourable ore-controlling structures, and widespread fluid boiling of magmatic hydrothermal fluids, which facilitated metal deposition during the Mesozoic, as well as the superposition of Mesozoic hydrothermal reworking of earlier Palaeozoic sedimentary ore bodies.

Keywords: ore-forming process; magmatism; structures and ore deposition; Mesozoic ore deposits; Tongling district; NE China

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Introduction

The Tongling ore cluster region is an uplifted area in the Middle-Lower Yangtze metallogenic belt located between the Lower Yangtze block and the North China block (Figure 1). During the Palaeozoic, the metallogenic belt occupied a passive continental margin. In the Mesozoic, the belt experienced intense intraplate tectono-magmatic activities, and its tectonic evolution was constrained by the collision between the Yangtze and North China blocks, the subsequent underflow of the Pacific and Izanagi plates underneath Eurasia (Sun et al. 2007; Ling et al. 2009), and later lithospheric delamination and extension in East China.

After several tectonic movements, the cover sequence in the Tongling region was deformed, and abundant Mesozoic intrusions were emplaced, inducing intense and diverse mineralizations. More than 180 ore deposits and occurrences have been discovered in the Tongling region and they are mainly clustered in five orefields: the Shizishan, Tongguanshan, Fenghuangshan, Xinqiao, and Jinlang orefields (Figure 2). On both sides of the Tongling region, abundant ore deposits are also concentrated in the Lujiang-Zongyang (abbreviated as Luzong), Fanchang, and Nanjing-Wuhu (abbreviated as Ningwu) volcanic basins of the metallogenic belt (Figure 1).

Because of the great economic value and scientific significance of the Tongling region, scientists have intensively studied its tectonic process, magmatic evolution, origin of ore-forming fluids and materials, and the metallogenic processes (Chang et al. 1991; Zhai et al. 1992; Tang et al. 1998; Mao et al. 2004, 2009; Meng et al. 2004; Hou et al. 2004, 2007; Xu et al. 2005a, 2005b, 2007a, 2007b; Yang et al. 2008b; Li et al. submitted; Yang and Lee 2011). The regional deep-seated structure has been studied using deep reflection seismic profiles (Lü et al. 2004a, 2004b). Caprock structures and their

![Figure 1](image_url)  
Figure 1. Geological location of the Tongling ore cluster area, Anhui Province, China. TLF, Tancheng-Lujiang fault; XGF, Xiangfan-Guangji fault; YCF, Yangxing-Changzhou fault. Black dots are magmatic intrusion-related Cu–Fe–Au deposits (after Pan and Dong 1999).
deformation mechanism are discussed in detail (Deng et al. 2004b, 2004c; Wu et al. 2004; Wang et al. 2011). Petrologic structure, chemical compositions of magmatic rocks, and their origins have been studied by various researchers (Xing and Xu 1995, 1999; Xing 1998; Xu and Lin 2000; Zhang et al. 2001; Wang et al. 2003a, 2004e, 2007; Wu et al. 2003b; Di et al. 2005; Zeng et al. 2005; Xu et al. 2006; Li et al. 2007a, 2007b; Yang et al. 2007; Cao et al. 2009; Xie et al. 2009b). The magmatic rocks and associated ores have been dated by different methods, including K/Ar (Zhai et al. 1996; Li 2004; Zeng et al. 2004), 40Ar/39Ar (Wu et al. 1996, 2000), molybdenite and pyrite Re–Os, Os–Os (Sun et al. 2003; Mao et al. 2004; Yang et al. 2004a; Mei et al. 2005; Xie et al. 2009a), pyrite Rb–Sr (Wang et al. 2004d), and zircon U–Pb (Wang et al. 2004a, 2004b, 2004c; Xu et al. 2004, 2008; Di et al. 2005; Zhang et al. 2006; Du et al. 2007b; Lu et al. 2007; Yang et al. 2007, 2008a; Wu et al. 2008; and Xie et al. 2008b). The age of Re/Os and Os/Os cited from Sun et al. 2003; Mao et al. 2004; Yang et al. 2004a; Mei et al. 2005; Xie et al. 2009a. The dating data is listed in Table 1.)

Figure 2. Geological map of the Tongling ore cluster area, Anhui province, China. (The map is modified after the 1:50,000 geological map accomplished by the 321 geological team in Anhui province, 1989. The age of zircon U–Pb cited from Wang et al. 2004a, 2004b, 2004c; Xu et al. 2004, 2008a; Di et al. 2005; Zhand et al. 2006; Du et al. 2007b; Lu et al. 2007; Yang et al. 2007, 2008a Wu et al. 2008; and Xie et al. 2008b. The age of Re/Os and Os/Os cited from Sun et al. 2003; Mao et al. 2004; Yang et al. 2004a; Mei et al. 2005; Xie et al. 2009a. The dating data is listed in Table 1.)
The tectonic deformation, magmatic evolution, and ore-forming process behaved as an interconnected system. Previous studies mainly focused on one or two aspects of the system, and a comprehensive framework of the Tongling region has not yet been constructed. Based on the results obtained by different disciplines and supplemented with some new evidence, the tectonic-magmatic-metallogenic model of the Tongling region with emphasis on the interaction of the various geological processes is hereby established in this article.

Tectonic framework and compressional deformation

Tectonic framework

After multiple tectonic movements, the crust of the Tongling region shows a low thickness of about 32 km (Wu et al. 1999). The deep seismic reflection profile across the region clearly displays crustal structure (Lü et al. 2004b). In the profile, the sub-Moho reflections support the occurrence of underplating, and a weak Moho also denotes that intense magmatism happened. The lower crust shows the typical reflection characteristics of a craton, suggesting no obvious magmatism. Strong reflections between the upper and lower crust is explained as a detachment between them. In addition, a transparent zone, representing a batholith, exists underneath the folded caprock (Figure 3). According to the gravity anomaly and ETM image, it is recognized that the region is confined by deep faults and traversed by basement faults, in which the EW-trending faults in the north part is the most obvious (Wang et al. 2011).

The caprock consists of a Palaeozoic basement and a sequence of Mesozoic sedimentary rocks. The Proterozoic low-grade metamorphic basement is exposed about 30 km south of the study region (Chang et al. 1991). The stratigraphic sequence cropping out in the study region ranges from Silurian to Triassic with thickness up to 3000 m (Figure 4). The sequence includes Silurian shallow marine sandstones interbedded with shales, Devonian continental quasi-molasse formation and lacustrine sediments, Carboniferous shallow marine carbonates, Permian marine facies alternating with a marine-continental ones, Early to Middle Triassic shallow marine carbonates, and Quaternary sediments. Jurassic and Cretaceous volcanic rocks are developed in surrounding area. The first angular unconformity in the outcropped sequence lies between the Middle Triassic Dongma’anshan Formation (T2d) and the Yueshan Formation (T2y), and it divides the caprock into upper and lower structural layers. Several parallel unconformities are developed in the lower structural layer, and many angular unconformities occur in the upper layer. The lower structural layer covers most of the region and contains most ore reserves in the region.

In the lower structural layer, the strata with different lithologies and thicknesses alternate. During deformation, the Devonian thick quartz sandstone, as well as the Lower Permian and Lower Triassic thick carbonates may behave as competent layers. The thin carbonates, mudstone, shale, and silty shale in the Silurian and Upper Permian, on the other hand, act as incompetent layers. The alternation of the competent and incompetent layers facilitates the development of bedding detachment faults and non-harmonic folds.

The characteristics of the surface structures are shown in Figure 2. Three types of fundamental structures can be observed. The NE-trending folds, most of which are S-shaped, are prominent. Bedding detachment faults and the NW and NNW-trending sinistral strike-slip faults cutting the folds are widely developed. An analogous experiment was performed to reflect the formation process of caprock structural framework under overall NW compression, and several important ore-controlling structures are identified (Deng et al. 2004a). Combining the experiment results and drill sections, it is discovered that reverse faults
Figure 3. (a) Stacked section of the Tongling deep seismic reflection; (b) line drawing of stacked section and interpretative section. FCVB, Fanchang volcanic basin; TLU, Tongling uplift (modified from Lü et al. 2004b).
Figure 4. Stratigraphy and mineralization developments of the Tongling, Anhui Province, China (modified after Geological Team 321, 1989 and Lü et al. 2007).
near the fold cores and non-harmonic folds containing multi-layered void spaces are likely to be developed.

In the caprock, structures with various attitudes and in different layers compose a network, which serves as a pathway or emplacement space for magma and related hydro-thermal fluids. The network is characterized by bedding-parallel faults and void spaces that are connected or cut by faults with high dip angles.

**Compression process**

The parallel unconformities in the lower structural layer suggest that the region remained tectonically quiescent from the Silurian to the Middle Triassic. The first angular unconformity between T2d and T3y indicates the start of intraplate horizontal compression. Because the assembly between the Yangtze and North China blocks took place during 210–240 Ma, as determined by the 40Ar/39Ar and Sm–Nd dating methods (Shen et al. 1994; Chavagnac and Jahn 1996; Rowley et al. 1997), it is deduced that this assembly triggered the horizontal deformation in the region. After the assembly ended, the active motion of the Pacific and Izanagi ocean plates underneath the Eurasian plate began to influence the tectonic and magmatic evolution in the Tongling region (Sun et al. 2007; Ling et al. 2009).

The block collision induced an overall intense NW compression, inducing the development of lithospheric and deep crustal faults. Because of the confinement of the deep faults, the Tongling region suffered a relatively independent deformation process. And some deep faults also served as concealed basement faults across the region.

The NE-trending folds and NW-trending strike-slip faults also suggest that the region mainly suffered continuous and intense NW compression. Based on the S-shaped folds, it is proposed that the region experienced progressive deformation, in which the compression was followed by a simple shear (Deng et al. 2004b; Wu et al. 2004) (Figure 2). Nevertheless, a non-coaxial and asymmetric compression model is proposed to be responsible for the formation of the S-shaped folds (Wang et al. 2011). In the deformation models, it is recognized that the caprock with multi-layered structures under an intense and complex deformation process are responsible for the development of non-harmonic folds and reverse faults.

The compressions induced by the plate collision also resulted in a thickened crust, which differs from the structure of the modern crust in the Tongling region (Wang et al. 2004c).

**Magmatic evolution and tectonic transformation**

**Geological occurrence and lithologic types**

Intrusive rocks in caprock occur mostly as stocks, dikes, and sills with 2–10 km² outcropping areas. In the Shizishan orefield, intrusions occur as stocks and dikes along faults to form a network system approximately 3 km long and 1 km wide (Deng et al. 2004a). The largest Fenghuangshan intrusive body associated with a series of skarn deposits with an area of about 10 km² is located near the southeast boundary of the region. The magma emplacement is largely controlled by the EW-trending basement fault crossing the Xinqiao, Shizishan, and Tongguanshan orefields (Figure 2) (Chang et al. 1991; Wu et al. 2003a).
The region comprises three major rock associations: (1) pyroxene diorite–pyroxene monzodiorite; (2) quartz diorite–quartz monzodiorite, which are the most important magmatic rocks in the Tongling region; and (3) granodiorite. Most magmatic bodies are virtually intrusive complexes consisting of both mafic and intermediate-acid intrusive rock types, such as the Baimangshan, Jiguanshan, Sujiadian, Caoshan, Yushan, and Shizishan magmatic bodies (Chang et al. 1991).

**Chemical compositions, emplacement age, and tectonic setting**

In the Harker variation diagrams, most intrusive rocks in the region are categorized as high-K calc-alkaline series (Wang et al. 2003a). Several models have been suggested for the formation of the intrusive rocks, including (1) the mixing of mantle- and crust-derived magmas, or assimilation and fractional crystallization of a mantle-derived magma, with major contributions from an ancient crustal component (Chen et al. 1993; Chen and Jahn 1998; Wu et al. 2000; Deng and Wu 2001); (2) the partial melting of lower crustal materials in the Yangtze continental block (Yang and Lin 1988; Du and Li 1997; Zhang et al. 2001; Wang et al. 2004c); (3) the production of rocks with SiO₂ ≤ 55% by the crystallization of basaltic magmas derived from an enriched mantle, with limited assimilation of lower crustal materials; and in this model, rocks with SiO₂ > 55% were generated by mixing of mantle-derived basaltic magmas and adakite-like magmas derived from melting of the basaltic lower crust (Wang et al. 2003a, 2003b); (4) partial melting of subducted oceanic slab and subsequent crustal contamination (Ling et al. 2009).

Despite of the debates, the following opinions are well evidenced and recognized. The intrusive rocks in the Tongling region were produced by a magma mixture of at least two end-members, one mantle-derived and the other crust-derived, and the mixed magma experienced fractional crystallization during its ascent.

The mixing of the mantle-derived and crust-derived magmas is supported by the εNd(t) and (87Sr/86Sr)i values of the intrusions, the geochemical and mineralogical features of enclaves, and the Fe³⁺/(Fe²⁺ + Fe³⁺) ratios of biotites in the intrusions (Wu et al. 2000; Wang et al. 2003a, 2003b; Gao et al. 2006; Lou and Du 2006; Du et al. 2007a, 2007b; Xie et al. 2009b). The fractional crystallization process is evidenced by the fact that the SiO₂ content is inversely proportional to that of CaO, TiO₂, P₂O₅, MgO, and Zr and that the REE patterns of different intrusions are generally consistent.

The origin of the magmas reflects a complex deep process, which consists of delamination of the lower part of the thickened lithosphere, lithospheric thinning, asthenospheric upwelling, and crust–mantle interactions (Wang et al. 2003a; Xie et al. 2009b).

Zircon U–Pb dating shows that the emplacement ages of the magmas varied from 132.7 ± 4.8 Ma to 151.8 ± 2.6 Ma, mainly from 134 to 142 Ma (Figure 2) (Wang et al. 2004a, 2004b, 2004c; Xu et al. 2004, 2008; Di et al. 2005; Zhang et al. 2006; Du et al. 2007a; Lu et al. 2007; Wu et al. 2008; Yang et al. 2007, 2008a; Xie et al. 2009b). The narrow age range indicates the different intrusions emplaced semi-synchronously. The emplacement duration represents the transition interval from lithospheric thickening to delamination, that is from regional compression to extension.

The zircon U–Pb ages of the Mesozoic volcanic rocks in the Luzong and Ningwu volcanic basins range from 134.8 ± 1.8 Ma to 127.1 ± 1.2 Ma (Table 1) (Fan et al. 2008; Zhou et al. 2008; Yan et al. 2009). The greatest age of the intrusions in the Tongling region is similar to the smallest age of the volcanic rocks in the volcanic basins; it is thus proposed that the onset of lithosphere thinning and extension occurred at about 134 Ma in the Tongling region and its vicinity. The zircon U–Pb ages of the A-type intrusions widely
Table 1. Dating data of magma emplacements and ore-forming events in the Tongling region, Anhui Province, China.

<table>
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<tr>
<th>Orefield</th>
<th>Ore deposit</th>
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<th>Mineral</th>
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<th>Age (Ma)</th>
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<td>LA-ICPMS</td>
<td>144.2 ± 2.3</td>
<td>Zeng et al. (2005)</td>
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<td>142.2 ± 1.6</td>
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<td>Mao et al. (2004)</td>
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<td>Di et al. (2005)</td>
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Magma transport process and its effect on the tectonic framework

Magma transport network and migration process at deep and shallow levels

Based on the pressure calculation for the enclaves in intrusions and the crustal structure detected by deep seismic reflection, three magma chambers are proposed to exist in the crust (Wu et al. 2000; Du et al. 2007a). The deep and middle magma chambers developed around the Moho and the interface between the upper and lower crust, respectively. A concealed magma chamber existed at about –10 km, from which the ore-forming magma transported into the caprock.

In regional extension, the tectonic framework may be changed to some extent, and detachment faults along the interfaces formed. Meanwhile the steeply dipping compression fault displayed dilational characteristics: vertical weakness zones in the middle and lower crust may be developed. These steeply dipping structures can connect the multilayered detachments in the crust, as is similar to the spatial assembly of different structures in the caprock. The magma stemming from the deep magma chamber was transported upwards along the vertical structures and aggregated in the detachments, forming the middle and shallow chambers (Du 1999). Because the lower crust shows little evidence of magmatic activity, mesoscale pervasive flow, rather than diapirism, is supposed to be the transport pattern between the chambers, in which magma moves upwards through an extensive network developed in hot, low-viscosity country rocks where diking is inhibited (Leitch and Weinberg 2002; Weinberg 1998; Wu et al. 2004).

In the upper crust, the basement faults and the above NE-trending high-angle reverse faults served as the main magma pathways, and the magma emplaced in the pathways and the saddle void spaces within the folds.

In addition, the zircon U–Pb age and the K–Ar, Rb–Sr, and $^{40}$Ar/$^{39}$Ar ages are almost identical for the same intrusive, even though the closure temperatures of these isotopic systems are very different (Xie et al. 2009b). It is thus suggested that the felsic magmas experienced fast transport and cooling. Based on the fast transport of the magmas, the wide development of cryptobreccias denoting a high abundance of volatiles, and the geological occurrences of the intrusions, it is deduced that the magma transported into caprock from the shallow magma chamber rapidly via a diking pattern. The diking pattern indicates that magma with volatiles at its top migrated rapidly upwards along pre-existing weak structural planes in an elastic medium (Emerman and Marrett 1990; Petford et al. 1993, 1994). Pulse generations of the dikes because of continuous fractioning in the shallow magma chamber may be partly responsible for the concentrated emplacement of magmas and the multiple lithological components in one intrusion (Deng et al. 2006; Petford and Koenders 1998).

Influence of the magma emplacement on the caprock structures

To further study the strata deformation after several tectonic movements, trend surface analysis of the S–D, D–C, C–P, P$_2$–P$_3$, and P–T boundaries is performed based on their elevations sampled evenly in a composite 1:50,000 geological and topographic map (Deng...
et al. 2007). Trend surface analysis has been used consistently by geologists to separate map data into a regional component and one with local fluctuations (Davis 1986).

After superposing trend surfaces of adjacent boundaries (such as superposing the S–D boundary on the D–C boundary), it is discovered that the lower trend surface always pierces the upper one. Moreover, the position and orientation of the pierced part of the different superposed trend surfaces are similar and in accordance with the regional EW-trending magmatic-metallogenic belt comprising the Shizishan, Tongguanshan, and Xinqiao orefields (Figure 1). This indicates that the caprock on the EW-trending basement fault is subject to bending resulting from magmatic emplacement.

In the Fenghuangshan intrusion, the foliation and lineation defined by the dark minerals and enclaves in the intrusion margin (Figure 1), the strike of the fold hinge, as well as the flow cleavage of the ductile shear zone in the contact, are parallel to the intrusion boundary, indicating a final ballooning emplacement of the intrusion and a corresponding compression to the nearby strata (Zhang and Li 1999; Wu et al. 2004). The ballooning emplacement can be explained as a result of the rapid supply speed, that is the fast transport, of the magma, as is consistent with its diking pattern.

The stratal trend surface simulations and the internal and contact deformation of the large intrusion both indicate the great kinetic energy of the magmas as they ascended, further supporting the diking pattern and its influence on the caprock deformation.

The major ore-controlling structures in the caprock, which experienced regional compression and later extension, were further reworked by the bending resulting from magma emplacements. The bending can activate the vertical and bedding structures around the intrusions, providing suitable physical conditions for multi-layered emplacement and long migration of ore-forming fluids (Deng et al. 2007).

Ore-forming process

Metallogenic diversity and superposition of ore-forming processes

Ore deposit types in the Tongling region mainly include skarn, stratabound hydrothermal, porphyry, and cryptobreccia. The Fenghuangshan orefield consists of contact skarn and porphyry deposits, whereas the Tongguanshan, Xinqiao, and Shizishan orefields are composed of more types, such as stratabound skarn and hydrothermal deposits, as illustrated in Figure 5, which shows an overall distribution of the ore deposits in the Tongling region.

The skarn deposits, characterized by Cu and Au mineralization, are dominant in the region. Skarn ores are composed of chalcopyrite, pyrrhotite, pyrite, garnet, diopside, quartz, calcite, epidote, chlorite, and wollastonite, with a few containing sphalerite, galena, and native gold. Mineralization of the skarn deposits can be generally divided into five stages. Stage 1 is characterized by anhydrous skarn minerals (garnet, diopside, and wollastonite) and calcite. Stage 2 is represented by an assemblage of actinolite, tremolite, epidote, and chlorite. Stage 3 is characterized by the formation of magnetite as the main mineral. Stage 4 is the main ore stage and is characterized by the formation of chalcopyrite and bornite, together with quartz, pyrite, siderite, and calcite. Stage 5 is represented by the calcite and sulphides, such as pyrite, sphalerite, and galena (Pan and Dong 1999; Lai et al. 2007; Li et al. submitted).

Some skarn orebodies with jagged and sharp boundaries developed along the intrusion contact zone. Ore minerals are deposited in tensional spaces distributed unevenly along the contact zone, and some of the tensional spaces are genetically related to the activities of the magmatic hydrothermal (Liu et al. 2008). For example, in the open pit of the Jinniudong
Figure 5. Metallogenic model of the deposit distribution in the Tongguanshan, Shizishan, Xin-qiao, and Fenghuangshan orefields, Tongling area, China. (The figure is based on fieldwork and the references Chang et al. 1991; Xu and Zhou 2001; Wu et al. 2003a, 2003b.) (1) Huangshilao deposit; (2) Maanshan deposit; (3) Dongguashan deposit; (4) Huashupo deposit; (5) Laoyaoling deposit; (6) Datuanshan deposit; (7) Xishizishan deposit; (8) Dongshizishan deposit; (9) Hucun deposit; (10) Caoshan pyrite deposit; (11) Xinqiao deposit; (12) Jinniudong deposit; (13) Fenghuangshan deposit; (14) Xianrenchong deposit.

Figure 6. Mineralization phenomena in the open pit of the Jinniudong skarn deposit, Fenghuangshan orefield, Tongling ore cluster area. (a) Ore pit in the Jinniudong deposit; (b) and (d) cryptoexplosive breccia ore; (c) sulphide orebody in skarns.

deposit located in the Fenghuangshan orefield, orebodies are contained in the tensional fractures in the skarns and cryptoexplosive breccias (Figure 6). Moreover, replacement skarns of both calcic and magnesium types within sedimentary strata along the bedding faults are widely developed and host so-called stratabound skarn orebodies (Figure 7). In the stratabound skarn orebodies, cryptoexplosive breccias are barely observed, because the bedding-parallel fault could keep the pressure balance between the intrusions and
surrounding skarns. An ore deposit can comprise several stratabound skarn orebodies, which are controlled by the multi-layered ore-controlling bedding-parallel faults (Figure 7).

The polymetallic stratabound hydrothermal orebodies, such as those in the Huangshilao deposit in the Tongguanshan orefield and the Xinqiao deposit, are developed mostly on the D–C boundary. The Xinqiao deposit, situated 24 km east of Tongling city, is a large-scale Cu–S–Fe–Au polymetallic deposit (Figure 1). In the deposit, there are two different types of sulphide mineralization. One is the stratabound orebody restricted to the D–C boundary and the other is the skarn mineralization restricted to the intrusion contact. However, significant economic reserves have only been explored in the stratabound orebody. A horizontal extension of 2550 m and a vertical extension of 1810 m with an average thickness of 21 m have been confirmed for the stratabound orebody by drilling (Figure 8). The stratabound mineralization is dominated by pyrite with minor amounts of chalcopyrite, magnetite, pyrrhotite, galena, sphalerite, quartz, and dolomite (Xu and Zhou 2001). In the Xinqiao ore deposit, 300 groups of Au–S–Fe–Cu–Zn concentrations of ores were collected for performing a cluster analysis, as shown in Figure 9. The cluster analysis shows that the Fe and S are highly correlated, indicating that pyrite is dominant in the ores. In addition, numerous occurrences characterized by pyrite mineralization around the D–C boundary are widely developed in the region (Figure 5). The mineral compositions of the stratabound hydrothermal ores are very different to those in the skarn ores, indicating that the origins of the two types of deposits are possibly distinct.

Ore deposits with various types located at different depths are clustered in one single orefield. From a cross-section view, the main orebodies exist as multiple floors from the top to the bottom of the orefield, composing a multi-layered mineralization network. For example, in the Shizishan orefield, the Dongguashan porphyry and stratabound skarn deposit exist in the deep part, Huashupo and Datuanshan stratabound skarn deposits are in

![Figure 7. Sections in the Huashupo ore deposit of the Shizishan orefield, Tongling ore cluster area (modified from Chang et al. 1991).](image-url)
the middle, Laoyaling and Xishizishan stratabound skarn deposits are in the upper part, and Dongshizhishan cryptobreccia deposit and Baocun, Baimongshan, and Jiguanshan skarn deposits are developed in the shallow (Figure 5).

Figure 8. Typical exploration sections in the Xinqiao deposit, China (compiled based on the exploration data of 803 Geological Team 1971).

Figure 9. Cluster analysis of the Au–S–Fe–Cu–Zn concentrations in the stratabound hydrothermal ores in the Xinqiao deposit, Tongling ore cluster area.
Most ore deposits in the Tongling region are genetically related to the magmatic rocks. The molybdenite samples were collected from the different skarn orebodies for precise Re–Os dating. The determined mineralization ages are identical to formation ages of intrusive rocks within errors (Sun et al. 2003; Meng et al. 2004; Mei et al. 2005) (Figure 2). In addition, sulphur and lead isotopes of sulphides both suggest that most ore-forming materials come from magmatic rocks, and REE distribution patterns of most ores are also similar to the adjacent intrusions (Tian et al. 2005, 2007; Xie et al. 2008a; Yang et al. 2011; Yang and Lee 2011). The hydrogen and oxygen isotope compositions of the fluid inclusions in vein quartz of different mineralization stages in the skarn deposits show that the ore-forming fluids mainly originated from magmatic fluid with a minor mixture of meteoric water (Zhou et al. 2000; Ren et al. 2006; Qiu et al. 2007). Qin et al. (2003, 2004) discovered sulphides in amphibole cumulate xenoliths and amphibole megacrysts in Mesozoic magmatic rocks, verifying that the magma brought metals from the deep.

However, several mineralizations, including the Laoyaling molybdenite mineralization in black shale of the Upper Permian Dalong Formation and the polymetallic ore deposit at the D–C boundary, are shown to be synsedimentary via geological phenomena, dating, and isotopic data (Zhou et al. 2000; Yang et al. 2004b) (Figures 4 and 5). The black shale from the Laoyaling Mo orebody has been dated to 234.2 ± 7.3 Ma by the Re–Os technique, which is much earlier than the regional Mesozoic intrusions, and younger than the Later Permian deposition age, denoting that the Mo ore is sedimentary in origin and possibly suffered a later hydrothermal disturbance (Yang et al. 2004a). In terms of the ore compositions, and the isotopic and dating evidence, the Xinqiao and Huangshilao deposits were inferred to be first formed via pyrite accumulation in synsedimentary mineralization during the Hercynian period, then superimposed by the Yanshanian magmatic hydrothermal fluids, during which they became enriched in Au, Cu, and Zn elements (Chang et al. 1991; Hou et al. 2004). The superposition of the different ore processes is prominent in the Tongling region, increasing the deposit tonnage and facilitating polymetallic mineralization. The superposition mineralization on the D–C boundary makes it host the greatest ore reserve in the caprock.

Magmatic hydrothermal ore-forming processes

Ore-controlling structures

The ore-controlling structures are composed of those related to the intrusive boundary and those in the strata. The structures in the strata were first formed under intense compression and later reactivated by regional extension and magma intrusion. The previous compressional structures became dilational and facilitated fluid migration and element deposition.

Several types of structures are considered to control migrations of magmatic hydrothermal fluids. The most important is the multi-layered bedding-parallel fault, which controls stratabound orebodies. The great length of the stratabound orebodies, such as the orebody up to several kilometres long in the Huangshilao deposit, means that the fluids can migrate far along the detachment fault. The widespread non-harmonic folds are emplacement localities for fluids; for example, an excellent non-harmonic fold was developed in the Xinqiao deposit and partly controls the emplacements of magmatic bodies and orebodies (Figure 8). High-angle reverse faults can behave as pathways for hydrothermal fluids. The ore-controlling structural network in the strata is also characterized by interconnected bedding faults and steeply dipping ones. For instance, in an ore hand specimen of the Caoshan deposit in the Shizishan orefield, the ore-forming hydrothermal is observed to transport
first along the reverse fault, which shows dilational characteristics, and then to migrate along the bedding-parallel faults as the hydrothermal ascends (Figure 10).

**Fluid evolution process in skarn deposits**

When magma with a large number of volatiles is rapidly emplaced in the caprock and encounters void spaces, fluid boiling can be caused because of the sudden pressure drop. The fluid boiling is evidenced by the cryptobreccia ores, in which the breccias are sealed by quartz (or calcite) and sulphide veins or by felsic materials, and also revealed by fluid inclusions formed in the metallogenic stages 4 and 5 in skarn deposits (Table 2). For instance, in the open pit of the Jinnudong deposit in the Fenghuangshan orefield, the cryptobreccia ores, in which the marble breccias are sealed by the calcite and sulphide veins, are widely developed around the intrusive (Figure 6). The skarn deposits in the different orefields experienced similar fluid evolutions with decreasing temperatures and salinities from early to late stages, as manifested by fluid inclusions (Table 2). From the early to late stages, $\delta^{18}$O$_{\text{H}_2\text{O}}$ usually declines, suggesting a greater involvement of meteoric water, as is exemplified by the Dongguashan deposit (Xu et al. 2005a, 2005b; 2007a, 2007b). Thus, it is concluded that the fluid evolution is characterized by immiscibility in the early stage and by fluid mixing in the late stage.

**Element-enrichment features during skarn mineralization**

Because of the ore-forming process in a relatively complex structural network, the spatial distributions of ore-forming elements should show much irregularity. Five drillcores that are nearly 1000 m in length, located in the Dongguashan, Changlongshan, Huashupo,
Table 2. Fluid inclusions in skarn deposits of the Tongling region, Anhui Province, China.

<table>
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<tr>
<th>Orefield</th>
<th>Ore deposit</th>
<th>Ore-forming stage</th>
<th>Host mineral</th>
<th>FL type</th>
<th>Th°C</th>
<th>Salinity (%NaCl, equ.)</th>
<th>Geological significance</th>
<th>Reference</th>
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I, Gas-rich fluid inclusions; II, liquid-rich fluid inclusions; IIa, liquid-rich inclusions without daughter minerals; IIb, liquid-rich inclusions with daughter minerals; III, gas-liquid inclusions; IV, multi-phase fluid inclusions.
Hucun, and Datuanshan skarn deposits in the Shizishan orefield, were chosen for analysing the characteristics of element enrichment. The Datuanshan drillcore is dominated by marble and the other four by skarns.

The five drillcores were sampled from top to bottom with an interval of 10 m, and the ore-forming elements in the samples were analysed (Wang et al. 2008). The concentration curves of the ore-forming elements in the typical drillcores are irregular, as shown in Figure 11, and thus analysed by the fractal models (Wang et al. 2010a).

The Hurst exponent in the self-affine fractal and multifractal spectrum was utilized to analyse the distributions and assemblages of ore-forming elements to better understand the element transport during the formation of the skarn deposit (Deng et al. 2008; Wang et al. 2008). The Hurst exponent was proposed by Hurst et al. (1965) to discriminate random and persistent distributions. Via the Hurst exponent, it is reflected that the elemental distributions in the marble-dominated drillcore, where the original characteristics of the sedimentary rocks generally remain, show approximately random distributions. The elemental distributions in the skarn-dominated drillcores are generally persistent, and the persistence indicates that the mineralized segments developed repeatedly along the drillcores, as is according to the multi-layered structures of the ore-controlling bedding faults and orebodies (Deng et al. 2008; Wang et al. 2010b).

The multifractal spectrum is powerful in characterizing singular measures arising in a variety of physical situations, including the spatial element distribution during ore-forming processes. The multifractal spectrum is a reverse bell shape, with a width $\Delta \alpha$ and a height $\beta$.

![Figure 11. Element concentration curves along the drillcores located in the Dongguashan, Huashupo, and Datuanshan ore deposits respectively, Shizishan orefield, Tongling ore cluster area (modified from Wang et al. 2010b).](image-url)
difference $\Delta f(\alpha)$ between the two ends of the spectrum. An increase in $\Delta \alpha$ means a transition from a homogeneous (random, space filling) to a heterogeneous (ordered, complex, clustered) pattern. A positive $\Delta f(\alpha)$ means the spectrum is right hooked, indicating that there are more small values within the dataset than large ones; otherwise, they are dominated by larger ones (Zeleke and Si 2006; García Moreno et al. 2008). Wang et al. (2008) studied the multifractal parameters of the ore-forming element distributions in the drillcores, discovered that the $\Delta f(\alpha)$ of most elements between two drillcores show proportional relationships, and thus proposed that different deposits show similarities in the element enrichments. In this article, the multifractal parameters are analysed further. The $\Delta f(\alpha)$ and $\Delta \alpha$ of various elements in the Changlongshan drillcore against those in the Dongguashan drillcore and those in the Hucun drillcore were plotted in Figure 12. In Figures 12(a) and (b), the $\Delta f(\alpha)$ of most ore-forming elements are positive, indicating that the elements are locally enriched in the drillcores. Although generally proportional relationships among the elements in Figures 12(a) and (b) are easily observed, most plots in Figure 12(a) and part plots in Figure 12(b) are away from the diagonal line. It is revealed that the elemental enrichment characteristics in one drillcore still show much variance compared to those in another drillcore. The $\Delta \alpha$ plots, as illustrated in Figure 12(c) and (d), still show inconsistent element-enrichment characteristics between the drillcores. It is

Figure 12. Plots of the multifractal parameters of the element distributions in skarn deposits in the Shizishan orefield, Tongling ore cluster area. (a) $\Delta f(\alpha)$ plots between Changlongshan and Hucun deposits; (b) $\Delta f(\alpha)$ plots between Changlongshan and Dongguashan deposits; (c) $\Delta \alpha$ plots between Changlongshan and Hucun deposits; (d) $\Delta \alpha$ plots between Changlongshan and Dongguashan deposits.
demonstrated by further analysis of multifractal parameters that the skarn deposits in the same orefield show diverse element-enrichment characteristics.

**Evolution of the Tongling tectonic-magmatic-metallogenic system**

The evolution of the tectonic-magmatic-metallogenic system of the Tongling ore cluster region is outlined in this article. The regional evolution is divided into three stages (Figure 4).

The first stage ranging from S to T2 is a relative tectonic quiescence period, during which several parallel unconformities and multi-layered synsedimentary orebodies formed. In the second and third stages ranging from T2 to K1, the Tongling region suffered intense intraplate tectono-magmatic activations in a tectonic environment evolving from compressional to extensional.

Stage 2 from the Middle Triassic (T2) to the Late Jurassic (J3) is the tectonic compressional stage; the region suffered NW compression resulting from the collision between the North China block and the Yangtze block. Continuous and intense compression resulted in a thickened lithosphere. The NE-trending folds and bedding-parallel faults induced by compression were dominant in the caprock. The bedding faults containing void spaces between various strata are commonly connected by various types of nearly vertical faults.

Stage 3 lasted roughly from 150 to 134 Ma, defined by the emplacement age of the regional intrusions. The magmatic activity was triggered by the delamination of the thickened lithosphere, and this stage is considered as a transition from a compressional to extensional environment. The lithospheric delamination and asthenosphere upwelling caused crust–mantle interactions and the mixing of mantle- and crust-derived magmas. The mixed magma experienced fractional crystallization during its ascent. The structural framework formed by the previous compression was reworked and shows more tensional characteristics to facilitate the magma ascent.

In the crust, the magma ascended along the deep faults or structural weakness zones probably as mesoscale pervasive flow at depth and aggregated at the detachment faults to form multi-layered magma chambers. The magma generated from the shallow magma chamber at about 10 km migrated into the caprock in a diking model. Because of the inherent kinetic energy of dikes, the magma emplacement caused the bending of the strata and further reactivation of the existing structural network. Magma emplacement further enhanced the vertical transport of ore-bearing fluid, promoting the formation of a multi-layered mineralization network.

The magma emplacements and the following magmatic hydrothermal activities induced the formation of deposits with various types, in which skarn deposits are dominant. Some orefields were composed of multi-layered orebodies, constrained by the spatial features of ore-controlling structures. The different skarn deposits generally show diverse element-enrichment characteristics and similar fluid evolution. In the early stage, ore-forming fluid activity was influenced by a rapid decrease of the magma external pressure and characterized by fluid immiscibility in skarn deposits. Superpositions of the Mesozoic hydrothermal fluids on the synsedimentary orebodies formed in the first evolution stage are outstanding in the region.

**Conclusions**

The tectonic-magmatic-metallogenic system of the Tongling ore district is characterized by the following features:
(1) The system experienced two major tectonic transitions. In the Middle Triassic, the tectonic regime changed from quiescence to intense compression. The second tectonic transition, from compression to extension, occurred during the interval from 134 to 150 Ma. The main ore deposits formed during the second transition.

(2) Because of the transition of the tectonic regime, superposition of Mesozoic magmatic hydrothermal deposition on the previously formed Palaeozoic sedimentary ore bodies occurred throughout the region during the quiescence stage.

(3) Intense Mesozoic mineralization in the Tongling region was due to the abundant metals derived from mantle, favourable ore-controlling structures, and widespread fluid boiling attending hydrothermal fluid evolution, which facilitated metal deposition.

(4) The ore-controlling structure system in the cover sequence formed during strong tectonic compression and was reworked by the deformation that resulted from magma emplacement, and is reflected in the multi-layered bedding faults cut by steeply dipping faults. This structural assemblage resulted in the spatial multi-layered distribution of bedding-parallel ore bodies in a number of deposits.

**Acknowledgements**

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Comparative study of ore-forming fluids of hydrothermal copper–gold deposits in the lower Yangtze River Valley, China

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Fluid-inclusion and stable isotope studies were carried out on five types of Mesozoic (Yanshanian) hydrothermal copper–gold deposits in the lower Yangtze River Valley. Deposits include (1) copper in cryptoexplosive breccia pipes, (2) skarn copper, (3) porphyry copper, (4) high-temperature quartz vein-type copper and gold, and (5) medium–lower temperature fracture zone gold. This research has allowed a comparison between various types of ore-forming fluids. Melt-fluid inclusions in garnet from the matrix of the breccia pipe at the Shizishan copper deposit reveal the existence of a water-rich magma. In all deposit types, fluid temperatures and salinities were higher at early stages and generally decreased with time. Magmatic water is dominant in the high-temperature ore-forming fluids, whereas meteoric water was involved only in the medium–lower temperature Xiaomiaoshan gold deposit and in the post-mineralization stage of the Shaxi porphyry copper deposit. Fluid boiling played an important role in the mineralization of most deposits, particularly at Shizishan, where multi-stage boiling was associated with the formation of cryptoexplosive breccia, skarn, quartz-sulphide, and quartz-carbonate-sulphide stages. Boiling of an aqueous magmatic fluid system at high temperatures reflects the release of crystallization heat and increase of total volume of the magma–fluid system, and hence it can be referred to as active boiling. On the contrary, boiling of a fluid at lower temperatures is typically triggered by pressure release due to fracturing or dilation in the surrounding rocks, and is thus referred to as passive boiling. In general, passive boiling occurs more commonly at the higher levels of a hydrothermal mineral system and at later stages of the ore-forming process.

Keywords: ore-forming fluid; boiling; hydrothermal deposit; copper; gold; lower Yangtze Metallogenic Belt

Introduction

The lower Yangtze River Valley is a major metallogenic province, well known in China for its numerous skarn and porphyry-skarn mineral deposits, with important resources of copper and gold. A considerable volume of literature deals with the tectonic evolution, magmatism, and metallogenesis of this region (Sato et al. 1986; Chang et al. 1991; Zhai et al. 1996; Li et al. 1997; Gu et al. 2007; Chen et al. 2007a). Some authors have studied
the nature of ore-forming fluids for individual deposits of the Yangtze River Valley (Xu et al. 1999; Yang et al. 2002; Lu et al. 2007; Xu et al. 2008; Yang and Lee, submitted), but reports providing data on the ore-forming fluids of this metallogenic province are relatively scarce (Yang and Lee, submitted). Based on a recent study of the Shizishan and Tongniujing deposits, this article aims to make a comparison of the main features, origin, and evolution of the fluids responsible for these hydrothermal copper-gold mineral systems.

**Regional geology and metallogeny**

The lower Yangtze River Valley is situated between the early Precambrian Dabie Uplift and the late Precambrian Jiangnan orogenic belt (Figure 1). The Dabie Uplift is divided by the Xinxian–Luotian–Wuhe–Shuihou fault zone (Figure 1) into two parts: northern and southern Dabie blocks (Dong and Dai 1993; Cong et al. 1994). The northern Dabie block is composed mainly of Archaean and early Proterozoic gneisses and migmatites, which form the basement to an Early–Middle Triassic volcanic arc on the southern margin of the North China plate (Cong et al. 1994). The fault extending from Xinxian to Luotian and Wuhe to Shuihou marks the Middle Triassic (Indosinian) collision between the North China Craton and the Yangtze Craton. As a result of subduction, collision, and exhumation, numerous diamond- and coesite-bearing eclogite bodies with ages of 220–230 million years (Li et al. 1993; Wang and Liou 1993; Zhuang 1998) occur to the immediate south of this fault zone. The southern Dabie block (Figure 1) is composed of schist and amphibolite of the lower Proterozoic Susong Group, and the middle and upper Proterozoic greenschist and phyllite in the Shui Xian and Zhangbaling areas (Figure 1), which are part of the basement of the Yangtze Craton, thrust up during continental collision (Gu et al. 2007). The greenschist and phyllite exposed along the Precambrian Jiangnan orogenic belt (Figure 1) are interpreted to be part of an island arc on the southern margin of the Yangtze Craton (see Gu et al. 2007).

During the upper Palaeozoic era, the lower Yangtze River region was a passive continental margin of the Yangtze Craton (Zhang 1997; Gu et al. 2007). Upper Palaeozoic sedimentary units consist of Devonian continental and offshore clastic rocks, Carboniferous and Permian marine carbonates, and terrigenous clastic rocks with a minor amount of pelagic siliceous rocks. Overlying these sediments are the Lower-Middle Triassic marine carbonates interlayered with clastic and argillaceous rocks. This passive continental margin and the oceanic crust to its north were subducted beneath the North China Craton and finally involved in its collision with the Yangtze Craton during Middle Triassic time (Indosinian orogeny: Qinling-Dabie orogenic belt). The post-collisional Middle Triassic Huangmaqing Formation, Upper Triassic Fanjiatang Formation, and Lower-Middle Jurassic Xiangshan Formation all contain continental clastic sediments (Gu et al. 2007). Intensive magmatism took place during the Late Jurassic and Early Cretaceous, locally producing volcanic rocks of shoshonite and high-K calc-alkaline series, and intrusive rocks of high-Na alkaline, calcic, and high-K calc-alkaline affinity, corresponding to mafic-intermediate and intermediate-felsic rocks, respectively (Tang et al. 1998; Chen et al. 2001; Xie et al. 2009). These magmatic activities and related mineralization are thought to have taken place in an aborted intracontinental rift environment (Gu and Xu 1987; Zhai et al. 1996).

Copper and gold mineralization in the lower Yangtze River Valley was formed during two major periods: Carboniferous and Late Jurassic to Early Cretaceous (Yanshanian). Numerous sediment-hosted massive sulphide deposits, such as the stratiform ore bodies at Wushan, Chenmenshan, Mashan, Xinqiao, Dongguashan, and Tongguanshan, developed during the Carboniferous (Figure 1). As described in detail by Gu et al. (1993, 2007),
massive sulphide ore bodies occur in the middle Carboniferous Huanglong Formation, in which minor amounts of dacite lava and rhyolitic volcaniclastic rocks have been locally found (Fu et al. 1977; Xu et al. 1980; Gu and Xu 1984; Chang et al. 1991; Zhai et al. 1992; Zhu 1992). In contrast, the Yanshanian (Mesozoic) tectono-thermal event is characterized by the development of hydrothermal deposits genetically linked to intermediate or felsic intrusives. The Yanshanian deposits encompass five main types (Figure 1): (1) copper in cryptoexplosive breccia pipes (e.g. eastern Shizishan and Yangjishan), (2) skarn copper (e.g. western Shizishan, Wushan, Tonglushan, and Yangjishan), (3) porphyry copper (e.g. Shaxi and Fengshandong), (4) high-temperature quartz vein-type copper and gold (e.g. Tongniujing – also called Yueshan in literature), and (5) medium–lower temperature, economically less important, fracture zone gold (e.g. Xiaomiaoshan). Carboniferous massive sulphide ores coexist with skarn- and/or porphyry-type ores in the same areas, such as the Tongguanshan, Dongguashan, Xinqiao, Wushan, and Chenmenshan mines (Gu et al. 2000, 2007).

**Deposit geology**

Representative hydrothermal deposits selected for our study are briefly described below.
Shizishan breccia pipe and skarn-type copper deposit

The Shizishan copper deposit (No. 7 in Figure 1) is located near the city of Tongling, Anhui Province, where the geology and tectonic evolution are described by Wang et al. (2010). This deposit comprises an eastern and a western ore zone, with the former characterized by ore bodies of the cryptoexplosive breccia pipe (Wang and Zhou 1982; Chang et al. 1991) developed in the eastern part of the Shizishan quartz-monzodiorite intrusion (Rb–Sr age of 137 million years, Tang et al. 1998), and the latter consisting of several skarn ore bodies along the western contact of the same intrusion with Lower Triassic marble rocks. The stratigraphically highest units intruded by the Shizishan quartz-monzodiorite belong to the Lower Triassic Tashan Formation, and thus, based on total thickness of the overlying strata, this intrusion was estimated to have intruded at a depth of about 700–1000 m below the surface, with a lithostatic pressure around 18–26 MPa.

The eastern Shizishan cryptoexplosive breccia pipe shows an irregular boundary at the surface, with a diameter of about 150 m, and extends to a depth of more than 500 m. It exhibits a funnel-shaped cross section (Figure 2). The fragments in the pipe are angular or subangular and chaotically arranged (Figure 3A and 3B). Most have sharp boundaries with baked and discoloured margins $\sim 1–2$ mm in width. Lithologically, they are dominated by quartz-monzodiorite (Figure 3A) with minor marble and pelitic hornfels, but some of them have been converted to skarn, as shown by intense garnet and diopside alteration (Figure 3B). The matrix of the breccia is characterized mainly by garnet, diopside, and scapolite (Figure 3A). Both the fragments and the matrix have been more or less replaced by late-stage sulphide minerals, which are dominated by pyrite, chalcopyrite, and arsenopyrite in association with quartz and carbonate minerals. On the weakly weathered surface, most of the iron from sulphides in the breccia has been converted to iron oxides, with copper mostly removed by rainwater (Figure 3A). The pipe grades laterally into intensely skarn-altered quartz-monzodiorite and marble. Copper concentration increases outwards from 0.7% in the pipe to 1% in the surrounding rocks, but the content of arsenopyrite decreases in the

Figure 2. Cross section of the cryptoexplosive breccia pipe copper ore bodies, eastern Shizishan (Chang et al. 1991).
Figure 3. Photographs of cryptoexplosive breccia in the Shizishan copper deposit. (A) Weakly weathered surface of cryptoexplosive breccia at eastern Shizishan, showing clear boundaries of quartz-monzodiorite fragments. Most of the iron from sulphides has been converted to iron oxides, but copper staining mostly removed by rainwater. (B) Cryptoexplosive breccia at eastern Shizishan with quartz-monzodiorite fragments replaced by fine-grained garnet and diopside, oxidized sulphides shown by the brown colour.

same direction (Chang et al. 1991). Other magmatic skarn bodies in the Shizishan district have been reported from within the quartz-monzodiorite and its wall rocks as lenses and knobs, several metres to tens of metres in size (Ling et al. 1998; Wu and Chang 1998).

The western Shizishan skarn-type mineralization comprises several parallel or sub-parallel ore bodies (Figure 4), the largest of which extends over 300 m, with a thickness
averaging 17 m. Copper mineralization occurs dominantly in skarn and partly in the quartz-monzodiorite and marble (Figure 4). Pyrite, chalcopyrite, and pyrrhotite are the main ore minerals. In strong contrast to the garnet-dominated breccia pipe in eastern Shizishan, diopside is the prevailing skarn mineral in the western Shizishan ore zone. The parallel or subparallel nature of the ore bodies seems to have resulted from branching of the quartz-monzodiorite into the marble along its bedding. Ores at western Shizishan average 1.24% Cu and 0.95 g/t Au (Tang et al. 1998). The stratiform ore body in the Carboniferous strata below the skarn-type ore bodies in Figure 4 is part of the Dongguashan massive sulphide copper deposit that is considered to have been formed by Carboniferous submarine exhalation (Gu et al. 2007). This ore layer is dominated by pyrite, pyrrhotite, and chalcopyrite and may have supplied part of the metals in the skarn-type ore bodies above by remobilization of the quartz-monzodiorite (Gu et al. 2007).

Field and microscope studies suggest that mineralization processes at Shizishan can be divided into four stages: cryptoexplosive breccia stage, skarn stage, quartz-sulphide stage, and quartz-carbonate stage. The quartz-sulphide stage is especially important for ore formation.

Shaxi porphyry copper deposit
Geology around the Shaxi porphyry copper deposit (No. 9 in Figure 1) is described by Yang et al. (2010). This deposit is hosted by quartz-diorite porphyry, with a whole-rock Rb-Sr isochron age of 127.9 ± 1.6 million years and an initial $^{87}$Sr/$^{86}$Sr ratio of 0.7058, intruded in the Middle Silurian argillaceous siltstone and the Lower-Middle Jurassic sandstone (Figure 5) (Chang et al. 1991; Xu et al. 1999). Most of the ore bodies are lenticular or tabular in shape and occur in the apical portions of the intrusion with few ore bodies in the surrounding strata. Mineralization extends from the surface to a depth of more than 600 m (Xu et al. 1999). Chief ore components are chalcopyrite, pyrite, molybdenite, bornite, and magnetite with gangue minerals comprising quartz, anhydrite, illite, and carbonates. Alteration mineral assemblages grade upwards from anhydrite + biotite + K-feldspar in the inner part of the intrusion to quartz + sericite to epidote + chlorite + carbonate. Correspondingly, ore mineral assemblage grades upwards from magnetite and minor molybdenite through chalcopyrite + bornite + chalcocite and chalcopyrite + bornite + tetrahedrite + pyrite to chalcopyrite + pyrite, and further to pyrite + sphalerite + galena. Veinlets and disseminations of copper sulphides occur mainly in the outer portion of the biotite and K-feldspar alteration zone and in the quartz and sericite alteration zone. Ore grades range from 0.44 to 0.68% Cu, with about 0.5 ppm Au. From drill core analyses, reserve of this deposit is estimated at about 500,000 t Cu (Chang et al. 1991; Qiu et al. 1991; Tang et al. 1998).

Based on cross-cutting relations, early-, main-, and post-mineralization stages can be distinguished (Xu et al. 1999). The early mineralization stage is characterized by K-feldspar alteration and sulphide disseminations. Copper sulphides and pyrite together with anhydrite and quartz characterize the main mineralization stage, whereas the post-mineralization stage is represented by veinlets of quartz, gypsum, and carbonates with minor sulphides (Yang et al. 2010).

Tongniujing high-temperature quartz vein-type copper–gold deposit
The Tongniujing high-temperature quartz vein containing copper and gold (No. 10 in Figure 1) is hosted by the Yueshan quartz-diorite porphyry (Figures 6 and 7), which was...
intruded into red sandstone and siltstone of the Middle Triassic Huangmaqing Formation, yielding an age of 136 million years by the $^{40}\text{Ar}/^{39}\text{Ar}$ method on hornblende (Chen et al. 1991). The term high-temperature deposit refers to a mineralization event that occurred at temperatures of between 300 C and 500 C (Yao and Sun 2006). This temperature range corresponds to that of hypothermal deposits termed hypo-mesothermal by Lindgren (1933). The Tongniujing veins, particularly the high Mo contents and associated K-feldspar and

Figure 5. Cross section of the Shaxi porphyry copper deposit (from Geological Company No. 327, Bureau of Geology and Mineral Resources, Anhui Province).

Figure 6. Geology of the Tongniujing deposit at mine level —10 m.
biotite alteration, taken together with homogenization temperatures of fluid inclusions (300–450°C; see below) of the main ore-forming stage, indicate that these veins were formed at high temperatures.

The deposit includes three veins (Figure 7) striking N60°E, along a tension-shear fracture zone. The largest vein has a thickness varying from 1 to 6 m and a total length of over 700 m (Figure 6). It dips SE at angles of ∼70–80°, extending to a depth over 200 m (Figure 7). The mine began to produce copper–gold ores in 1973 and was shut down in 1996 due to exhaustion of the reserve, with a total output of 23,000 t Cu at 1.33%, 1293 t Mo at 0.07%, 353 kg Au at 0.22 ppm, and 8611 kg Ag at 4 ppm.

Predominant constituents of the vein are quartz and lesser carbonates with chalcopyrite, molybdenite, pyrite, and a small amount of electrum as the main ore minerals. The host quartz-diorite is affected by hydrothermal alteration, characterized by an assemblage of K-feldspar, biotite, actinolite, epidote, chlorite, sericite, and carbonate with sulphide disseminations. Quartz-diorite fragments cemented by quartz, carbonates, and sulphides can be seen in some localities. Interestingly, gold concentration of the ores decreases downward, but molybdenum concentration increases, possibly due to a corresponding upward decreasing temperature of metal transport and deposition.

**Xiaomiaoshan fracture zone gold deposit**

The Xiaomiaoshan gold deposit (No. 1 in Figure 1), with a resource of 3156 kg Au, is located in the Zhangbaling Meso- and Neoproterozoic terrane at the northern margin of
the lower Yangtze region. Tectonic setting and geology of this terrane are described by Huang et al. (2010). The deposit area is dominated by Neoproterozoic Na-rich rhyolitic lava and volcaniclastic rocks, metamorphosed to lower greenschist facies and intruded by a Yanshanian quartz-monzonite (Huang et al. 2002, 2010). A lamprophyre dike cutting the quartz-monzonite yielded a whole-rock Rb–Sr isochron age of 129.7 ± 1.6 million years.

The deposit includes five ore zones controlled by fractures in the metamorphosed volcanic rocks. These zones generally trend 15–20° with widths of between 0.5 and 2 m, depth extension greater than 100 m, and a maximum length of 1500 m. These ore zones dip SE at angles of 75–85°. Native gold occurs as replacement product both in altered fracture zones and in quartz veins (Figure 8) in association with pyrite, minor chalcopyrite, and galena. Alteration of the hosting volcanic rocks is represented by silicification, chloritization, sericitization, kaolinization, and pyritization. The ores average 5.07 g/t Au with a maximum of 8.22 g/t Au.

**Ore-forming fluids**

**Fluid inclusions**
Vapour-rich inclusion, liquid-rich inclusion, and daughter-bearing liquid-rich inclusion are the three major fluid-inclusion types found ubiquitously in the above-mentioned hydrothermal copper–gold deposits in the lower Yangtze River Valley metallogenic province. However, compositions, homogenization temperatures, and salinities of these three inclusion types vary significantly from deposit to deposit and from one mineralization stage to another. Fluid inclusions in the same mineral grain commonly show dispersed gas/liquid
ratios, which indicates there must be a dispersed trapping temperature for these fluid inclusions. In addition, melt-fluid inclusions occur in garnet of the Shizishan deposit.

**Temperature and salinity**

Fluid-inclusion determinations were performed on a Linkam THMS 600 after preheating the samples at 200°C for 2 hours to remove secondary inclusions. Both heating and cooling procedures, whenever possible, were done on the same inclusions. The cooling has been calibrated with USGS synthetic fluid inclusions. The precision of temperature measurements is ±0.1°C at temperatures lower than 0°C and ±1°C at temperature higher than 31°C. To avoid overheating during stepwise temperature rising, at temperatures approaching that of phase conversion, temperature of the stage was first adjusted 1°C lower than the last step, and then set to rise by an interval of 0.2°C. Double determinations were carried out for each inclusion to preclude the possibility of leakage. Temperature-salinity conversions were done following the formula given by Bodnar (1993):

\[
\text{Salinity} = 0.00 + 1.78X - 0.0442X^2 + 0.000557X^3
\]

where \(X\) represents absolute temperature of the freezing point. Salinities of halite-bearing inclusions were obtained from halite-disappearing temperatures and the solubility curve of NaCl given by Keevil (1942).

**Shizishan deposit**

Homogenization temperatures of 105 inclusions and salinities of 57 inclusions have been obtained for ores of various stages from the Shizishan deposit, but only the data with both temperature and salinity are plotted in Figure 9.

![Figure 9. Temperature versus salinity plots of fluid inclusions from Shizishan. Field I - for matrix of the cryptoexplosive breccia; field II - for skarn; field III - for the quartz-sulphide stage; and field IV - for late-stage veins. Two points for garnet represent salinities of the liquid phases in the melt-fluid inclusions and the temperature of the upper determination limit of the heating stage that is obviously lower than the actual homogenization temperatures of the inclusions. Arrow indicates the direction in which the point should move towards its actual position.](image-url)
Garnet with $\sim 39 \text{–} 99 \text{ mol.} \%$ andradite and $\sim 1 \text{–} 61 \text{ mol.} \%$ grossular is the main component in the matrix of the eastern Shizishan breccia pipe. Fluid inclusions are relatively scarce and are scattered, with size varying between 5 and 45 $\mu$m. Most of them are two-phase inclusions containing a vapour and a liquid phase, with vapour content ranging from $\sim 45$ to $65 \text{ vol.} \%$. In addition, melt-fluid inclusions were earlier reported by Zhao et al. (1995) for garnet from the breccia pipe (Figure 10A). The present authors also observed melt inclusions in this breccia. These inclusions are also randomly distributed and are $\sim 10 \text{–} 45 \mu$m in size with irregular boundaries. They are composed of a silicate glass, an aqueous liquid phase, and a vapour bubble and commonly have one or more daughter crystals. The glass in these inclusions is optically isotropic, but some parts of it have a vague granular appearance at high magnifications, presumably indicating devitrification. Volume proportion of the vapour bubble is conspicuously variable from 15 to 80%. The daughter crystal that is cubic, colourless, and isotropic and shows a higher refractive index than the glass is probably halite. Homogenization temperatures of seven inclusions are higher than the upper determination limit of the heating stage (600°C), and two of them successfully gave salinities of 42.0 and 56.2 wt.% NaCl equivalent, respectively, for the liquid phases. They are plotted in Area I in Figure 9.

Diopside from the skarn at the contact zone between quartz-monzodiorite and marble has both vapour- and liquid-rich inclusions with a size range of $\sim 8 \text{–} 31 \mu$m. Some inclusions contain daughter mineral(s). These inclusions gave homogenization temperatures ranging from 422 to 467°C and salinities from 38.0 to 45.1 wt.% NaCl equivalent.

Figure 10. Photographs of fluid inclusions from the Shizishan copper deposit. (A) Melt-fluid inclusion in garnet including a vapour bubble with aqueous solution and glass, plane polarized light. (B) Vapour-rich inclusions coexisting with liquid-rich inclusions in quartz, plane polarized light. (C) Liquid-rich inclusions without daughter in calcite, plane polarized light. (D) Liquid-rich and daughter-bearing inclusions coexisting with daughter-free inclusions in quartz, crossed nicols. Inclusion symbols: V, vapour phase; L, liquid phase; G, glass; D, daughter.
Calcite patches in the skarn have plenty of vapour-rich inclusions with homogenization temperatures ranging from 443 to 472 °C and salinities from 10.2 to 10.7 wt.% NaCl equivalent. Sixteen temperature determinations for diopside and calcite from the skarn gave an average of 458 °C, and the data are plotted with salinity in Area II of Figure 9.

Calcite and quartz blebs in the ores representing the quartz-sulphide stage are characterized by clustered vapour- and liquid-rich (Figure 10B and 10C) inclusions, ~10–56 µm in size. Some of the liquid-rich inclusions contain one or more daughter grains (Figure 10D). The inclusions gave homogenization temperatures of 337–439 °C with an average of 390 °C and salinities of ~3.0–30.0 wt.% NaCl equivalent. They are shown in Area III of Figure 9.

Vapour- and liquid-rich inclusions commonly coexist in late-stage quartz-carbonate veins and are 5–53 µm in size. Some of the liquid-rich inclusions are daughter-bearing. These inclusions gave homogenization temperatures varying in a range of 158–336 °C with an average of 265 °C and salinities of 2.1–40.4 wt.% NaCl equivalent. They are shown in Area IV of Figure 9.

From the above-mentioned data on inclusion assemblages, temperatures, and salinities in combination with ore geology, it can be suggested that the mineralizing fluids for the Shizishan deposit have undergone early fluid immiscibility from the magma and possibly four episodes of fluid boiling. Melt-fluid inclusions in garnet are characterized by ratio of variable volumes of vapour, liquid, and melt phases, indicating that these inclusions were not trapped as a homogeneous fluid-rich magma, but as a heterogeneous system of two phases, a silicate melt and an aqueous-rich fluid (e.g. Roedder 1992; Roedder and Bodnar 1997; Gu et al. 2010). These two phases were possibly developed by fluid immiscibility from the magma at temperatures exceeding 600 °C.

Garnet at Shizishan occurs in the cryptoexplosive breccia pipe as a principal cementing material of rock fragments. The mechanism of breccia pipe formation has been explained by Burnham (1997) to involve an episode of boiling subsequent to immiscible fluids evolving from the magma. Therefore, it appears reasonable to infer that garnet precipitation could have succeeded an episode of boiling that is responsible for the formation of the breccia pipe, although no vapour-rich, low-salinity inclusions have been found in garnet. Sainty (1992) pointed out that boiling may often occur without vapour-rich inclusions being trapped.

The second episode of boiling occurred together with the development of skarns, resulting in the coexistence of vapour-rich and daughter-bearing liquid-rich inclusions in diopside, both being homogenized at similar temperatures. The third and fourth episodes correspond to the quartz-sulphide and quartz-carbonate stages. The coexistence of vapour-rich, low-salinity inclusions with liquid-rich, high-salinity inclusions in quartz and calcite and the comparable homogenization temperatures of all these inclusions demonstrates that boiling did occur also at these two stages.

Shaxi deposit

Xu et al. (1999) have carried out detailed studies on fluid inclusions from the Shaxi deposit. Three types of fluid inclusions are recognized: vapour-rich, liquid-rich, and daughter-bearing inclusions. Vapour-rich inclusions, 9–20 µm in size, commonly show negative crystal form of quartz and occur mostly in the potassium silicate alteration zone in the central part of the deposit. Liquid-rich inclusions represent the most common inclusion type, the majority of which are subround or ellipsoidal in outline with a size range of 3–30 µm. Like vapour-rich inclusions, daughter-bearing inclusions are
largely distributed in the potassium silicate alteration zone with negative crystal form of quartz. They are from 5 to 15 µm in size, with halite as the dominant daughter phase.

Xu et al. (1999) determined homogenization temperatures and salinities of the fluid inclusions in quartz for the Shaxi deposit. The inclusions from the potassium silicate alteration zone, representing the early mineralization stage, gave temperatures ranging from 460 to 520 °C with a peak at 460 °C and salinities of 52–58 wt.% NaCl equivalent. Temperatures of the main mineralization stage vary in the range of 280–420 °C with a peak around 370 °C, but salinities exhibit a bimodal distribution between 41 and 52 wt.% and 9 and 17 wt.% NaCl equivalent. The high-salinity inclusions are normally daughter-bearing, whereas the low-salinity ones contain only a liquid and a vapour phase. The later stage is characterized by inclusion temperatures ranging from 110 to 260 °C with a peak around 170 °C and salinities of 8–24 wt.% NaCl equivalent. In general, both fluid temperature and salinity decreased with time in the Shaxi deposit. The temperature of the main mineralization stage is comparable with those of typical porphyry copper deposits of China (Rui et al. 1984; Lu et al. 2004; Chen et al. 2007b; Chen and Li 2009; Chen and Wang 2010).

Tongniujing deposit

Samples for fluid-inclusion studies were taken from mine levels −10 m, −60 m, −110 m, −150 m, and −200 m (Figure 11). The three types of inclusions, that is, the vapour-rich, liquid-rich, and daughter-bearing inclusions, occur in all five levels and mostly range between 6 and 12 µm. Fluid inclusions from other mine levels vary in abundance and phase proportions of individual inclusion type. Daughter-bearing inclusions are the most abundant type at level −10 m, and liquid-rich inclusions are abundant at level −60 m, whereas liquid-rich and daughter-bearing inclusions are almost equally abundant at levels −110 m, −150 m, and −200 m. Within the daughter-bearing multi-phase inclusions, the vapour/(vapour + liquid) ratio is 0–10 vol.% at level −10 m, 10–20 vol.% at level −60 m, 10–30 vol.% at level −110 m, 15–40 vol.% at level −150 m, and 25–40 vol.% at level −200 m. Vapour-rich inclusions with vapour/(vapour + liquid) ratios ranging between 50 and 90 vol.% are the most abundant at level −10 m.

Homogenization temperatures and salinities of fluid inclusions in quartz from various levels of the Tongniujing copper–gold vein were measured by the present authors. It is shown in Figure 11 that salinity values lower than 30% NaCl equivalent are scarce, and ores were precipitated from fluids of higher salinities (mainly 30–48 wt.% NaCl equivalent) at temperatures between 300 and 450 °C. There are also fluid inclusions with homogenization temperatures lower than 300 °C, but these inclusions have also high salinities (31–44 wt.% NaCl equivalent). Among those that have both temperature and salinity data, the inclusion that gives the lowest homogenization temperature (192 °C) has a salinity of 31 wt.% NaCl equivalent. Figure 11A–11E shows that the fluid temperature generally decreases upwards in the ore system. This is in accordance with the decreasing trend of Mo/Au ratio in the ores from level −200 m upwards. In contrast, fluid salinity does not show any systematic variation upwards (Figure 11F–11J).

Comparable to gold-sulphide-quartz veins in granitoid plutons of the Taihang region, northern China (Zhu and Zeng 2001), ores from all levels of the Tongniujing deposit are characterized by daughter-bearing multi-phase inclusions. Salinity of the inclusions varies mainly in the range between 30 and 48 wt.% NaCl equivalent, indicating that the fluids are dominated by magmatic water.
Xiaomiaoshan

Fluid inclusions in the Xiaomiaoshan gold veins are less abundant and of small size. Their size varies between 4 and 24 µm and mostly between 5 and 10 µm. They are dominated by two-phase inclusions with gas/liquid ratio between 15 and 40%. These two-phase inclusions homogenized between 91 and 348°C, and mostly in the range of 160–280°C (Figure 12). Salinity varies between 0.7 and 16.5 wt.% NaCl equivalent. Occasionally, daughter-bearing three-phase inclusions are found, but only two yielded homogenization temperatures of up to 360 and 378°C, and salinities of up to 42 and 44 wt.% NaCl equivalent (Figure 12), respectively. These data indicate that gold mineralization occurred principally at middle- to low temperatures. Based on the equation of Sourirajan and Kennedy (1962), fluid pressure of the main mineralization stage has been
calculated between 3 and 13 MPa. Assuming a fluid pressure nearly equal to the lithostatic pressure, the depth at which gold mineralization occurred is estimated at ∼100–500 m.

Figure 12 shows that there is a positive correlation between temperature and salinity of the Xiaomiaoshan fluid inclusions and that three inclusion groups can be discerned. Group I (Figure 12) daughter-bearing inclusions give particularly high temperature and salinity; Group II shows medium temperature and salinity with values of 155–348°C and 1.6–16.5 wt.% NaCl equivalent, respectively; and Group III is low in temperature and salinity with values ranging from 91 to 139°C and 0.7–1.9 wt.% NaCl equivalent, respectively. The coexistence of fluid inclusions of these three groups is likely to indicate fluid mixing. Groups I and III approximate high- and low-salinity end members. Good mixing of these two end members in various proportions resulted in a wide spectrum of inclusions with variable salinity and limited abundance in Groups I and III.

**Stable isotopes**

Much research has been performed on sulphur isotopes in the hydrothermal copper and gold deposits of the lower Yangtze River Valley. The general consensus is that the sulphur in the Yanshanian hydrothermal deposits of this region came essentially from the magma, with a minor proportion derived from the surrounding rocks (Pan and Dong 1999; Zhou and Yue 2000). Therefore, we focused isotope determinations for the Shizishan deposit on hydrogen, oxygen, and carbon. All samples were prepared by hand-picking under a binocular microscope. Quartz, representing the main mineralization stage of the deposit (Area III in Figure 9), was leached by HCl solution to eliminate intergrown carbonate minerals and preheated at 200°C for 2 hours to remove adsorbed water and secondary inclusions, and then analysed for oxygen and hydrogen isotope compositions. Oxygen was liberated by reaction with BrF5 in Ni bombs. Inclusion fluids obtained from the quartz by decrepitation were used for determination of hydrogen and carbon isotopes. Isotope measurements were performed using a mass spectrometer at 252 in State Key Laboratory of Ore Deposit Research, Nanjing University. Repeated analyses gave the reproducibility of better than ±0.2‰ for δ18O, δD, and δ13C. Calculations for oxygen isotope compositions of the fluids were done based on the formula 1000 ln α = 3.38 (10^6/T^2) – 3.40 for 200–500°C (Clayton et al. 1972).
Table 1. Determinations and calculation results of hydrogen, oxygen, and carbon isotope compositions of ore-forming fluids from the Shizishan deposit.

<table>
<thead>
<tr>
<th>Mineralization stage</th>
<th>Sample number</th>
<th>Mineral assemblage</th>
<th>Th (°C)</th>
<th>δ¹⁸O_qz, (SMOW)</th>
<th>δD_fluid,(SMOW)</th>
<th>δ¹³C_fluid,(PDB)</th>
<th>δ¹⁸O_water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz-sulphide</td>
<td>M 944</td>
<td>py-cp-qz</td>
<td>333</td>
<td>12.4</td>
<td>-67</td>
<td>-2.9</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>M 953</td>
<td>py-cp-qz</td>
<td>379</td>
<td>12.7</td>
<td>-69.5</td>
<td>5</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>M 949</td>
<td>py-cp-qz</td>
<td>322</td>
<td>12.1</td>
<td>-73.9</td>
<td>0.9</td>
<td>8.2</td>
</tr>
<tr>
<td>Quartz-carbonate</td>
<td>M 858</td>
<td>py-cp-car</td>
<td>298</td>
<td>12.7</td>
<td>-67.3</td>
<td>-0.7</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>M 946</td>
<td>py-cp-car</td>
<td>390</td>
<td>12.9</td>
<td>-66.5</td>
<td>-3</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Note: car, carbonates; cp, chalcopyrite; py, pyrite; qz, quartz; Th, homogenization temperature of fluid inclusions in quartz; *, Calculated based on Clayton et al. (1972).

Figure 13. Hydrogen and oxygen isotope compositions of inclusion fluids for the Shizishan, Shaxi, and Tongniujing deposits. Deposit symbols: cross: Shizishan (our data); triangle: Tongniujing (data from Zhou and Yue 2000); open circle: principal mineralization stage of Shaxi (data from Xu et al. 1999); filled circle: post-mineralization stage of Shaxi (data from Xu et al. 1999); and open square: Xiaomiaoshan (data from Xu Zhaowen, unpublished).

Results of hydrogen and oxygen isotope compositions for the Shizishan (Table 1), Shaxi, Tongniujing, and Xiaomiaoshan deposits are shown in Figure 13. It can be seen that all the samples from the Shizishan deposit plot in the magmatic water box; two points for the main mineralization stage of the Shaxi deposit also plot within the magmatic water box, whereas three others are outside but close to the left boundary of the magmatic water area. Plots for the Tongniujing deposit are located further to the left. These plots indicate that fluids of these samples are dominated by magmatic water with less meteoric water involved. By contrast, fluids of the Xiaomiaoshan deposit and the post-mineralization stage of the Shaxi deposit are shifted evidently towards the meteoric waterline (Figure 13), suggesting significant involvement of meteoric water.
δ13C values of CO2 separated from inclusion fluids in quartz from the Shizishan deposit ranges from −3.0 to 5.0‰ (Table 1). Such carbon isotope data are similar to those of Carboniferous carbonate sediments of the lower Yangtze River Valley (−3.5 to +4.5‰, Lin et al. 2002), implying that much of the CO2 in the fluids might have been derived from the surrounding carbonate strata during ore formation. CO2 in the Shaxi deposit, by contrast, is likely to have come from the magma itself, as indicated by its lower δ13C values of approximately −2.7 to −6.5‰ (Xu et al. 1999). The strong and negative deviation of δ13C of the Shaxi deposit from marine carbonates is in accordance with the absence of carbonate rocks in the surrounding Jurassic and Silurian rocks.

Discussion

From the foregoing, it can be seen that the ore-forming fluids of the most important four types of copper–gold deposits in the lower Yangtze River region, that is, the cryptoexplosive breccia copper, skarn copper, porphyry copper, and high-temperature quartz vein-type copper–gold are dominated by magmatic water. However, meteoric water was involved in the porphyry copper and quartz vein types, particularly at the post-mineralization stage of the porphyry copper deposit. The cryptoexplosive breccia stage of the Shizishan deposit and the early mineralization stage of the Shaxi porphyry copper deposit are quite similar in that their ore-forming fluids were high in temperatures (>440°C) and salinities (>40 wt.% NaCl equivalent). Such fluids are comparable to those from many other porphyry copper deposits reported in literature (Aubouin 1990; Roedder and Bodnar 1997; Lu 2000; Chen et al. 2007b; Chen and Wang 2011). Fluids of high salinities can be derived either by immiscible phase separation directly from magma or by boiling (Roedder 1992; Webster 1997; Shmulovich et al. 1999; Chen et al. 2004; Fan et al. 2006) or by effervescence (Wilkinson 2001) of fluids.

Homogenization temperature of the high-salinity melt-fluid inclusions in the garnet that occurs in the matrix of the cryptoexplosive breccia well exceeds the upper determination limit of the heating stage (600°C). As a matter of fact, previous authors (Zhao et al. 1995; Ling et al. 1998; Wu and Chang 1998) did report temperatures higher than 900°C and even up to 1190°C for melt inclusions in skarn garnet from the Shizishan deposit. Such temperatures exceed the solidus of a water-rich granitic magma (e.g. Johannes and Holtz 1996). Therefore, we advocate the use of the term ‘magmatic skarn’ for this type of garnet skarn as also proposed by other authors (Zhao et al. 1993; Ling et al. 1998; Wu and Chang 1998) to make a distinction from classical skarn formed by contact metasomatism. The fact that garnet occurs either as cementing material of the quartz-monzodiorite fragments or as veinlets or impregnations within the fragments, coupled with the existence of melt-fluid inclusions in it, indicates that such a kind of skarn-forming magma was water-rich and of low-viscosity. This magma may have been derived by differentiation and by carbonate assimilation of a parental quartz-monzodiorite magma (Ling et al. 1998; Wu and Chang 1998). In contrast, the diopside skarn at the contact zones surrounding the Shizishan quartz-monzodiorite is likely to have been produced by fluid reaction with sedimentary carbonates. During the formation of this skarn, the fluids of the Shizishan deposit decreased in temperature to 468–422°C and salinity to 38–46 wt.% NaCl equivalent. These values accord with the fluid-inclusion data of anhydrous skarn minerals in many other skarn-type deposits (Fommeilles 1989; Huang 1994; Chen et al. 2007b).

Copper–gold ores at Tongnuijing were precipitated from fluids comparable to those of porphyry-type deposits in relatively higher temperatures and salinities (Zaw et al. 1994; Chen and Li 2009). When these fluids entered a dilatant space, rapid pressure reduction
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(pressure quenching, Burnham 1997) triggered boiling. Fluid inclusions in this vein-type deposit have three prominent features: (1) inclusions with salinities lower than 30 wt.% NaCl equivalent are scarce in the deposit (Figure 11); (2) inclusions at mine level of −10 m (the highest level of the deposit) are most abundant in daughter minerals; and (3) daughter-bearing multi-phase inclusions at this level are higher in vapour/vapour + liquid ratio than those at deeper levels. These features may indicate that water loss and boiling occurred in an open system during ore formation, particularly in the upper levels.

In the Xiaomiaoshan deposit, no evidence for fluid boiling has been found, but fluid mixing of two end members is noticeable. Inclusions of Group I (Figure 12) with salinities higher than 40 wt.% NaCl equivalent and highest temperatures probably represent a magmatic fluid, and this should have been trapped in the earliest stages of the ore-forming process. Fluids for Group III (Figure 12) with salinities lower than 3 wt.% NaCl equivalent probably represent a meteoric end member. This is substantiated by the lower δ18O values of the inclusion fluids from the ore veins (Figure 13). Interestingly, despite the fact that the temperature decrease of the fluid inclusions from Groups I through Group II to Group III is essentially continuous, no inclusions with salinities of between 20 and 40 wt.% NaCl equivalent have been found. This salinity gap coupled with continuous temperature decrease is an indication that the low-salinity fluid was heated when it mixed with the high-salinity fluid.

Boiling of ore-forming fluids is a ubiquitous phenomenon in Mesozoic hydrothermal copper–gold deposits of the lower Yangtze River Valley, and multi-stage boiling has been recognized in the Shizishan deposit (Zhou and Yue 2000; Xiao et al. 2002; Lu et al. 2007; Chu et al., submitted). The mechanical energy for the formation of breccia pipes, such as that at Shizishan, was explained by Burnham (1997) to have been produced by an episode of boiling in the apical zone of an intrusive body. The energy for boiling was provided by the release of crystallization heat and exsolution of volatiles. Therefore, such a kind of boiling could be referred to as active boiling (or second boiling). Pre-mineralization active boiling as at Shizhishan resulted in the formation of fractures and breccia pipes that provided pathways and spaces for migration and precipitation of ore-forming components. In contrast, syn-mineralization boiling could be a trigger for ore precipitation, possibly due to a rapid temperature drop. A diabatic expansion and concomitant pH increase of the fluids will result in destruction of metal complexes involving HCO3−, HS−, and Cl−, as acidic components such as CO2, H2S, and HCl, preferentially enter the vapour phases (Drummond and Ohmoto 1985; Chen et al. 2000). In addition, due to lowered temperature of the fluids, internal energy of the post-mineralization system is no longer sufficient to initiate boiling. However, boiling at this stage can be triggered by decompression or fracturing induced by volume contraction of the surrounding rocks on cooling or by tectonism (e.g. Norton and Cathles 1973; Bischoff 1991; Burnham 1997). Such a kind of boiling could be referred to as passive boiling (or first boiling). Some late-stage quartz-carbonate veins with minor sulphides in the Shizishan, Shaxi, and Tongniujing deposits are hosted by dilational fractures and are likely to be linked with passive boiling.

Hydrogen and oxygen isotope values indicate that meteoric water did not have much contribution to the ore-forming fluids of the cryptoexplosive breccia and skarn types at Shizishan, but a certain amount was probably involved in the porphyry-type deposit at Shaxi and the copper-gold vein at Tongniujing. Strong involvement of meteoric water occurred during the post-mineralization stage of the Shaxi deposit and in the fracture zone-type Xiaomiaoshan gold deposit that was formed at relatively lower temperatures. More contribution of meteoric water at later stages and lower temperatures could have resulted from the opening of contraction fractures and hence the channels for water circulation on cooling.
Conclusions

Our comparative fluid-inclusion study of typical hydrothermal copper and gold deposits of the lower Yangtze River Valley indicates that magmatic water dominated the high-temperature ore-forming fluids, whereas in the medium–lower temperature Xiaomiaoshan gold deposit and in the post-mineralization stage of the Shaxi porphyry copper deposit meteoric water was commonly involved. In a particular deposit, both fluid temperature and salinity were higher at early stages and generally decreased over time. Fluid boiling, either actively or passively driven, took place commonly and in some cases episodically, in these hydrothermal deposits, and played an important role in mineralization. Melt-fluid inclusions in garnet of the explosive breccia at Shizishan imply that, other than their replacive origin, some so-called skarn minerals can also be formed by direct crystallization from water-rich magmas.

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Geochemical and zircon U–Pb study of the Huangmeijian A-type granite: implications for geological evolution of the Lower Yangtze River belt

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The Early Cretaceous Huangmeijian Pluton is an A-type granite located on the northern bank of the Lower Yangtze River in Anhui Province, east-central China. It intruded the SE edge of the Early Cretaceous Luzong volcanic basin. The moderate- to coarse-grained granite is mainly composed of alkali feldspar, plagioclase, and quartz and has a typical A-type geochemical signature. LA-ICP-MS zircon dating yielded a weighted mean $^{206}$Pb/$^{238}$U age of 127.1 ± 1.4 Ma, similar to other A-type granites in the Lower Yangtze River belt, indicating an Early Cretaceous extensional environment. Temperatures calculated using the Ti-in-zircon thermometer suggest that the magma formed under high-temperature conditions (720–880°C). The low calculated \( \text{Ce(IV)}/\text{Ce(III)} \) ratio based on zircon rare earth element patterns indicates low oxygen fugacity for this A-type magma. Previous studies suggested that eastern China was an active plate margin related to the Early Cretaceous subduction of the Pacific and Izanagi plates. The ridge between these two plates probably passed under the Lower Yangtze River belt, forming A-type granites and adakites. The Huangmeijian Pluton is roughly the same age within error but is marginally older than the Baijuhuajian A-type granite in the eastern part of the Lower Yangtze River belt. A-type granite genesis in the Lower Yangtze River belt only lasted for 2–3 million years and slightly predates the transition from regional extension to compression. All these can be plausibly interpreted by the ridge subduction model, that is, A-type granites formed because of mantle upwelling through the slab window during subduction of the ridge separating the Pacific and Izanagi plates.

Keywords: A-type granitic intrusion; geochemistry; LA-ICP-MS zircon dating; Huangmeijian Pluton; Luzong volcanic basin; east-central China

Introduction

The Lower Yangtze River belt (LYRB), which ranges from Wuhan in Hubei province in the west to Zhenjiang in Jiangsu province in the east, is an important metallogenic belt in eastern China (Chang et al. 1991; Zhai et al. 1992, 1996; Pan and Dong 1999; Xing 1999; Deng et al. 2002). Most of the deposits in the LYRB formed during the Early Cretaceous...
period (140 ± 5 Ma) (Sun et al. 2003; Mao et al. 2006; Yang et al. 2007), and they are closely associated with adakites of the same age (Zhang et al. 2001a, b; Wang et al. 2004a, b, 2006, 2007). Much attention has been focused on the geological evolution of this region (e.g. Xing and Xu 1994, 1995; Chen and Jahn 1998; Zhou and Li 2000; Chen et al. 2001; Sun et al. 2007; Fan et al. 2008; Yuan et al. 2008; Xie et al. 2008; Zhou et al. 2008a, b; Ling et al. 2009; Xie et al. 2009; Yang et al. 2011). In addition to adakite, there are a large number of Cretaceous A-type granites along both banks of the LYRB (Zhang et al. 1988; Xing and Xu 1994; Fan et al. 2008; Wong et al. 2009). The age and formation of A-type granite is important for understanding the geological evolution of the LYRB.

The genesis of A-type granites in the LYRB remains controversial. A-type granite is anhydrous, alkaline, and anorogenic, which generally indicates formation in an extensional environment (Loiselle and Wones 1979; Eby 1990, 1992; Bonin 2007). The extensional environment in the LYRB was proposed to be either back-arc and post-collision extension settings (Du et al. 2007; Cao et al. 2008) or intracontinental shearing effect associated with mantle upwelling (Fan et al. 2008). Alternatively, it has been attributed to slab rollback of subducting Pacific plate (e.g. Wong et al. 2009) or a ridge subduction (Ling et al. 2009) based on the drifting history of the Pacific plate (Sun et al. 2007). The ridge subduction model implies that A-type granites in the LYRB would be progressively younger from west to east. Previously published dating results have not observed this (e.g. Zheng et al 1995; Fan et al. 2008; Wong et al. 2009).

In this contribution, we analysed the geochemistry and zircon ages of the Huangmeijian A-type granite on the northern bank of the LYRB to gain a better understanding of the genesis of A-type granite in the LYRB and firmer constraints on the geological evolution of the LYRB.

Geological background

The LYRB is situated in the northern margin of the Yangtze block in central eastern China (Figure 1A). The northern and northwestern boundaries of the region are the Xiangfan-Guangji and the Tancheng-Lujiang faults, which separate the Dabie orogenic belt in the north and the Yangtze block in the south, respectively. The southern boundary is the Jiangshan-Shaoxing fault that separates the Yangtze block from the Cathaysia block (Figure 1A). Late Mesozoic igneous rocks are widely outcropped in the LYRB. These igneous rocks intrude into Neoproterozoic low-grade metamorphic rocks and Palaeozoic to Triassic sedimentary strata, and are classified into three associations: Na-rich alkaline mafic, K-enriched, and high potassium calc-alkaline associations (Chang et al. 1991). According to tectonic, magmatic, and metallogenic characteristics, the LYRB can be divided into three associated belts: inner belt, north outer belt, and south outer belt (Xing and Xu 1995; Xing 1999). The inner belt, distributed along both banks of the Lower Yangtze River, has intense mineralization of Cu, Fe, S, and Au (Pan and Dong 1999; Xie et al. 2009; Huang et al. 2011; Yang and Lee 2011; Yuan et al. 2011; Sun et al. 2010, 2011), which are closely associated with adakites (Wang et al. 2004a, b, 2006, 2007; Ling et al. 2009). The north outer belt has Cu deposits, such as the Shaxi Cu deposit (Yang et al. 2007, 2011; Yu et al. 2008). The south outer belt contains mainly porphyry-type Mo, Cu, and Pb–Zn deposits (Xing 1999; Mao et al. 2006). Two A-type granite belts are distributed parallely on both banks of the Lower Yangtze River (Xing and Xu 1994) (Figure 1B). The Huangmeijian granite, situated at the southeast edge of Luzong Basin in Anhui province, is one of the largest A-type granite plutons on the northern bank of the Lower Yangtze.
River. It intruded in the Middle and Lower Jurassic sediment rocks in the east and in the Upper Cretaceous volcanic rocks in the west. No Jurassic volcanic rock in the Luzong Basin has been confirmed so far (Zhou et al. 2008b). Huangmeijian granites are faint red with moderate- to coarse-grained texture and are mainly composed of potassium feldspar (80–85%), quartz (10–15%), and plagioclase (5–10%) (Figure 2).

Figure 1. (A) Regional geological map of Lower Yangtze River. (B) Geological map of the Huangmeijian granite. Modified after Chen (2001).
Whole-rock major and trace element analyses

The major and trace elements of the bulk rock samples were analysed at the Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Whole-rock samples were first powdered in an agate mill to less than 200 mesh, and then fluxed with Li$_2$B$_4$O$_7$ to make homogeneous glass disks at 1150–1200°C using a V8C automatic fusion machine produced by the Analymate Company in China. The bulk rock major elements were analysed by X-ray fluorescence spectrometry (Rigaku 100e), with a sample/flux ratio of 1 : 8. Analytical precision for major elements was better than 1% (Ma et al. 2007).

For trace element analyses, samples were first digested with a mixture of HF and HNO$_3$ in screw top PTFE-lined stainless steel bombs at 185°C for 2 days, and insoluble residues were dissolved in HNO$_3$ after being heated to 145°C for 3 h using closed high-pressure bombs to ensure complete digestion. Pure RH standard solutions were used for internal calibration and GSR-1, BHVO-1, and OU-6 were used as reference materials to monitor data quality. Bulk rock trace elements were analysed using ICP-MS, with accuracies of better than 5% for most elements (Liu et al. 1996).

Zircon U–Pb dating and zircon trace element analyses

Zircons were separated using a conventional method, which involved powdering samples to 80 mesh, desliming in water, density separation, magnetic separation, and finally handpicking.
Zircon grains were then mounted in epoxy and polished down to nearly a half section to expose internal structures. Cathodoluminescent and optical microscopy images were taken to ensure that the least fractured, inclusion-free zones in zircon were analysed. Zircon U–Pb dating and trace elements were analysed at the Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The LA-ICPMS system is composed of an Agilent 7500a ICP-MS coupled with a Resonetic RESOLution 50-M ArF-Excimer laser source (λ = 193 nm). Laser energy was 80 mJ and frequency was 10 Hz with ablation spot of 31 μm in diameter and 40 s ablation time. Both a double-volume sampling cell and a Squid pulse-smoothing device were used to improve data quality (Tu et al. 2009). Helium gas was used as the carrier gas to the ICP source. NIST610 and TEM were used as external calibration standards and 95Zr as the internal standard. The calculation of isotope ratios, trace elements, and Ce anomalies were performed using software from the Research School of Earth Sciences, Australian National University; the age was calculated by Isoplot (Version 3.23).

Results

Whole-rock major and trace elements

Ten samples were analysed for major and trace element compositions. The Huangmeijian granite is characterized by high SiO2 (64.3–74.1 wt.%), Al2O3 (13.4–17.4 wt.%), Fe2O3T (2.12–3.62 wt.%), Na2O (4.30–5.56 wt.%), K2O (4.85–6.99 wt.%), lower TiO2 (0.15–0.53 wt.%), MgO (0.02–1.13 wt.%), CaO (0.12–0.53 wt.%), and P2O5 (0.01–0.10 wt.%). In comparison to other rocks of similar age in the LYRB (Table 1), the samples are classified as alkali-feldspar quartz-syenite. They are metaluminous or metaluminous-peraluminous rocks with A/CNK (molar Al2O3/(CaO + Na2O + K2O)) values of 0.96–1.12 (Figure 3B). In Hacker diagrams, TiO2 and Fe2O3T decrease with increasing SiO2, indicating fractional crystallization of Ti–Fe oxide (Figure 4).

Most of the samples have low Sr (7.20–27.4 ppm) and high Nb (71.8–118 ppm) and Rb (322–572 ppm) concentrations; they also have high rare earth elements (REEs), with total REE concentrations of 210–667 ppm. A chondrite-normalized REE diagram shows that the Huangmeijian samples are LREE enriched (LaN/YbN = 7.19–15.7) with flat heavy REE and negative Eu anomalies (Eu/Eu* = 0.09–0.87), which indicates the removal of plagioclase by fractional crystallization (Figure 5). The decrease in Sr and Ba and slight increase in Rb with increasing SiO2 may also be due to plagioclase fractionation. Negative anomalies in Ba, Sr, and Eu, as shown in the primitive mantle-normalized trace element diagram (Figure 6), suggest fractional crystallization of feldspar. In contrast, Nb, Ta, Zr, and Hf are not depleted, implying little contribution of crustal- or subduction-related material in the magma source. The depletion of Ti coupled with high Nb and Ta concentrations suggests crystallization of ilmenite, with little influence of rutile or titanite. Ilmenite, rutile, and titanite are the three popular Ti minerals (Liou et al. 1998). Rutile and titanite usually have high concentrations of Nb and Ta (Manning and Bohlen 1991; McDonough 1991; Green 1995; Rudnick et al. 2000; Foley et al. 2002; Xiong et al. 2005; Xiao et al. 2006; Ding et al. 2009; Liang et al. 2009). In contrast, ilmenite usually has much lower Nb and Ta (Ding et al. 2009). Thus, crystallization of ilmenite takes Ti out of the magma, leading to depletion of Ti in the granite without significant decrease of Nb and Ta.
Compared to Baijuhuajian A-type granite in northeastern Quzhou, western Zhejiang Province, in the northwest region of the NW-trending Jiangshan-Shaoxing fault zone (Wong et al. 2009), samples from Huangmeijian have lower SiO$_2$ and higher CaO, TiO$_2$, Fe$_2$O$_3$ $^T$, P$_2$O$_5$, Sr, and Ba. In Hacker diagrams, samples from both rocks have a good negative linear relationship between SiO$_2$ and CaO, TiO$_2$, Fe$_2$O$_3$ $^T$, P$_2$O$_5$, Sr, and Ba. In a chondrite-normalized REE diagram, Huangmeijian samples have higher light REE (LREE) and lower heavy REE (HREE) patterns, with stronger negative Eu anomaly.
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Enrichment of the LREE indicates an enriched origin, thus the composition of Huangmeijian granite is relatively more enriched than that of Baijuhuajian granite (Table 2).

**LA-ICPMS U–Pb zircon dating**

The results of LA-ICP-MS analysis are listed in Table 3. Zircon CL images of sample 08HMJ02 are shown in Figure 7. Zircons from this sample are euhedral with lengths ranging from 250 to 350 μm and are characterized by a dark brown colour, which is very likely due to high U and Th concentrations. No inherited cores were observed in these zircons. U and Th concentrations varied widely (U from 370 to 2470 ppm, Th from 140 to 2170 ppm), with Th/U ratios ranging from 0.15 to 1.63, indicating a magmatic origin (Hoskin and Black 2000; Belousova et al. 2002; Sun et al. 2002). All results are concordant or nearly concordant. The data can be divided into two groups as shown in the zircon U–Pb age histogram: one group with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 127.1 ± 1.4 Ma
(MSWD = 0.82, n = 12) and the other group with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 142.3 ± 1.6 Ma (MSWD = 0.39, n = 10) (Figure 8). Given that both groups are magmatic zircon, the younger ages represent the crystallization age of the magma.
Zircon trace element patterns

The zircon chondrite-normalized REE diagram shows an Eu negative anomaly and slight Ce positive anomaly in most zircon analyses. Only a few zircon grains have a slight Ce negative anomaly (Figure 9, Table 4). The older zircons have consistent chondrite-normalized REE patterns, whereas the younger zircons have chondrite-normalized REEs
Table 3. LA-ICPMS zircon U–Pb isotope composition and age of the Huangmeijian granite.

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<th>Th (ppm)</th>
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<th>Ce(IV)/ Ce(III)</th>
<th>Isotopic ratios</th>
<th>Age (Ma)</th>
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with a large range of LREEs, especially La (Figure 9). The ratio of Ce(IV)/Ce(III) ranges from 2.30 to 42.0 (Table 3). The younger zircon group shows a small range of Ce(IV)/Ce(III) ratios (Figure 10), whereas the older zircon group shows a relatively larger range of Ce(IV)/Ce(III) ratios. The low Ce(IV)/Ce(III) ratio indicates that the Huangmeijian granite formed at low oxygen fugacity (Ballard et al. 2002; Liang et al. 2006). The large range of Ce(IV)/Ce(III) ratios of the older zircon group is likely due to capturing zircon grains of different origins, for example high oxygen fugacity adakitic intrusions (Xie et al. 2009) and other rocks of similar ages. Titanium concentration in the zircons ranges from 2.99 to 831 ppm, with younger zircons showing relatively low Ti concentrations. According to Ti concentrations and the formula of Watson et al. (2006), calculated temperatures of zircon formation range from 720°C to 1140°C. Zircons with younger ages have a smaller temperature range (720–820°C) as shown in Figure 11. By contrast, the older zircon group has a larger range of temperature, which again suggests its diverse origins, that is, inherited or captured.

**Petrogenesis and tectonic implications**

**The Huangmeijian Pluton: an A-type affinity**

The term ‘A-type granite’ was first proposed by Loiselle and Wones (1979) to distinguish a special group of granitic rocks that occurs in an extensional tectonic environment like rift zones or anorogenic settings. This group of granite shares common characteristics of high FeO_T/(FeO_T + MgO) and K_2O/Na_2O ratios, high K_2O content, and enrichment of incompatible elements such as REEs (except Eu), Zr, Nb, and Ta. A-type granite also has high TiO_2/MgO ratios (Douce 1997). Concentrations of Ba, Sr, and Eu, as well as water fugacity, are low for A-type granite (Loiselle and Wones 1979).

The Huangmeijian granite has all the geochemical characteristics of A-type granite. It contains high total alkalis (K_2O + Na_2O = 8.90–12.1 wt.%) and plots into the alkaline area of the SiO_2–AR diagram (Figure 12). ACNK ranges from 0.96 to 1.15, showing a metaluminous-peraluminous nature. The high Fe* [FeO_T/(FeO_T + MgO) = 0.93–0.99] of the Huangmeijian granite is also a typical characteristic of A-type granite.

The trace element composition of the Huangmeijian granite also shows characteristics of A-type granites. The Huangmeijian granite is enriched in HFSE (Zr, Nb, Y) and REEs, whereas depleted in Ba, Sr, P, Ti, and Eu. The total concentrations of Nb, Zr, Ce, and Y (549–1489 ppm) > 350 ppm and the Nb/Ta (10.4–17.6) and Zr/Hf (25.1–71.5) ratios also show characteristics of A-type granites. The ratio of Y/Nb (0.49–0.81) indicates an intra-plate formation environment and mainly mantle origin (Eby 1992).

Various discrimination diagrams are used to constrain their genetic environment and discriminate A-type granite from other kinds of granite. In the Pearce diagram, samples from the Huangmeijian granite are plotted in the within-plate area (Pearce et al. 1984) (Figure 13A), and they are mainly formed in the rift valley environment as shown in Figure 13. In FeO_T/MgO, Nb, Zr versus 10,000 Ga/Al diagrams, all Huangmeijian granite samples are plotted into the A-type granite area except for two samples (Figure 13B–D), and are characterized by high FeO_T/MgO ratio and high 10,000 Ga/Al ratio (2.95–3.91). These are typical characteristics of A-type granite.

**Petrogenesis of the Huangmeijian granite**

Although A-type granite is generally attributed to extensional environment, its petrogenesis is still controversial. One model proposed that A-type granite is the result of fractionation
Figure 7. CL images of representative zircon grains for the Huangmeijian granite. The dark colour is likely due to high Th, U concentrations.
Figure 8. (A) Concordia diagram of the Huangmeijian granite (08HMJ02). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age is 127.1 ± 1.4 Ma. (B) Concordia diagram of the Huangmeijian granite (08HMJ02). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age is 142.3 ± 1.6 Ma. (C) Histograms of weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age for zircons from the Huangmeijian granite. Given that all the zircons have high Th/U, such that they are magmatic, the younger group represents the crystallization of the Huangmeijian granite.
of basaltic magmas, with or without crustal contamination (Loiselle and Wones 1979; Turner et al. 1992; Smith et al. 1999; Anderson et al. 2003). Another model attributed it to the melting of deep crust materials such as granulitic meta-igneous sources that were previously depleted by extraction of a hydrous felsic melt (Collins et al. 1982; Clemens et al. 1986; Whalen et al. 1987). The latter model conflicts with the fact that A-type granite has high TiO₂/MgO and K₂O/Na₂O ratios (Creaser et al. 1991; Douce 1997). Experimental results suggest that the refractory granulitic residues from partial melting of a wide range of crustal rocks are characteristically depleted in alkalis relative to Al and depleted in TiO₂ relative to MgO (Creaser et al. 1991; Douce 1997). Re-melting of these residues cannot produce granitic liquids with the high (Na₂O + K₂O)/Al₂O₃ and TiO₂/MgO ratios that are characteristic of A-type granite. Moreover, to produce granites containing chemical and isotopic signatures of both mantle and crust, various models have been proposed, for example, fractionation of variously contaminated, mantle-derived alkali basalt (Bonin

Figure 9. Zircon chondrite-normalized REE diagram for the Huangmeijian granite.

Figure 10. Zircon Ce(IV)/Ce(III) versus ²⁰⁶Pb/²³⁸U age diagram for the Huangmeijian granite.
Table 4. Zircon trace element data for Huangmeijian granite (ppm).

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</table>
mixing of crustal melts with OIB magma (Eby 1990, 1992), and evolution of mantle-derived mafic and intermediate magmas (Turner et al. 1992).

Major and trace element compositions of the Huangmeijian A-type granite give constraints on its origin. The overall high and large ranges of Nb (71.8–118 ppm), Ta (4.32–8.05 ppm) concentrations, as well as low Y/Nb (0.49–0.81) ratios and Zr concentration, indicate an origin of mantle source with a little crustal contamination. Given that the crust has a higher ratio of Y/Nb (>2), crustal contamination increases the value of Y/Nb (Eby 1992). The incompatible element ratio diagrams show that the Huangmeijian A-type

Figure 11. SiO₂–AR diagram for the Huangmeijian granite.

Figure 12. Zircon temperature versus \(^{206}\text{Pb}^{238}\text{U}\) age diagram for the Huangmeijian granite.
granite has chemical characteristics similar to OIB (Figure 14). This also indicates magma origin from the enriched mantle with little crustal contamination during mantle upwelling. The Nd isotope characteristics of the Huangmeijian A-type granite also support the enriched mantle source origin, with $\varepsilon_{\text{Nd}}$ of $-2.50$ (Xing and Xu 1994).

Regional extension and tectonic evolution of the LYRB

The geodynamic mechanism for the formation of A-type granite in the LYRB is controversial. One proposed model is that A-type granite in the LYRB formed in back-arc and post-collision extension settings related to the Triassic collision between the North and South China blocks (Du et al. 2007; Cao et al. 2008). The Triassic collision, however, occurred in the Qinling-Dabie orogenic belt (Meng and Zhang 1999; Li et al. 2000; Sun et al. 2002; Zheng et al. 2003; Zhou et al. 2008c), whereas A-type granites distribute mainly in the LYRB (Xing and Xu 1994; Fan et al. 2008; Ling et al. 2009; Wong et al. 2009). It is difficult to form A-type granite up to several hundred kilometres away from the orogenic belt after about 100 Ma through post-collisional extension. Alternatively, the extension environment has been attributed to an intracontinental shearing associated with mantle upwelling (Fan et al. 2008; Zhou et al. 2008a, 2008b). This model, however, does not explain why mantle upwelling occurred within a short period of time (only 2–3 Ma). Some

![Figure 13. (A) Discrimination diagrams for granites (Pearce et al. 1984). The Huangmeijian granites are plotted in the field of WPG (= within-plate granite). (B) FeO/MgO versus 10000 Ga/Al diagram (Whalen et al. 1987). The Huangmeijian granitic samples are plotted in the field of A-type granite. (C and d) Discrimination diagrams for granites (Whalen et al. 1987). Samples of the Huangmeijian granite are plotted into the area of A-type granites.](image)
A-type granite rocks in the eastern part of the region were assumed to be the result of slab rollback (Wong et al. 2009) based on the drifting history of the Pacific plate (Koppers et al. 2001; Sun et al. 2007). The Pacific plate may have started to subduct underneath eastern China during the Late Jurassic (Zhou and Li 2000; Li and Li 2007; Wang et al. 2011), but a simple slab rollback model cannot plausibly explain why A-type granites in the LYRB formed within a short period of time in the Early Cretaceous and distributed linearly from west to east. Moreover, none of these models paid any detailed attention to adakites and other rocks of the Early Cretaceous in the region, which are spatially closely associated with but slightly predate A-type granites. Based on the distribution of adakite, A-type granite, and Nb-enriched volcanic rocks, a ridge subduction model has also been proposed (Ling et al. 2009). According to this model, A-type granites formed when a slab window opened during the late stage of the ridge subduction (Ling et al. 2009).

Figure 14. (A) Yb/Ta versus Y/Nb and (B) Y/Nb versus Ce/Nb diagrams for the Huangmeijian granite (Eby 1992). OIB = oceanic island basalt; IAB = island arc basalt. Fields with dashed lines represent A1- and A2-type granites of Eby (1990).
From the Late Jurassic to the Early Cretaceous, there were two plates subducting under eastern China. They were the Pacific plate, subducting towards the southwest, and the Izanagi plate subducting towards the northwest (Maruyama et al. 1997, Sun et al. 2007). Because of the different directions and different velocities between the Pacific and the Izanagi plates, the ridge between these two plates moved westward during the subduction and subducted under the Lower Yangtze River region at about 140 Ma. The ridge gradually opened as the subduction continued, forming a slab window and consequently, A-type granites (Ling et al. 2009). The asthenospheric mantle is characterized by dry and high temperatures. Previous studies on ridge subduction have already suggested that A-type granite associated with ridge subduction probably resulted from asthenospheric mantle material upwelling through the slab window and evolved at shallow crust in low pressure condition (Thorkelson and Breitsprecher 2005).

The Huangmeijian A-type granite has the characteristics of high genesis temperature, with oxygen fugacity lower than that of adakites in the region. We suggest that the Huangmeijian A-type granite resulted from the ridge subduction. During the ridge subduction, the ridge between the Pacific and the Izanagi plates opened; consequently, enriched mantle materials melted due to hot mantle materials upwelling through the slab window.

Previous dating results showed that Huangmeijian A-type granite (125.4 ± 1.7 Ma; Fan et al. 2008) formed at exactly the same time as the Baijuhuajian A-type granite (125.6 ± 3.2 Ma; Wong et al. 2009), several hundred kilometres to the east. Interestingly, the K–Ar age of the Huangmeijian granite is identical to its zircon U–Th age (Zheng 1995). Considering the high temperature of the Huangmeijian granite, this is unusual. Our new result (127.1 ± 1.4 Ma) is marginally older than previous results. The age difference between our result and that of Baijuhuajian A-type granite is 1.5 Ma, which is about the same as the 2σ error of our result and the 1σ error of the Baijuhuajian age. This suggests that the age difference is real at a confidence level of approximately 60%. This is consistent with the ridge subduction model as the slab window opened from the west and migrated eastward.

As mentioned above, compared to the geochemical characteristics of the Baijuhuajian A-type granite, the Huangmeijian granite is enriched in LREEs and depleted in HREEs with lower SiO₂, indicating a more enriched mantle source for the Huangmeijian granite. Enriched mantle source was common in eastern China before 110 Ma (Xu 2001, 2006). Given that the Baijuhuajian granite is located in the east, closer to the subduction zone, it is likely that more enriched mantle materials there were removed by early subduction, such that the granite itself is less enriched compared to Huangmeijian.

Conclusions

Geochemical data indicate that the Huangmeijian granite, exposed along the northern bank of the LYRB, is a typical A-type granite characterized by high Fe* (FeO_t/(FeO_t + MgO)), enrichments of incompatible elements [REEs (except Eu), Zr, Nb, and Ta], and depletion in Ba, Sr, and Eu. High genesis temperature and low oxygen fugacity are consistent with its mantle origin. Negative εNd values indicate the evolvement of enriched mantle ± crustal materials. Zircon U–Pb ages of the Huangmeijian A-type granite range from 127 to 142 Ma, which can be classified into two groups with the younger representing its crystallization age (127 Ma). Together with previous studies, we suggest that the genesis of Huangmeijian A-type granite was due to the slab window related to a Cretaceous ridge subduction in the LYRB, which opened at ≥127 Ma.
Acknowledgements

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Petrogenesis of volcanic and intrusive rocks of the Zhuanqiao stage, Luzong Basin, Yangtze metallogenic belt, east China: implications for ore deposition

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The Mesozoic Luzong volcanic basin is located in the Lower Yangtze River fault-depression, along the northern margin of the Yangtze Block. Volcanic and plutonic rocks are widely distributed in the basin and are spatially related to Cu, Fe, Au, Pb, and Zn ore deposits. The magmatic rocks are dominated by an alkali-rich shoshonitic suite of volcanics and intrusives, including both a trachybasalt-basaltic trachyandesite-trachyte series and a diorite-monzonite-syenite-alkali feldspar granite series. Volcanic sequences within the Luzong Basin are subdivided into four stages, namely the Longmenyuan, Zhuanqiao, Shuangmiao, and Fushan stages with magmatism occurring between 136 and 124 Ma. Most mineral deposits were formed during the Zhuanqiao stage from about 134 to 131 Ma, during a longer (140–130 Ma) period of transition from compression to extension within the Luzong Basin.

Major element concentrations in the Zhuanqiao volcanic rocks range from 53.97 to 62.59 wt.% SiO\textsubscript{2}, 0.57–0.94 wt.% TiO\textsubscript{2}, 3.52–6.07 wt.% Na\textsubscript{2}O, and 3.60–8.66 wt.% K\textsubscript{2}O. Combined K\textsubscript{2}O + Na\textsubscript{2}O totals lie between 7.87 and 12.49 wt.%, and K\textsubscript{2}O + Na\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} ranges between 0.47 and 0.71. In comparison, the Zhuanqiao intrusions have SiO\textsubscript{2} concentrations between 52.19 and 67.70 wt.%, TiO\textsubscript{2} between 0.26 and 1.13 wt.%, Na\textsubscript{2}O between 1.33 and 6.55 wt.%, and K\textsubscript{2}O between 2.15 and 8.25 wt.%, with K\textsubscript{2}O + Na\textsubscript{2}O values ranging from 5.92 to 12.39 wt.% and K\textsubscript{2}O + Na\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} ratios between 0.37 and 0.75. The Zhuanqiao volcanic rocks have an average ΣREE (rare earth element) content of 223.17 ppm, whereas the average ΣREE of the Zhuanqiao intrusives is 250.06 ppm. Weak negative Eu anomalies (Eu/Eu* between 0.69 and 1.00) characterize the volcanics, whereas a larger range with more significant negative Eu anomalies (Eu/Eu* values of 0.35–0.94) is present in the plutonics. The Zhuanqiao volcanic rocks and plutons have (Nb/Th)\textsubscript{PM} ratios of 0.05–0.14 and 0.02–0.14 and (La/Sm)\textsubscript{PM} of 3.33–4.95 and 3.36–7.29, respectively. Initial \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{143}\text{Nd}/^{144}\text{Nd}\) ratios and \(\varepsilon_{\text{Sr}}(t)\) and \(\varepsilon_{\text{Nd}}(t)\) of the Zhuanqiao volcanic rocks are 0.7059–0.7067, 0.51194–0.51218, 22.0–33.3, and −10.2 to −5.5, respectively; those of the intrusives are 0.7060–0.7082 and 0.51203–0.51214 and 23.3–54.7 and −8.6 to −6.4, respectively. The geochemistry presented here suggests that both volcanic and intrusive Zhuanqiao stage magmatic rocks were cogenetic and were probably derived from an enriched mantle (EM) source, most probably metasomatized mantle relating to the EM type-I (EM-I). The Zhuanqiao stage magmatism apparently was controlled by differentiation and assimilation of crustal material in a high-level magma chamber.

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Formation of the Zhuanqiao stage magmatic rocks coincided with the formation of much of the Cu and Fe mineralization within the Luzong Basin. This coeval magmatism and mineralization during the Zhuanqiao stage can be subdivided into three differing mineral deposit affinities: magmatism associated with magmato-hydrothermal vein Cu (e.g. the Jingbian, Shimenan, and Chuanshandong deposits), porphyry-hosted Fe (e.g. the Luohe and Nihe deposits), and skarn Fe (e.g. the Longqiao deposit). Combining geological characteristics with variations in SiO₂, K₂O + Na₂O, and MgO enabled the division of the Zhuanqiao stage magmatism in the Luzong Basin into geochemically distinct units associated with these differing styles of mineralization.

Keywords: magmatic rocks; ore deposit; Zhuanqiao magmatism; Luzong volcanic basin; Yangtze metallogenic belt

Introduction
The Yangtze metallogenic belt occupies the middle and lower reaches of the Yangtze River, within the fracture zone on the northern margin of the Yangtze Block. The area hosts various Fe, Cu, Au, and polymetallic deposits within smaller secondary tectonic features (Chang et al. 1991; Zhai et al. 1992). Within the metallogenic belt, the Luzong volcanic basin is an important area for iron, copper, lead, and zinc mineralization. Volcanic rocks and intrusives within the Luzong Basin are spatially related to the mineralization; this study aims to determine whether this spatial relationship is also a genetic relationship, and, if so, whether individual mineral deposit types are associated with differing types of magmatism. The identification of genetic links between mineral deposits and magmatic units can then be used in mineral exploration to target volcanic and plutonic areas for specific commodities and types of ore deposit.

In the 1990s, research in the Luzong volcanic basin focused on basic descriptions of the mineral deposits and implications for regional metallogenesis (Chang et al. 1991; Hu et al. 1991; Ren et al. 1991; Zhai et al. 1992; Zhang 1992; Liu 1994; Ni et al. 1994; Wang et al. 1996; Wu et al. 1996; Tang et al. 1998; Pan and Dong 1999; Wei and Zhang 1999). More recent research has focused on the temporal–spatial framework, evolution, and geodynamic processes in the Luzong Basin and the influence that these processes had on metallogenesis (Liu et al. 2002; Chen et al. 2005; Yan et al. 2005; Mao et al. 2006; Wang et al. 2006, 2011; Liu et al. 2007; Xie et al. 2007; Zhou et al. 2007, 2008; Fan et al. 2008; Yuan et al. 2008; Xie et al. 2009; Chu et al. submitted; Deng et al. 2011, submitted; Li et al. 2011; Sun et al. 2011; Yang et al. 2011; Zhang et al. 2011). The recent discovery of the large Nihe iron deposit (>200 million tons Fe), which is thought to be genetically associated with a Zhuanqiao stage dioritic porphyry body, suggested a genetic link between the type of magmatism and the mineral deposits. This metallogenetic specialization of magmatic bodies is the focus of this article; here, we discuss the volcanic and intrusive magmatism of the Zhuanqiao stage of evolution of the Luzong Basin, the relationship this magmatism had to metallogenesis, and the implications for targeting individual mineral deposit types within the Yangtze metallogenic belt.

Geological background
The Mesozoic Luzong volcanic basin is located in the Lower Yangtze River fault-depression zone along the northern margin of the Yangtze Block. This basin is controlled by NE, near E–W, SN, and NW-trending fault zones, is considered to be a fault basin formed by the reactivation of pre-existing faults (Ren et al. 1991; Zhou et al. 2008), and contains approximately 800 km² of outcropping volcanic units. Rocks within the basin are dominantly of
Triassic, Jurassic, Cretaceous, and Quaternary ages; thin Silurian, Devonian, Carboniferous, and Permian sequences are also present towards the margins of the basin.

The Mesozoic volcanic rocks within the basin can be divided into four formations: from bottom to top, these are the Longmenyuan, Zhuanqiao, Shuangmiao, and Fushan Formations (Figure 1). The basal Longmenyuan Formation is present only at the outer edges of the basin, consists of hornblende trachyandesites, and has a thickness of >440 m. The Zhuanqiao Formation is present at the centre of the basin, is typically pyroxene-trachyandesite in composition, and is >1082 m thick. The trachybasalts and trachydacites of the Shuangmiao Formation are present in the central and southern sections of the basin and are >588 m thick. Overlying these units is the uppermost Fushan Formation; this unit outcrops in the centre of the basin, has a thickness of over 454 m, and is dominated by trachytic lavas.

Silurian–Jurassic age diorite, monzonite, syenite, and granite intrusions are also present within the Luzong volcanic basin (Figure 1). Zhou et al. (2008) and Yuan et al. (2008) suggested that these intrusions could be divided into four groups corresponding with the four volcanic formations described above, that is, splitting all magmatism in the basin into the Longmenyuan, Zhuanqiao, Shuangmiao, and Fushan stages.

**Ore deposits and mineralization**

A number of major ore deposits are present in the Luzong Basin. These include the Luohe, Longqiao, Nihe, and Xiaoling iron deposits; the Dabaozhuang pyrite deposit; the Shaxi Cu deposit; the Yueshan Pb-Zn-Ag deposit; the Fanshan alunite deposit; the Shimenan and
Tiantoushan vein Cu-Au deposits; and the Bamaoshan Cu-Au deposit (Figure 1). These mineral deposits can be split into three distinct mineral deposit types associated with Zhuanqiao magmatism. These are vein magmato-hydrothermal Cu deposits (such as the Jingbian, Shimenan, and Chuanshandong deposits), porphyry-hosted Fe deposits (such as the Luohu and Nihe deposits), and skarn Fe deposits (such as the Longqiao deposit). All three mineral deposits appear to have formed in a basin-wide mineralizing event that occurred around 131 Ma.

The vein magmato-hydrothermal Cu deposits are closely associated with syenites, porphyritic syenites, and trachytic porphyries (Zhou et al. 2008). Ore minerals within these deposits are dominated by chalcopyrite, pyrite, bornite, specularite, and chalcocite and are associated with an alteration assemblage of amorphous silica, sericite, chlorite, and carbonate. The coeval porphyry-hosted Fe deposits are hosted by porphyritic diorite or trachyanodesite porphyry units (Fan et al. 2008). These deposits consist of pyrite, magnetite, hematite, and chalcopyrite and are associated with alkali feldspar, anhydrite, gypsum, and amorphous silica alteration. The third major mineral deposit type, the skarn Fe deposits, is related to porphyritic syenite or trachytic porphyry units, is dominated by magnetite and pyrite, and is associated with garnet, phlogopite, sericite, and tourmaline alteration (Zhou et al. 2008).

Sampling, sample preparation, and analytical methods

Volcanic rock samples analysed during this study are from the Zhuanqiao Formation in the middle of the Luzong Basin. A number of intrusives corresponding to the volcanic rocks of the Zhuanqiao Formation were also sampled, namely, the Xiewani (pyroxene-monzonite), Bamaoshan (monzonite), Jiaochong (quartz-syenite), Longqiao (syenite), Bajiatan (pyroxene-monzonite), and Jianshan Plutons (biotite-monzonite).

Samples of the least vesicular, least altered, and least weathered volcanic rocks and intrusions were collected, cleaned of any weathered surfaces, crushed using steel plates, and ground in agate mills. Samples were then analysed for major and trace element concentrations, and Sr and Nd isotopes.

Major and trace element concentrations were determined at the Centre of Excellence in Ore Deposits (CODES), University of Tasmania, Australia. Major element concentrations were determined by X-ray fluorescence (XRF) spectrometry. Trace element concentrations were determined by solution inductively coupled plasma-mass spectrometry (ICP-MS) using a PE Elan 6000 instrument. Prior to analysis, 100 mg of sample was digested with 1 ml of HF and 0.5 ml of HNO₃ in screw top PTFE-lined stainless steel bombs at 190°C for 12 hours. After this initial digest, an insoluble residue was dissolved using 8 ml of 40% HNO₃ (v:v) heated to 110°C for 3 hours. Analytical calibration was accomplished using aqueous standard solutions. The precisions of ICP-MS analysis were better than ±5% and the analytical precisions of the XRF were 1–2%.

Sr and Nd isotopic analysis was conducted at the Isotope Laboratory, Chinese Academy of Geological Sciences in Yichang. Analysis was performed using a 7-collector Finnigan MAT-261 mass spectrometer. \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios were normalized against the value of 0.71024. \(^{143}\text{Nd}/^{144}\text{Nd}\) ratios were normalized against the value of 0.7219. The notations of \(\varepsilon_{\text{Sr}}(t)\) and \(\varepsilon_{\text{Nd}}(t)\) are according to DePaolo (1981). The standard errors for Sr and Nd isotopes are reported at the 2σ confidence level.

The new geochemical data in this study are reproduced in Tables 1 and 2. The discussion in this article is based on our new data, as well as the published data from Zhao et al. (2003), Ren et al. (1991), Liu et al. (2002), Wang et al. (2006), Xing and Xu (1998), Liu.
Table 1. Major (wt.%) and trace (ppm) element compositions of magmatic rocks in the Luzong Basin.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zhuanqiao Formation</th>
<th>Xiewani Pluton</th>
<th>Bamaoshan Pluton</th>
<th>Jiaochong Pluton</th>
<th>Longqiao Pluton</th>
<th>Bajiatan Pluton</th>
<th>Jianshan Pluton</th>
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(1994), which are not listed due to space limitations, but the complete set of the data is available from the authors free of charge upon request.

**Geochemistry**

**Major and trace element concentrations**

SiO$_2$ abundances of the Zhuanqiao stage volcanic rocks range from 53.97 to 62.59 wt.% with an average value of 57.87 wt.%, TiO$_2$ from 0.57 to 0.94 wt.%, Na$_2$O from 3.52 to 6.07 wt.%, K$_2$O from 3.60 to 8.66 wt.%, and K$_2$O + Na$_2$O values ranging from 7.87 to 12.49 wt.% with an average value of 9.84 wt.%. K$_2$O + Na$_2$O/Al$_2$O$_3$ ratios range from 0.47 to 0.71. SiO$_2$ concentrations of the Zhuanqiao stage intrusions range from 52.19 to 67.70 wt.% with an average value of 59.19 wt.%, whereas TiO$_2$ concentrations vary from 0.26 to 1.13 wt.%, Na$_2$O from 1.33 to 6.55 wt.%, K$_2$O from 2.15 to 8.25 wt.%, and K$_2$O + Na$_2$O values ranging from 5.92 to 12.39 wt.% with an average value of 9.73 wt.%. K$_2$O + Na$_2$O/Al$_2$O$_3$ ratios have a similar range as the volcanics from 0.37 to 0.75. Both volcanic rocks and intrusions have high alkali contents, characteristic of alkaline magmatic rocks.

Using a total alkali versus silica (TAS) diagram, volcanic rocks can be classified as basaltic trachyandesites, trachyandesites, trachytic dacites, and trachytes (Figure 2A). The compositions of these volcanics broadly overlap with the intrusives, which are classified as monzodiorites, monzonites, quartz-monzoites, and syenites (Figure 2B). Plotting SiO$_2$ against K$_2$O indicates that both volcanics and intrusives of the Zhuanqiao stage are shoshonitic (Figure 3). In the Harker plot (Figure 4), volcanics and intrusives are compositionally similar: CaO, TiO$_2$, P$_2$O$_5$, FeO$_T$ (FeO + Fe$_2$O$_3$ x 0.9); and MgO decrease with increasing SiO$_2$, indicative of olivine, pyroxene, ilmenite, and apatite fractionation during magmatic evolution. There is a rapid decrease in Na$_2$O with increasing SiO$_2$, indicating potential plagioclase differentiation took place during the formation of either intrusives or volcanics. With increasing evolution of both volcanic and intrusive magmatic systems, coincident decreases in Fe, Mg, and Ca are evident.

The volcanic rocks have an average ΣREE content of 223.17 ppm whereas the plutonic rocks have a ΣREE average of 250.06 ppm. Weak negative Eu anomalies (Eu/Eu* between 0.69 and 1.00) are observed in the volcanic rocks, whereas a larger range with more significant negative Eu anomalies (Eu/Eu* values of 0.35–0.94) are present in the plutonic rocks.

### Table 2. Nd, Sr isotopes composition of magmatic rocks in the Luzong Basin.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zhuanqiao Formation</th>
<th>Xiewani Pluton</th>
<th>Bamaoshan Pluton</th>
<th>Jiaochong Pluton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithology</td>
<td>Trachyandesite</td>
<td>Pyroxene-trachyandesite</td>
<td>Pyroxene-monzonite</td>
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<td>$^{147}$Sm/$^{144}$Nd</td>
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<tr>
<td>$^{143}$Nd/$^{144}$Nd</td>
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<td>0.51204</td>
<td>0.51219</td>
<td>0.51214</td>
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<tr>
<td>($^{143}$Nd/$^{144}$Nd)$_i$</td>
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<td>0.51194</td>
<td>0.51211</td>
<td>0.51204</td>
</tr>
<tr>
<td>$^{87}$Rb/$^{86}$Sr</td>
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<td>−7.1</td>
<td>−8.4</td>
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<tr>
<td>$^{87}$Sr/$^{86}$Sr</td>
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<td>1.1120</td>
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<tr>
<td>($^{87}$Sr/$^{86}$Sr)$_i$</td>
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<td>0.7088</td>
<td>0.7083</td>
<td>0.7121</td>
</tr>
<tr>
<td>$^{86}$Sr/$^{87}$Sr</td>
<td>0.7062</td>
<td>0.7067</td>
<td>0.7062</td>
<td>0.7066</td>
</tr>
<tr>
<td>$^{86}$Sr/$^{87}$Sr</td>
<td>24.7</td>
<td>33.3</td>
<td>26.1</td>
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</tr>
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</table>
indicates that the latter crystallized from magmas that differentiated more plagioclase or were sourced from partial melting of rocks that had residual plagioclase. Chondrite-normalized REE patterns (Figure 5) indicate that both volcanics and plutonics are light rare earth element (LREE) enriched, with both having high (La/Yb)$_N$ ratios (11.45–19.24 for volcanics and 8.08–23.45 for plutonics). The Zhuanqiao stage volcanics and plutonics are enriched in Rb, Th, U, La, Ce, Zr, and Hf and have negative Ba, Ta, Nb, Sr, and Ti anomalies (Figure 6). Both plutonics and volcanics also have large variations in Zr.
concentrations (159–479.4 ppm for volcanics and 133–726 ppm for plutonics). The volcanic rocks and plutonics have (Nb/Th)PM ratios of 0.05–0.14 and 0.02–0.14, with (La/Sm)PM ratios of 3.33–4.95 and 3.36–7.29, respectively.

Nd and Sr isotopic compositions

Initial \(^{87}\)Sr/\(^{86}\)Sr and \(^{143}\)Nd/\(^{144}\)Nd ratios and \(\varepsilon_{\text{Sr}}(t)\) and \(\varepsilon_{\text{Nd}}(t)\) are calculated based on the ages determined by Zhou et al. (2008). The initial \(^{87}\)Sr/\(^{86}\)Sr and \(^{143}\)Nd/\(^{144}\)Nd ratios and \(\varepsilon_{\text{Sr}}(t)\) and \(\varepsilon_{\text{Nd}}(t)\) values of the volcanic rocks are 0.7059–0.7067, 0.51194–0.51218, 22.0–33.3, and
−10.2 to -5.5, respectively, whereas the plutonics have ratios of 0.7060–0.7082 and 0.51203–0.51214 and the values of 23.3–54.7 and −8.6 to −6.4. Both volcanics and plutonics within the Luzong Basin have a consistently narrow range of initial $^{87}\text{Sr}/^{86}\text{Sr}$ values and negative $\varepsilon_{\text{Nd}}(t)$ values.

**Discussion**

**Origin, evolution, and geodynamic setting**

The Zhuanqiao stage volcanics and intrusives in the Luzong Basin share very similar geochemical features, namely, similar rock types on TAS diagrams (Figure 2), shoshonitic affinities (Figure 3), similar trends on Harker plots (Figure 4), similar chondrite-normalized...
REE patterns (Figure 5), similar trace element spidergram anomalies (Figure 6), and finally a narrow range of initial $^{87}\text{Sr}^{86}\text{Sr}$ and negative $\varepsilon_{\text{Nd}}(t)$ values. This strongly suggests that the volcanics and intrusives were cogenetic and underwent very similar differentiation and igneous evolution histories, most probably in a high-level magma chamber rather than during ascent or emplacement. The volcanic rocks and intrusions data are adjacent to the enriched mantle I (EM-I) field of Zindler and Hart (1986) in Figure 7, indicating the source of magma is probably metasomatic mantle associated with EM-I. Major element variations (Figure 4) indicate that differentiation of olivine, pyroxene, ilmenite, and apatite, with little differentiation of plagioclase, occurred during the evolution of the high-level magma chamber that acted as a source for both volcanic and plutonic units. The large variations in Zr and TiO$_2$ contents of magmatic units and enrichments of Zr (Figure 6) can all be ascribed to igneous differentiation processes and enrichments of incompatible elements. Compared with mantle-derived rocks, crustal rocks are enriched in highly incompatible elements (e.g. Th, LREE) and exhibit negative Ta, Nb, P, and Ti anomalies; decreasing $(\text{Nb}/\text{Th})_{\text{PM}}$ ratios are also thought to be related to increasing assimilation of crustal material (Lightfoot and Hawkesworth 1988; Lightfoot et al. 1990; Keays and Lightfoot 2010). The enrichments of Th, La, and Ce; negative Ta, Nb, and Ti anomalies (Figure 6); and low $(\text{Nb}/\text{Th})_{\text{PM}}$ ratios (0.05–0.14) indicate that the parental magmas of both volcanics and intrusives underwent crustal contamination. This evidence of contamination contradicts the uncontaminated magmatism suggested by Liu et al. (2002) and Xie et al. (2007). The new evidence presented here strongly suggests that the Zhuanqiao stage magmatism underwent differentiation with subsidiary assimilation of crustal material in a high-level magma chamber, before eruption of the volcanic sequences and emplacement of the plutonic units within the Luzong Basin.

Based on field geological characteristics and laser ablation (LA)–ICP-MS isotopic dating of zircon from both intrusives and volcanics, Zhou et al. (2008), Yuan et al. (2008), and Fan et al. (2008) divided the intrusives within the Luzong Basin into two periods and

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Figure 7. Scattergram of $^{87}\text{Sr}^{86}\text{Sr}$$_i$ versus $^{143}\text{Nd}^{144}\text{Nd}$$_i$ for volcanic rocks and intrusions (after Zindler and Hart 1986). MORB: mid-ocean ridge basalt, OIB: ocean island basalt, EM (I, II): enriched mantle components, DMM: depleted mantle component.
four stages. These stages correspond to the four volcanic stages documented in the Luzong Basin, and the authors concluded that magmatism within the basin occurred between 136 and 124 Ma. The researchers also conclude that the Zhuanqiao magmatic events occurred from 134 to 131 Ma. Wu et al. (2003) suggested that lithospheric thinning in eastern China took place in the late Mesozoic, with a maximum thinning during the Early Cretaceous (130–120 Ma). This thinning was related to the subduction of the Pacific plate and led to intensive magmatism and mineralization. Yuan et al. (2008) indicated that the Luzong Basin underwent a change in tectonic regime from compression to extension in the Early Cretaceous (140–130 Ma). The chemistry of the Zhuanqiao volcanics is suggestive of a transition between volcanic arc (VAG) and inner plate tectonic settings (Figure 8), whilst the coeval intrusions are transitional between VAG and syn-collisional (syn-COLG) granites and within-plate granites (WPG) (Figure 9), providing further evidence of a transitional tectonic regime. Furthermore, the trachybasalt–trachydacite dominated Shuangmiao Formation that overlies the Zhuanqiao Formation is bimodal in composition (mafic-felsic), indicative of a typical extensional regime. Hence, Zhuanqiao stage magmatic rocks record the transition from compressional to extensional tectonic regimes.

**Metallogenic specialization**

Knowledge of metallogenic specialization, or, in other words, the distinct relationship between certain types of magmatic rocks and certain mineral deposits, is essential for targeting during mineral exploration. In this article, we can differentiate three geochemically distinct groups of magmatic rocks. These three groups are intimately associated with the three major types of mineral deposit within the Zhuanqiao magmatic stage within the Luzong Basin, namely, vein magmatic hydrothermal Cu deposits, porphyry-hosted Fe deposits, and skarn Fe deposits.

Magmatic rocks related to the vein magmatic-hydrothermal copper deposits typically have 58–62 wt.% SiO₂, 8.5–10.5 wt.% K₂O + Na₂O, 1.8–2 wt.% MgO, 5.5–7 wt.% FeO, and a felsic index (FI) of 68–80. In comparison, the magmatic rocks related to porphyry-hosted

![Figure 8](https://example.com/figure8.png)  
**Figure 8.** Tectonic discrimination plot for volcanic rocks (after Dupuy et al. 1992).
iron deposits typically contain 45–53 wt.% SiO₂, 6–10 wt.% K₂O + Na₂O, 2.3–4.9 wt.% MgO, 7–9.5 wt.% FeO_T, and have an FI of 40–70. Finally, the magmatic rocks related to the skarn iron deposits typically have 52–66 wt.% SiO₂, 8–12 wt.% K₂O + Na₂O, 0.4–2 wt.% MgO, 4–10 wt.% FeO_T, and an FI of 52–66. These units also have high Th/Yb values, reaching a maximum of 35. This indicates that the changing composition of the plutonic and volcanic rocks during the Zhuanqiao magmatic stage controlled the formation of the three differing types of mineral deposit within the Luzong Basin (Figure 10); this information can be used to target specific mineral deposit types and commodities within the Yangtze metallogenic belt.

Conclusions

The volcanic and plutonic rocks of the Zhuanqiao stage in the Luzong Basin were cogenetic and were derived from metasomatized mantle involving an EM-I-type source. The Zhuanqiao magmas formed during a transition from compressional to extensional tectonic regimes, favourable for the formation of Cu and Fe mineral deposits. The igneous evolution of the Zhuanqiao stage parental magma was dominated by differentiation and assimilation of crustal material in a high-level magma chamber prior to eruption and/or emplacement.

Mineral deposits associated with the Zhuanqiao stage magmatism can be divided into three metallogenic series, namely, vein magmatohydrothermal Cu deposits, porphyry-hosted Fe deposits, and skarn Fe deposits. Using a combination of field geological characteristics and major element variations, we showed that the concentrations of bulk-rock SiO₂, K₂O + Na₂O, and MgO can be effectively discriminated between the magmatic units associated with each metallogenic sequence and each type of mineral deposit. This will enable the evaluation of the metallogenic affinity and mineralization potential of the
Zhuanqiao stage magmatism, enabling better targeting of prospective magmatic bodies during mineral exploration within the Yangtze metallogenic belt.

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Petrogenetic–metallogenetic setting and temporal–spatial framework of the Yueshan district, Anhui Province, east-central China

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The Yueshan district is located in the Anqing–Guichi ore deposit area of the Middle–Lower Yangtze Metallogenic Belt. Two groups of intrusive rocks and three main types of ore mineralization occur in this district: diorite plutons (e.g. Yueshan, Zongpu, Wuheng, and Yangshan) and granite plutons (Hongzhen and Dalongshan), Cu–Au–(Fe) skarn deposits (e.g. Anqing, Tiepuling), Cu–Mo–Au–(Pb–Zn) hydrothermal vein-type deposits (Tongniujing), and hydrothermal uranium mineralization (Dalongshan). Detailed geological and geochemical work suggests that the Cu–Au–(Fe) skarn deposits and the Cu–Mo–Au–(Pb–Zn) hydrothermal vein-type deposits have a close spatial and genetic relationship with the dioritic plutons, whereas the hydrothermal uranium mineralization is associated with A-type granite plutons. Based on the highly precise dating of metal deposits and related plutons in the Yueshan district, such as the molybdenite Re–Os, Os–Os dating, \textsuperscript{39}Ar–\textsuperscript{40}Ar dating of potassium-bearing minerals and quartz, several Rb–Sr isochrons, SHRIMP zircon U–Pb dating + single-grain zircon U–Pb dating, and the SHRIMP zircon U–Pb dating of Hongzhen granite pluton, we suggest that the extensive magmatism and mineralization in the Yueshan district took place in two episodes: (1) the first episode involved the mineralization of both skarn and vein-type hydrothermal deposits, c.a. 136–139 Ma, related to diorite plutons emplaced at 138.7 ± 0.5 Ma; (2) the second episode attended the hydrothermal uranium mineralization at 106.4 ± 2.9 Ma, related to granite intrusive activity at 126.8 ± 1.0 Ma. These two times of Yueshan petrogenetic–metallogenetic development appear to be consistent with a tectonic environment transition from compression to extension.

Keywords: granitoid magmatism; mineralization; hydrothermal deposits; Yueshan district; Middle–Lower Yangtze Metallogenic Belt

Introduction

The Middle–Lower Yangtze Metallogenic Belt in eastern China is one of the most important Cu, Fe, and polymetallic mineralization belts. This belt is located in the Yangtze fracture zone in the northern margin of the Yangtze plate (Figure 1), the tectonic framework such as fault uplift and fault basin and various Cu, Fe, Au, and polymetallic deposit assemblage formed with long-term tectonization, magmatic activity, and metallogenesis (Chang \textit{et al.} 1991; Zhai \textit{et al.} 1992; Tang \textit{et al.} 1998; Pan and Dong 1999; Mao \textit{et al.} 2006; Zhou \textit{et al.}}
2007, 2008a, 2008b; Li et al. 2008). The ore deposits number more than 200 deposits and cluster in seven typical ore deposit concentrated areas: southeastern Hubei Province, Jiu–Rui (Jiujiang–Ruichang), Anqing–Guichi, Tongling, Lu–Zong (Lujiang–Zongyang), Ning–Wu (Nanjing–Wuhu), and Ningzhen large-scale ore deposit concentrated areas from west to east, in which Lu–Zong and Ning–Wu ore deposit concentrated areas are mainly located in a fault depression volcanic basin (fault basin) and are predominated by iron mineralization. Tongling, Anqing–Guichi, Jiu–Rui, and Ningzhen ore deposit concentrated areas are located in an uplift area (fault uplift) and predominated by copper and gold mineralization. The southeastern Hubei Province is intermediate of fault uplift and fault basin and is predominated by iron, copper, and gold mineralization.

The Yueshan district is the main district of Anqing–Guichi ore deposit concentrated area, located in the easternmost portion of the Middle–Lower Yangtze Metallogenic Belt, and represents one of the most important mining districts, where more than 90% of Cu–Fe–Au–Mo–U–(Pb–Zn) ore deposits are hosted in diorite intrusive rocks or along their contacts with the Early Triassic limestone and dolomite rocks (Zhou et al. 2005), and some hydrothermal uranium mineralization are associated with granite plutons. Over the last few decades, researchers have contributed to a better understanding of the genesis of these deposits, the source of metals, ore-forming fluids, and the contribution from plutons and sedimentary strata (Cai 1980; Gu and Xu 1986; Ishihara et al. 1986; Liu and Chang 1988; Wu and Liu 1988; Zhao et al. 1990; Chang et al. 1991; Hu and Hu 1991; Zhai et al. 1992; Zhou 1993; Zhou and Yue 1996; Li et al. 1997; Zhou et al. 1997, 2005, 2007; Tang et al. 1998; Wu 1998; Zhao et al. 1998, 1999; Zhou and Li 2000; Wang et al. 2004;
Yang et al. 2007, 2010; Zhang et al. 2008). But there are few integrated studies that investigate the temporal and spatial relationships between processes of ore deposition and magma emplacement linking these processes to the regional geologic settings. This article integrates new results of a large quantity of isotopic datings from previous publications on magmatism, tectonics, and mineralization of the Yueshan district and presents zircon U–Pb ages of Hongzhen granite plutons by use of a sensitive high-resolution ion microprobe (SHRIMP). Emphasis is placed on comparing the spatial, temporal, and genetic relationships between magmatism and mineralization and the geodynamic setting. The aim of this study is to provide a comprehensive understanding of the age, genesis, and geodynamic control of the magmatism and mineralization of the Yueshan district and provide new evidence of constraints on the geological evolution of the middle–lower Yangtze metallogenic belt.

**Geological background**

The Yueshan mineral district is situated to the west of Anqing city, southeast Anhui Province, eastern China, and tectonically located in the east of the Yangtze Block and to the east of the Dabieshan orogen (Figure 1). The tectonostratigraphic sequence of the Yueshan district consists of three major lithostructural units (Figure 1). These are (1) Precambrian Dongling Formation, which represents the regional basement with an age of 1895 ± 38 Ma (Xing et al. 1993), composed of feldspathic gneiss intercalated with plagioclase–amphibole schists (Zhou et al. 1995, 2000); (2) Cambrian to Triassic sedimentary rocks, consisting of shallow marine carbonate rocks, sandstone, and shale; and (3) Jurassic to Cretaceous sedimentary rocks, consisting of continental clastic and volcanic rocks and red bed formations. Dolomite and brecciated limestone of the Triassic Yueshan and Lanlinghu Formations are the most important host rocks for the Cu–Au deposits, which are overlain by sandstone of the Tongtoujian Formation. The regional structures in this district include multiple deformational events and regional scale faults, such as the NE-trending and nearly E–W faults that controlled the distribution of plutons and associated mineralization (Zhou et al. 2005). In addition, the Dongling metamorphic core complex is the most important tectonic component in the Yueshan district; the core of this complex consists of Dongling metamorphic rocks, and its limbs are mainly composed of Cambrian–Jurassic strata (Li 1993; Xing et al. 1993; Tang et al. 1998; Zhu et al. 2007) (Figure 1).

In the Yueshan district, there are many plutons intruded into the Permian, Triassic, and Jurassic sequences, which are distributed along detachment faults between different layers and the converged location of both groups of the structures and exposed as stocks, dikes, and sills with individual outcrop areas in the range of 90 km² to < 1 km² (Figure 1). These plutons mainly consist of diorite, quartz monzodiorite, granodiorite, and granite.

In or near the contact of the plutons and the sedimentary rocks occur many Cu–Fe–Au–Mo–U–(Pb–Zn) and uranium deposits (Zhou et al. 2005). The main ore deposits include Anqing copper deposit, Tiepuling deposit, Longmenshan copper deposit, Dapai iron deposit, Liujiawa deposit, Tongliujing deposit, Caiguashan deposit, Yanjialaowu deposit, and Dalongshan deposit (Figure 1).

**Distributions and compositional variations of the Cretaceous magmatism**

**Spatial relationships and geochronology**

Throughout the Yueshan district, magmatic rocks can be subdivided into the diorite plutons zone (mainly in Yueshan, Wuheng, Zongpu, Yangshan) and the granite plutons zone.
These diorite plutons are distributed in the northwest regions of this district. From the southwest to northeast occur the Yangshan, Yueshan, Zongpu, and Wuheng plutons. Among these plutons, the Yueshan pluton is located in the centre of this area and with an irregular shape (approximately 11 km²). The Hongzhen and Dalongshan plutons are distributed in the southeast regions of this district and in the southwest and northeast margins of this district, respectively. The NE-trending Hongzhen granite body appears just to the southeast of the NE-trending Dongling metamorphic core complex. The Dalongshan pluton with an outcrop area of about 90 km² occurs as a NNE-trending sub-ellipsoid hosted by Jurassic sandstones and latites. These two granite plutons, together with the Huangmeijian and Chengshan plutons and so on, comprise the Anqing–Lujiang quartz-syenite belt (Zhang et al. 1988; Shen et al. 1989).

Available K–Ar, Ar–Ar, and Rb–Sr ages published in different journals (Table 1) indicated that the diorite magmatism was active between 88 and 147 Ma. The Wuheng pluton with an irregular shape has been dated at 129 Ma (K–Ar age of whole rock, Zhou et al. 2005). The Yangshan and Zongpu plutons have, respectively, been dated at 133 Ma (K–Ar age of biotite) and 132 Ma (K–Ar age of hornblende) (Qiu and Dong 1993). Recently, more precise SHRIMP zircon U–Pb dating of the Yueshan quartz diorite pluton yielded a weighted mean of $^{206}\text{Pb}/^{238}\text{U}$ age of 138.7 ± 0.5 Ma (Zhang et al. 2008), which could more precisely constrain the emplacement time of diorite plutons of Yueshan district. Previous isotopic dating of these two granite plutons, mainly by K–Ar and partly Rb–Sr and conventional U–Pb methods, yielded ages for most intrusive rocks ranging from 88 to 135.6 Ma (Table 1). These data, if correct, would imply that the Yueshan district had a protracted magmatic history. With the aim to provide a comprehensive understanding of the age of magmatism of this region, we present the SHRIMP zircon U–Pb dating of the Hongzhen granite pluton in this study.

**Analytical methods**

The sampling location of Hongzhen granite plutons is shown in Figure 2. Zircons for U–Pb geochronology were extracted from samples H-01 using standard mineral separation techniques (crushing, heavy liquids and magnetic separation) and were processed in the laboratory of the Academy of the Geological Survey of Hebei Province, China. Representative zircon grains are colourless, transparent column crystals and were handpicked and mounted on an epoxy resin disc and then polished. The discs were polished, cleaned, and then gold-coated. Prior to isotopic analysis, all grains were photographed under transmitted and reflected light and subsequently examined using the cathodoluminescence (CL) image technique (Figure 2). Selected for U–Pb SHRIMP dating were the zircons whose CL images indicate that they are euhedral–subhedral with striped absorption and obvious oscillatory zoning rims. The U–Pb isotope analysis was performed on a SHRIMP hosted in the Australian National University, with procedures similar to Compston and Williams (1992) and Williams (1998). During the SHRIMP analysis, spot size was averaged to 30 μm and each spot was rastered over 120 μm for 3 min to remove common Pb on the surface or contamination from the gold coating. The TEM zircon standard was used for interelement fractionation correction and the 572 Ma standard zircon SL13 for determining U, Th, and Pb concentrations. The isotope data were processed by Ludwig’s (Ludwig 2003) Isoplot and Glitter (4.0 version) programs; the uncertainties in analysis are 1σ. The weighted mean ages are quoted at 95% confidence level. Corrections of common Pb were applied using the $^{204}\text{Pb}$-correction method (Black et al. 2004).
Results

SHRIMP U–Pb analytical data are summarized in Table 2 and graphically illustrated in the concordia diagrams (Figure 3). Zircon CL images of sample H-01 are shown in Figure 3. Zircons from this sample are euhedral with lengths ranging from 100 to 200 μm. No inherited cores were observed in these zircons. Uranium and Th concentrations of zircon have a large range (U from 54 to 557 ppm, Th from 53 to 367 ppm), with Th/U ratios ranging from 0.4 to 1.9. All results are concordant or nearly concordant. The weighted mean 206Pb/238U age of the sample H-01 is 126.8 ± 1.0 Ma (MSWD = 2.6, n = 19), which are the best estimates of the crystallization age of Hongzhen granite plutons.
Petrology and geochemistry

The plutons in Yueshan district are medium- to fine-grained or inequigranular in texture, and the mineralogy consists of plagioclase (50–75%), hornblende (8–20%), K-feldspar (3–15%), quartz (5–15%), biotite (1–2%), minor pyroxene (<1.0%), and accessory minerals (<1%) including titanite, apatite, and magnetite. The Zongpu and Wuheng plutons consist of quartz diorite and granodiorite with fine- to medium-grained granular texture. Their mineral association is similar to the Yueshan intrusive rocks. The Yangshan pluton comprises only quartz diorites with medium-grained granular texture; it has a higher biotite (5–15%) and lower hornblende content (5–10%) than those of the Yueshan intrusive rocks. The Hongzhen granite pluton is composed of granite with fine to medium granular texture, with a mineral assemblage comprising plagioclase (20–35%), K-feldspar (25–40%), quartz (30–32%), biotite (3–8%), minor hornblende (<5%), and accessory minerals (<1%) including titanite, magnetite, and apatite. The Dalongshan pluton is composed of quartz-syenite and alkali-feldspar-granite, with fine to medium granular texture, a mineral assemblage comprising perthite (25–35%), quartz (30–35%), orthoclase (10–15%), plagioclase (10–15%), amphibole (3–8%), biotite (2–5%), and minor amounts of some accessory minerals (magnetite, apatite).

Published major and trace element analysis results of the magma rock of Yueshan district (Wang et al. 2004; Zhou et al. 2005) show that these rocks have mostly high potassium except for several samples from Yueshan and Zongpu plutons that have medium potassium (Figure 4). There is a wide range in SiO₂ content in the samples from 56 to 75%, but there is clearly a compositional gap of 66–70% SiO₂, which separates the intermediate felsic diorite pluton rocks from the granites in Hongzhen granite pluton. In the diorite
Table 2. Zircon SHRIMP U–Pb dating data of granite from Hongzhen pluton.

<table>
<thead>
<tr>
<th>Spot no.</th>
<th>Concentration (10^−6)</th>
<th>n(207Pb)/n(206Pb)</th>
<th>n(207Pb)/m(235U)</th>
<th>n(206Pb)/m(238U)</th>
<th>n(208Pb)/m(232Th)</th>
<th>206Pb/238U</th>
<th>207Pb/235U</th>
<th>208Pb/232Th</th>
<th>206Pb/238U</th>
<th>207Pb/235U</th>
<th>208Pb/232Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-01-01.D</td>
<td>266 156 1.7</td>
<td>0.0500 0.0022</td>
<td>0.1121 0.0061</td>
<td>0.0193 0.0002</td>
<td>0.0063 0.0001</td>
<td>123.9</td>
<td>5.9</td>
<td>127.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-01-02.D</td>
<td>108 130 0.8</td>
<td>0.0515 0.0025</td>
<td>0.1551 0.0071</td>
<td>0.0190 0.0002</td>
<td>0.0064 0.0001</td>
<td>129</td>
<td>6.2</td>
<td>125.4</td>
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<td></td>
</tr>
<tr>
<td>H-01-03.D</td>
<td>207 143 1.5</td>
<td>0.0523 0.0027</td>
<td>0.1244 0.0075</td>
<td>0.0196 0.0002</td>
<td>0.0064 0.0001</td>
<td>125.4</td>
<td>7.3</td>
<td>122.4</td>
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<tr>
<td>H-01-04.D</td>
<td>320 172 1.9</td>
<td>0.0478 0.0022</td>
<td>0.1136 0.0063</td>
<td>0.0200 0.0002</td>
<td>0.0065 0.0001</td>
<td>129.1</td>
<td>6.1</td>
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<td>H-01-05.D</td>
<td>265 148 1.8</td>
<td>0.0546 0.0022</td>
<td>0.1374 0.0061</td>
<td>0.0197 0.0002</td>
<td>0.0063 0.0001</td>
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<td>5.6</td>
<td>130.9</td>
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<tr>
<td>H-01-06.D</td>
<td>91 91 1</td>
<td>0.0517 0.0029</td>
<td>0.1274 0.0079</td>
<td>0.0193 0.0002</td>
<td>0.0062 0.0001</td>
<td>123.1</td>
<td>7.3</td>
<td>121.8</td>
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<td>H-01-07.D</td>
<td>74 85 0.9</td>
<td>0.0465 0.0033</td>
<td>0.1108 0.0092</td>
<td>0.0198 0.0003</td>
<td>0.0065 0.0002</td>
<td>127.4</td>
<td>8.9</td>
<td>131.2</td>
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<td>H-01-08.D</td>
<td>557 321 1.7</td>
<td>0.0489 0.0017</td>
<td>0.1458 0.0046</td>
<td>0.0196 0.0001</td>
<td>0.0060 0.0001</td>
<td>124.4</td>
<td>4.4</td>
<td>121.8</td>
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<td>H-01-09.D</td>
<td>160 84 1.9</td>
<td>0.0496 0.0028</td>
<td>0.1397 0.0077</td>
<td>0.0199 0.0002</td>
<td>0.0062 0.0001</td>
<td>126.3</td>
<td>7.3</td>
<td>124.3</td>
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<td>H-01-10.D</td>
<td>449 256 1.8</td>
<td>0.0476 0.0017</td>
<td>0.1337 0.0049</td>
<td>0.0200 0.0002</td>
<td>0.0063 0.0002</td>
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<td>H-01-11.D</td>
<td>166 100 1.7</td>
<td>0.0482 0.0038</td>
<td>0.1798 0.0111</td>
<td>0.0207 0.0004</td>
<td>0.0060 0.0002</td>
<td>129.7</td>
<td>10.4</td>
<td>121.2</td>
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<tr>
<td>H-01-12.D</td>
<td>59 150 0.4</td>
<td>0.0464 0.0023</td>
<td>0.1199 0.0062</td>
<td>0.0195 0.0002</td>
<td>0.0064 0.0002</td>
<td>125.2</td>
<td>6.6</td>
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<td>242 125 1.9</td>
<td>0.0507 0.0047</td>
<td>0.1685 0.0142</td>
<td>0.0209 0.0007</td>
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<td>H-01-14.D</td>
<td>54 53 1</td>
<td>0.0523 0.0042</td>
<td>0.1328 0.0118</td>
<td>0.0198 0.0003</td>
<td>0.0064 0.0002</td>
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<td>128.3</td>
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<td>H-01-15.D</td>
<td>269 151 1.8</td>
<td>0.0519 0.0022</td>
<td>0.1452 0.0063</td>
<td>0.0201 0.0002</td>
<td>0.0063 0.0001</td>
<td>128</td>
<td>7.6</td>
<td>127.3</td>
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<tr>
<td>H-01-16.D</td>
<td>527 367 1.4</td>
<td>0.0481 0.0012</td>
<td>0.1428 0.0034</td>
<td>0.0199 0.0002</td>
<td>0.0062 0.0001</td>
<td>126.8</td>
<td>3.3</td>
<td>124.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-01-17.D</td>
<td>118 305 0.4</td>
<td>0.0513 0.0014</td>
<td>0.1489 0.0042</td>
<td>0.0203 0.0002</td>
<td>0.0062 0.0001</td>
<td>128.9</td>
<td>3.9</td>
<td>124.7</td>
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<td></td>
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<tr>
<td>H-01-18.D</td>
<td>127 82 1.6</td>
<td>0.0500 0.0014</td>
<td>0.1296 0.0087</td>
<td>0.0196 0.0003</td>
<td>0.0062 0.0001</td>
<td>124.9</td>
<td>8.3</td>
<td>124.6</td>
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<td>H-01-19.D</td>
<td>142 322 0.4</td>
<td>0.0499 0.0014</td>
<td>0.1333 0.0039</td>
<td>0.0203 0.0001</td>
<td>0.0067 0.0001</td>
<td>129.4</td>
<td>3.7</td>
<td>134.3</td>
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</table>
Figure 3. U–Pb concordia diagram of zircons from granite of Hongzhen pluton.

Figure 4. K₂O versus SiO₂ plot for intrusive rocks from Yueshan district. (Data from Wang et al. 2004; Zhou et al. 2005; Yu et al. 1988).
plutons group, the Yueshan, Zongpu, and Wuheng plutons have similar compositional characteristics of major and trace elements, for example, high Al$_2$O$_3$ (15.0–17.0%), Na$_2$O (3.80–6.0%), MgO (1.58–6.16%), Sr (1300–2000 ppm), Ni (9–29 ppm), and V (65–175 ppm) contents. The quartz diorites of the Yangshan pluton show the highest Al$_2$O$_3$ (18.0–18.1%), TiO$_2$ (1.02–1.04%), Y (34–35 ppm), and Yb (2.82–2.86 ppm) contents. The Hongzhen granites are characterized by high SiO$_2$ (69–75%) and Ba (1387–1618 ppm) and low Al$_2$O$_3$ (13.6–15.0%), CaO (1.3–2.2%), TiO$_2$ (1.02–1.04%), MgO (0.44–1.05%), Sr (421–458 ppm), and Yb (0.85–0.89 ppm). The trace element composition of the Dalongshan granite also shows characteristics of A-type granite.

Based on petrology and geochemistry, Wang et al. (2004) classified these plutons into two groups. One group (the Hongzhen adakitic granites) is characterized by high SiO$_2$ (69–75%) content and K$_2$O/Na$_2$O (>1.0), low MgO (or Mg#) values, Ni and V concentrations, low εNd (t) (–17.01 to –18.13), and high (87Sr/86Sr)$_i$ (0.7071–0.7072). The other group (the Yueshan and Zongpu adakitic rocks) is characterized by relatively low SiO$_2$ (58–67%) content and K$_2$O/Na$_2$O (<1.0), high MgO (Mg#) values, Ni and V concentrations, as well as relatively high εNd (t) (–6.63 to –9.62) and low (87Sr/86Sr)$_i$ (0.7064–0.7069).

Based on the geochemical and isotopic studies (e.g. Zhou and Yue 1998; Zhou et al. 2001; Wang et al. 2004), several hypotheses for the origins of rocks have been suggested: slab melting, AFC processes involving basaltic magma, and lower crust melting. Summarizing the results of the recent study of Yueshan district and the neighbouring areas (Lu-Zong, Ning-Wu, Tongling, and Daye district), we concluded that materials of these diorite pluton rocks have been derived ca. 70% from the mantle and 30% from the crust. They were formed in open magmatic systems through wall-rock assimilation of crustal material and fractional crystallization of mantle-derived alkaline basalts. The granites of Yueshan district are similar to the plutons in the whole Anqing–Lujiang quartz-syenite belt and may have originated from the enriched mantle with little crustal contamination during the upwelling.

**Hydrothermal deposits**

Yueshan district is characterized by many polymetallic ore deposits with different scale and variable composition and ore type. Major ore deposits are localized at the eastern part of this district, which are characterized by skarn Cu deposit, vein-type hydrothermal deposit, some small Pb–Zn and uranium deposits (Table 3). The distribution and key characteristics of three major ore types are summarized below.

**Skarn deposits**

The skarn deposits are all located within the contact zones between the dioritic plutons and the Middle–Lower Triassic Yueshan and Lanlinghu Formations (e.g. Anqing copper deposit, Figure 5a) or in association with xenoliths of sedimentary rocks within diorite (e.g. Longmenshan and Tiepuling copper deposit, Figure 5b). Their precise temporal and genetic relationship to the magmatism will be discussed below.

This type of deposits possesses the main metal resources of the Yueshan district, for example, the Anqing skarn Cu deposit has 340,000 t Cu in total with a grade of ca. 2.7% Cu. Ore bodies have irregular shapes and various sizes controlled by the petrologic characteristics in contact zones (Figure 5a). Skarn ore bodies at the contact zone between the dioritic pluton and carbonate country rocks are composed of magnetite, hematite, chalcopyrite, pyrrhotite, pyrite, molybdenite, bornite, garnet, pyroxene, wollastonite, albite, actinolite–tremolite, muscovite, chlorite, epidote, sericite, quartz, and calcite. Garnet- and magnetite-bearing
Table 3. Characteristics of selected hydrothermal deposits in the Yueshan district.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Deposit and type</th>
<th>Size and grade</th>
<th>Intrusive rock</th>
<th>Host rocks</th>
<th>Ore minerals</th>
<th>Gangue minerals</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anqing</td>
<td>Cu–Mo skarn</td>
<td>340,000 t Cu and 2.7% Cu</td>
<td>Diorite and monzodiorite</td>
<td>Triassic carbonate</td>
<td>Chalcopyrite, pyrite, pyrrhotite, molybdenite, magnetite, bornite, hematite</td>
<td>Garnet, pyroxene, wollastontite, albite, actinolite, tremolite, muscovite, chlorite, epidote, quartz, and calcite</td>
<td>Zhou et al. (2007)</td>
</tr>
<tr>
<td>Longmenshan</td>
<td>Cu skarn</td>
<td>10,000 t Cu and 2.1% Cu</td>
<td>Diorite and monzodiorite</td>
<td>Triassic carbonate</td>
<td>Chalcopyrite, pyrite, magnetite, bornite, and hematite</td>
<td>Garnet, anhydrite, diopside, scapolite, albite, epidote, actinolite</td>
<td>Zhou et al. (2005)</td>
</tr>
<tr>
<td>Tiepuling</td>
<td>Cu skarn</td>
<td>110,000 t Cu and 2.0% Cu</td>
<td>Diorite and monzodiorite</td>
<td>Triassic carbonate</td>
<td>Chalcopyrite, pyrite, magnetite, bornite, and hematite</td>
<td>Garnet, anhydrite, diopside, scapolite, albite, epidote, actinolite</td>
<td>Zhou et al. (2005)</td>
</tr>
<tr>
<td>Tongniuing</td>
<td>Cu–Au–(Mo) vein type</td>
<td>100,000 t Cu and 2.7% Cu</td>
<td>Diorite and monzodiorite</td>
<td>Triassic carbonate</td>
<td>Chalcopyrite, molybdenite, bornite, pyrite, chalcocite, hematite, and magnetite</td>
<td>Quartz, calcite, dolomite, actinolite, and chlorite</td>
<td>Zhou et al. (2007)</td>
</tr>
<tr>
<td>Yanjialaowu</td>
<td>Cu–Au–(Pb–Zn) vein type</td>
<td>100,000 t Cu and 2.4% Cu</td>
<td>Diorite and monzodiorite</td>
<td>Triassic clastic</td>
<td>Chalcopyrite, pyrite, galena, sphalerite, magnetite</td>
<td>Calcite, quartz, chlorite, tremolite</td>
<td>Zhou et al. (2005)</td>
</tr>
<tr>
<td>Dalongshan</td>
<td>U vein type</td>
<td>490.6 t U and 0.710% U</td>
<td>Quartz synite and granite</td>
<td>Jurassic sandstone and siltstone</td>
<td>Chalcopryite, pyrite, galena, sphalerite, magnetite</td>
<td>Quartz, dolomite, calcite, and fluorite</td>
<td>Zhao et al. (2004)</td>
</tr>
</tbody>
</table>
exoskarns typically occur in an external zone associated with marbles. Diopside- and scapolite-bearing endoskarn and altered diorite-type ores occur within diorite.

Based upon the mineral assemblage of skarn deposits, ore-forming processes can be subdivided into two periods and five stages (Zhou et al. 2007). The skarn period, that is, the early period, consists of an early garnet–diopside skarn stage (stage 1); a magnetite-rich stage
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(stage 2); and a minor, late vein stage (stage 3). The quartz–sulphide period, that is, the late period, includes a quartz–sulphide stage (stage 4) and a quartz–carbonate stage (stage 5). Ore minerals of the quartz–sulphide stage are pyrrhotite, chalcopyrite, pyrite, molybdenite, and minor amounts of galena, sphalerite, bornite, native gold, and electrum. Wall-rock alteration is well developed around the ore bodies and consists of scapolite, diopside, garnet (andradite), albite, zoisite, tremolite, actinolite, chlorite, quartz, carbonates, kaolinite, and sericite.

Studies on early fluid inclusions (Zhou et al. 2007) show that temperature values for mineralizing stages in these skarn deposits are as follows: early garnet–diopside skarn stage, 440–650°C (average 532°C); magnetite stage, 380–585°C (average 480°C); late skarn stage, 364–430°C (average 412°C); early quartz–sulphide stage, 220–375°C (average 324°C); and late quartz–sulphide stage, 200–310°C (average 275°C). Fluid salinity is high for all major mineralization stages of the skarn deposits. A prominent feature is that the quartz–sulphide stage of the deposits is characterized by bimodal salinity values, which might indicate the presence of two coexisting ore-forming fluids or phases, most probably resulting from boiling processes (e.g. Roedder 1992; Webster 1997).

Phlogopite from the Anqing copper deposit has yielded a K–Ar dating of skarn mineralization age of 131 ± 1.1 Ma (Chang et al. 1991). Mao et al. (2004) analysed two molybdenite samples with ICP-MS and NTIMS methods to gain the Re–Os model ages. They are 134.7 ± 2.3 Ma, 137.9 ± 1.5 Ma (YU-1) and 137.4 ± 2.2 Ma, 142.6 ± 1.7 Ma (YU-2). For comparison, Mao et al. (2004) also analysed the same sample (YU-1) in another lab and gained the Re–Os model age of 139.1 ± 0.4 Ma with NTIMS method.

Vein-type hydrothermal deposits

The vein-type hydrothermal deposits in the Yueshan district are mostly located within contact zones between plutons and sedimentary rocks or within plutons. They occur as veins, veinlets, and stockworks in silicified rocks and breccias. The Tongliujing Cu–Au–(Mo) deposit is a typical example: the Tongliujing hydrothermal vein-type deposit has about 100,000 t Cu with a grade of Cu of about 2.3%.

Locations of ore bodies are controlled by fractures and rupture zones (Figure 5c). Ore minerals include chalcopyrite, molybdenite, bornite, and minor amounts of pyrite, chalcocite, hematite, and magnetite. Gangue minerals in veins are quartz, calcite, dolomite, actinolite, and chlorite. Based on mineral associations, the ore-forming process can be divided into three stages (Zhou et al. 2007): (1) oxide stage; (2) quartz–sulphide stage, mainly consisting of chalcopyrite, molybdenite, minor magnetite and bornite, pyrite, albite, chloride, epidote, sericite, and quartz; and (3) quartz–carbonate stage, mainly consisting of pyrite, chalcopyrite, hematite, chloride, sericite, quartz, and dolomite. The wall-rock alteration consists of an alkali metasomatic stage and a carbonate–quartz–kaolinite stage. The alteration zones are best developed around the ore shoots in the veins.

Fluid inclusion study results (Zhou et al. 2007) show that the temperature for mineralizing stages of the vein-type hydrothermal deposits varies between 300 and 430°C (average 385°C, oxide stage), 180 and 350°C (average 325°C, sulphide stage), and 130 and 200°C (average 172°C, quartz–carbonate stage). Fluid salinity feature is the same as for the skarn deposits and also high for all major mineralization stages of the vein-type hydrothermal deposits; the quartz–sulphide stage of the deposits is characterized by bimodal salinity values, which might indicate the presence of two coexisting ore-forming fluids or phases, most probably resulting from boiling processes.

The age of the Tongniujing vein-type hydrothermal deposit has been determined by different researchers and by different methods (Table 1). Molybdenite Re–Os and Os–Os
ages are 131 ± 1.4 and 136.1 ± 2.0 Ma, respectively (Sun et al. 2003). Quartz yields an Ar–Ar plateau age of 134.77 ± 0.70 Ma and an isochron age of 130.92 ± 0.76 Ma (Zhou et al. 2003).

**Hydrothermal uranium deposits**

The Dalongshan hydrothermal uranium mineralization occurs in the contact zone between the Dalongshan pluton and the Jurassic sandstone, and its distribution is controlled by flexures along the contact surface (Figure 5d) (Zhu et al. 1992), which was exploited from 1964 to 1993. This is a high-grade uranium deposit used as a fuel source for the Chinese nuclear energy industry. The main uranium mineral is pitchblende with small amounts of uraninite, metatorbernite, and autunite, which occur as vein-disseminated ores. Associated minerals are dominated by pyrite, with trace amounts of sphalerite, galena, molybdenite, chalcopyrite, marcasite, magnetite, hematite, niccolite, and millerite (Zhang and Min 1985). Gangue minerals are mostly quartz, dolomite, calcite, and fluorite. Wall-rock alteration has resulted in the formation of albite, quartz, hematite, hydromica, carbonate, and pyrite.

Microthermometry of fluid inclusions in vein quartz associated with pitchblende shows homogenization temperatures of 250–300°C (Zhu et al. 1992). The oxygen isotope ratios of ore-forming fluid were calculated to range from 10.7 to 8.3‰ in the pre-ore stage and from 7.5 to 5.8‰ in the ore-forming stage (Zhu et al. 1992), on the basis of oxygen isotope analysis of gangue quartz and fluid inclusion homogenization temperatures. It appears that both magmatic and surface waters were involved in the ore-forming process, with a progressive increase in the component of the surface water during the hydrothermal evolution (Zheng et al. 1990).

Pitchblende of the Dalongshan hydrothermal uranium deposit has yielded a U–Pb isochron dating of uranium mineralization age of 106.4 ± 2.9 Ma (Zhao et al. 2004).

**Discussion**

**Spatial–temporal relationships between magmatism and mineralization**

The distribution of plutons in the Yueshan district exhibits significant geographic variations: the diorite plutons are distributed in the northwest region, and the Hongzhen and Dalongshan plutons are distributed in the southwest and northeast margins of this district, respectively. The origin of the base and precious metal mineralization of Yueshan district has been related by several authors to the spatially associated plutons (e.g. Zhao et al. 2004; Zhou et al. 2005). The skarn deposits are all located within the contact zones between the dioritic plutons and the Middle–Lower Triassic Yueshan and Lanlinghu Formations, such as the Anqing copper deposit, Tiepuling copper deposit, Longmenshan copper deposit, and Dapai iron deposit. The vein-type hydrothermal deposits are located within the contact zones between plutons and sedimentary rocks or within plutons occur as veins, veinlets, and stockworks in silicified rocks and breccias, such as the Tongniujing vein-type hydrothermal deposit. The hydrothermal uranium mineralization occurs in the contact zone between the granite plutons and the Jurassic sandstone, and its distribution is controlled by flexures along the contact surface, such as the Dalongshan uranium deposit that occurs at the contact zone between the Dalongshan granite plutons and the Jurassic sandstone.
Previous and recently obtained isotope dating of regional magmatism and mineralization has revealed the general timing of these processes in the Yueshan district. Different researchers reported that the geochronological ages of minerals related to the ore stage demonstrates that the mineralization ages of skarn deposits and vein-type hydrothermal deposits in the Yueshan district were significantly different. Taking into consideration the accuracy of the dating method, the molybdenite Re–Os age (137.9 ± 1.5 Ma, 139.1 ± 0.4 Ma, Mao et al. 2004) and the Os–Os age (136.1 ± 2.0 Ma, Sun et al. 2003) should be the best representatives of the mineralization ages. Therefore the mineralization age for these hydrothermal deposits related to the Yueshan intrusion is around 136–139 Ma, which is close to the zircon U–Pb ages of Yueshan diorite pluton (138.7 ± 0.5 Ma). The Dalongshan hydrothermal uranium mineralization occurred in 106.4 ± 2.9 Ma; the precise age of related granite plutons is 126.8 ± 1.0 Ma as represented by the Hongzhen granite pluton. That means the uranium ore-forming hydrothermal system is temporally dictated by the cooling rates of the granite and may lag about 20 million years behind the emplacement timing of associated granite. So the magmatism and mineralization in the Yueshan district can be divided into two stages: the Cu–Au–(Fe) skarn deposits and Cu–Mo–Au–(Pb–Zn) vein-type hydrothermal deposits have a close spatial and temporal relationship with the dioritic plutons; the hydrothermal uranium mineralization is associated with granite plutons.

The two-stage magmatism and mineralization activities in the Yueshan district are also consistent with the results of Zhou et al. (2008b). They proposed the fact that magmatism and metallogeny in the Middle–Lower Yangtze Metallogenic Belt mainly took place between 145 and 120 Ma: the magmatic activities were from 145 to 135 Ma, with the main phase of high-K calc-alkaline volcanic rock series magmatic rocks and Cu–Au mineralization mainly happening in fault uplift (e.g. Du et al. 2007; Wu et al. 2008; Xie et al. 2009), and magmatic activities from 135 to 127 Ma, with the main phase of shoshonitic rock series (e.g. Wang et al. 1996; Yuan et al. 2008; Zhou et al. 2008a) and Fe mineralization. The later A-type granite (Xing and Xu 1998; Fan et al. 2008) formed between 127 and 123 Ma and occurred in fault uplift as well as in fault basin, related to uranium and gold mineralization.

**Genetic relationships between magmatism and mineralization**

Significant changes in style and composition of ore deposits on the aspects of spatial and temporal characteristics may be related to those of chemical compositional changes of local magmatic rocks and the nature of host rocks. Original explanations of the skarn and vein-type hydrothermal deposits in the Yueshan districts have close genetic relationships with the diorite magmatism and evolution of diorite plutons. Zhou et al. (2007) suggested that during the early and middle stages of mineralization, fluid consisted primarily of magmatic water and minor shifted magmatic and evolved magmatic waters. Meteoric water input increased during the middle to later stages. The ore-forming fluids that deposited the vein-type hydrothermal deposits resulted by mixing of magmatic or evolved magmatic water and meteoric water. The proportion of meteoric water increased substantially in the later stages. This change in fluid compositions had a negative impact on the Cu mineralization. Metals were derived mainly from the dioritic magmas by melt–fluid partitioning. Interaction between hydrothermal fluids and dioritic plutons has provided most of the ore-forming components, whereas the interaction between the hydrothermal fluids and Triassic and pre-Triassic sedimentary rocks has provided additional amounts of sulphur and other ore-forming materials.
The Hongzhen and Dalongshan plutons together with the Huangmeijian and Chengshan plutons display a strong association with granite-type hydrothermal uranium deposits (Zhang et al. 1988; Shen et al. 1989; Zhao et al. 2004). Oxygen isotope analysis results of Dalongshan uranium showed that the ore-forming fluid had $\delta^{18}O$ values of 10.7–8.3‰ in the pre-ore stage and 7.5–5.8‰ in the ore-forming stage (Zhu et al. 1992), indicating a prominent component of magmatic water in the ore-forming fluid. Therefore, the uranium mineralization bears a close genetic relationship to the magmatic activity and the subsequent cooling process during which the granite was emplaced into the surrounding rocks.

An explanation contributing to the differences between the metal proportions of the ore deposits in the Yueshan district can be derived from variations in the isotopic composition of the magmatic rocks. The Hongzhen granites have the lowest $\varepsilon^{Nd}(t)$ values (–17.01 to –18.13) close to that of the Yangtze lower crust, and the Yueshan and Zongpu intrusive rocks have relatively high $\varepsilon^{Nd}$ values (–6.08 to –9.62). The Hongzhen granites have initial $^{87}Sr/^{86}Sr$ ratios (0.7071–0.7072) slightly higher than the Yueshan and Zongpu plutons (0.7064–0.7069) (Wang et al. 2004). The Sr and Nd isotope compositions of the plutons reflect an increasing amount of crustal components from the northwest towards the southeast, which coincides with the Cu–Mo–Au–(Pb–Zn) mineralization and the uranium mineralization.

Geodynamic implications

Some researchers have discussed the tectonic setting of Yueshan district in the late Mesozoic from different aspects: Zhou et al. (2005) suggested that the mineralization of the Yueshan district took place in the extensional environment or in a transition of compressional to extensional environment. Yang et al. (2007) and Zhu et al. (2007) suggested that the magmatic rocks in the Yueshan district formed in the extensional environment. Zhang et al. (2008) pointed out that the Yueshan pluton formed in the setting of transition stage from the compressional to extensional environment.

The extensional environment in the Mesozoic of this region has been taken as the lithospheric delamination and upwelling of hot asthenosphere (Xu et al. 2002; Wang et al. 2006), roll-back of subducting palaeo-Pacific plate (e.g. Wong et al. 2009), and the ridge subduction between Pacific and Izanagi plates (Sun et al. 2007; Ling et al. 2009). However, during the late Mesozoic the palaeo-Pacific subduction zone was located between the Central Tectonic Line in Japan and the Longitudinal Valley of Taiwan (Wang and Mo 1995; Ren et al. 1998), more than 800 km away from the Lower Yangtze Metallogenic Belt. It is unlikely that mantle wedge metasomatism extended over such a large distance.

Zhou et al. (2007) pointed out that the formation time (133 Ma) of the Bajiatan pluton in the Luzong basin adjacent to the Yueshan district represented the transitional time of tectonic setting from the transition of compressional to extensional regime to the extensional regime in the Middle–Lower Yangtze Metallogenic Belt. On the basis of an integrated study of the two-stage magmatism and mineralization in the Yueshan district, we concluded that the first episode of diorite magmatic activities (138.7 ± 0.5 Ma) and the skarn and vein-type hydrothermal mineralization activity (136–139 Ma) of this study district took place in the setting of the transition of compressional to extensional regime and the second episode of the granite activity (126.8 ± 1.0 Ma) and the hydrothermal uranium mineralization activity (106.4 ± 2.9 Ma) took place in the setting of the extensional regime; the most probable dynamic mechanism responsible for this extension was the lithospheric thinning and the upwelling of hot asthenosphere.
Conclusions

(1) The plutons and related ore deposits in the Yueshan district formed during two episodes. The first event involved skarn and vein-type hydrothermal mineralization, which took place between 136 and 139 Ma; diorite plutons intimately related to these deposits were emplaced at 138.7 ± 0.5 Ma. A second intrusive event occurred at 126.8 ± 1.0 Ma; the related hydrothermal uranium mineralization activity occurred at 106.4 ± 2.9 Ma. Two-stage magmatism and mineralization in the Yueshan district is also consistent with high-K calc-alkaline magmatic activities from 145 to 135 Ma. Cu–Au mineralization mainly happened in uplifted fault blocks (e.g. Tongling area); in contrast, A-type granite formed between 127 and 123 Ma, which occurred in faulted uplift realms as well as in faulted basins, related to uranium and gold mineralization in the Middle–Lower Yangtze Metallogenic Belt, respectively.

(2) Skarn and vein-type hydrothermal Cu–Au deposits in the Yueshan district have close genetic relationships with the diorite magmatic evolution, whereas uranium mineralization bears a close genetic relationship to the magmatic activity and the subsequent cooling process as granite was emplaced into the surrounding rocks.

(3) The two episodes of magmatism and metallogenesis in the Yueshan district were related to a transition from a compressional to an extensional environment and may be related to lithospheric thinning and the upwelling of hot asthenosphere.

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Deformation model for the Tongling ore cluster region, east-central China

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The Tongling region, an important Cu + Au ore district, consists of a series of S-folds and is defined by an irregular set of boundaries. The regional structural framework was traditionally considered to be the result of coaxial compression, followed by simple shear. By analysing the spatial distribution of fold geometries and fault densities, we propose a new deformation model. Two tectonic stages, that is, early NW–SE compression, and later NE–SW compression, have been newly identified in this region. In the early stage, shortening produced by the collision between the Lower Yangtze block and the North China block mainly acted on the south-eastern and north-western boundaries; NE–SW-trending anticlines adjacent to the regional boundaries are tight to isoclinal and overturned, and the density of NW–SE-trending strike-slip faults is high as revealed by the large box dimensions of the spatial fault distribution. In addition, NW–SE compressions of the two stress boundaries are non-coaxial and asymmetric. With regard to the disposition of the irregular boundaries, non-coaxial and asymmetric compression led to the formation of S-folds and to obvious displacement between the north-eastern and south-western parts of the region. In the later stage, weak NE–SW compression, derived from the south-westward component of subduction of the Izanagi plate beneath the Eurasian plate, acted on the north-eastern boundary and redeformed the local structures to a minor extent. High fault density near the region boundaries promoted the formation of an interconnected fault system, which facilitated magma migration and emplacement, as well as the development of deposits genetically related to the igneous activity.

**Keywords:** Tongling; compression; compressional structures; S-folds; magmatic emplacement and ore deposits

Introduction

The Tongling region, located in Anhui province, east-central China, is geologically an uplifted part of the metallogenic belt of the middle-lower Yangtze River, which is a conjunction part between the Dabieshan orogen and the Lower Yangtze block (Figures 1 and 2). The Dabieshan orogen is the collision belt between the Lower Yangtze block and...
the North China block, and it was formed during the period 238–218 Ma, determined by different dating methods (Ames et al. 1993, 1996; Rowley et al. 1997; Wawrzenitz et al. 2006). In the metallogenic belt, the Tongling ore cluster region is adjacent to the NE–SW-trending Luzong and Ningwu volcanic basins to the west and to Fanchang volcanic basin to the northeast. The formations of these volcanic basins were controlled by the south-westwards subduction of the Izanagi plate beneath the Eurasian plate in the Late Jurassic
to Early Cretaceous (Sun et al. 2007; Li et al. 2011). Hence, the structural deformation in the Tongling region could be constrained by both the collision between the Lower Yangtze block and the North China block and the subduction of the Izanagi plate.

The Tongling region is one of the most important ore districts in China and named the ‘ancient copper capital of China’. It contains about 180 ore deposits and occurrences, including 2 large, 19 medium, and 33 small ones with industrial scale, most of which are genetically closely related to intermediate-acid intrusions (Chang et al. 1991; Hou et al. 2007; Deng et al. 2008; Wang et al. 2008; Cao et al. 2009; Li et al. submitted; Yang and Lee 2011). The transportation and location of ore-forming magma and magmatic hydrothermal are largely controlled by the structures in the caprock.

Therefore, the structural framework, ore-controlling structures and deformation mechanism in the Tongling region have been studied for decades to reveal its tectonic evolution and to understand the ore-forming process. It has been commonly recognized that S-folds are dominant in the region and control most of the orebodies (Chang et al. 1991; Zhai et al. 1999; Deng et al. 2004a, b, c). To explain the formation of the S-folds, a two-step deformation process, in which a double-lateral compression is followed by simple shear, was put forward (Wu et al. 2003). Otherwise, another model, named one-lateral compression and simple shear, was suggested (Deng et al. 2004a). The deformation process can be revealed by the analysis of the fold shape, fault-slip data, and fault density. However, the previous studies mainly focused on the fold geometric shapes, and seldom analysed the detailed spatial differences of fold geometry. The spatial distribution of the faults, which can provide information for both the deformation process and fluid migration, is barely discussed either.

Fold geometries can be obtained by analysing sections across the study area. In the sections obtained by the analogue experiments and numerical simulations with various mechanical features, it is shown that the folds are first developed at the force boundary and then transferred forwards. And the folds in the sections gradually change from a closed and overturned shape in the force boundary to an upright and open (or gentle) one far from the force boundary (Patricia 2003; Wang et al. 2006; Jacques and Ghislain 2009).

The fault-slip data can reflect the stress direction, and fault density represents the deformation intensity. The fault density can be described by means of a parameter, box dimension. The box dimension is widely used to study geological events related to fracturing. Aviles et al. (1987) and Okubo and Aki (1987) applied the method to research the geometric characteristics of the San Andreas fault, and discovered the relationship between the box dimensions of the fault and earthquakes. Deng et al. (2001) calculated the box dimensions of the faults in the Jiaodong ore district, China, and suggested that the mineralization is located in the areas with high box dimensions. In these applications, the studied area is usually divided into several parts, and the box dimensions of the different parts are calculated and compared.

In this article, fold geometry, fault-slip data, and fault density in the Tongling region are comprehensively analysed, and a new deformation model is proposed. The fold geometries and fault density analysis are based on both the 1:50,000 geological map and the fieldworks. The geological map, completed by the 321 geological team in Anhui province in 1989, has high quality, and recorded well the regional first-order folds and faults. The fieldworks are carried out aiming at verifying and supplementing the content in the geological map.

**Geological setting**

In the Tongling region, the stratigraphic sequence cropping out ranges from Silurian to Quaternary, as shown in Table 1 and Figure 3. The first angular unconformity in the stratigraphic sequence is developed between the Middle Triassic Dongmaanshan Formation (T2d) and
Table 1. Strata column in the Tongling ore cluster region.

<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Formation</th>
<th>Lithology describe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neogene-Paleogene</td>
<td></td>
<td></td>
<td>Clay, glutenite, conglomerate</td>
</tr>
<tr>
<td>Cretaceous</td>
<td>Upper</td>
<td>K2x</td>
<td>Conglomerate, sandstone, silty sandstone</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>K1g, K1k</td>
<td>The upper part includes conglomerate, sandstone, and andesite; the lower part is volcanic breccias.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>J3c, J3z</td>
<td>The upper is trachyte, the lower is rhyolite.</td>
</tr>
<tr>
<td></td>
<td>Mid-lower</td>
<td>J1+2xs</td>
<td>Conglomerate, sandstone, siltstone</td>
</tr>
<tr>
<td>Jurassic</td>
<td>Mid-lower</td>
<td>T2t</td>
<td>The upper part includes limestone, siltstone, and sandy mudstone; the lower part is limestone.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T2y, T2d</td>
<td></td>
</tr>
<tr>
<td>Triassic</td>
<td></td>
<td>T1n, T1h</td>
<td>The upper part includes limestone; the lower part includes limestone and siliceous.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T1y</td>
<td></td>
</tr>
<tr>
<td>Permian</td>
<td>Upper</td>
<td>P3d, P3l</td>
<td>Quartz sandstone, siltite shale, shale, mudstone</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>P3g</td>
<td>The upper part includes limestone and dolomite; the middle part includes silicate and siliceous shale; the lower part is limestone.</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>P3q</td>
<td></td>
</tr>
<tr>
<td>Carboniferous</td>
<td>Upper</td>
<td>C2c, C2h</td>
<td>Limestone and dolomite</td>
</tr>
<tr>
<td>Devonian</td>
<td>Lower</td>
<td>D3w</td>
<td>Shale, quartz sandstone, mudstone</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>S3m</td>
<td>Quartz sandstone</td>
</tr>
<tr>
<td>Silurian</td>
<td>Middle</td>
<td>S3f</td>
<td>Siltite mudstone, shale, quartz sandstone</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>S3g</td>
<td>Shale, siltite shale, siltstone</td>
</tr>
</tbody>
</table>

K2x, K1g, and K1k are the Upper Cretaceous Xuannan Formation, Lower Cretaceous Guangde Formation, and Lower Cretaceous Kedoushan Formation, respectively. J3c, J3z, and J1+2xs are the Upper Jurassic Chisha Formation, Upper Jurassic Zhongfencun Formation, and Middle and Lower Jurassic Xiangshan Group, respectively. T2t, T2y, and T2d represent the Middle Triassic Tongtoujian Formation, Yueshan Formation, and Dongmaanshan Formation, respectively. T1n, T1h, and T1y are the Lower Triassic Nanninghu Formation, Helongshan Formation, and Yinken Formation, respectively. P3d and P3l are the Upper Permian Dalong Formation and Longtan Formation, respectively. P3g and P3q mean the Middle Permian Gufeng Formation and Lower Permian Qixia Formation, respectively. C2c and C2h are the Upper Carboniferous Chuanshan Formation and Huanglong Formation, respectively. D3w is the Upper Devonian Wutong Formation. S3m, S3f, and S3g are the Upper Silurian Maoshan Formation, Middle Silurian Fentou Formation, and Lower Silurian Gaojiabian Formation, respectively.
Figure 3. Geological map of the Tongling region, China (modified from the 1:50,000 geological map accomplished by 321 geological team, Anhui province).
the Yueshan formation (T2y), which denotes a horizontal compression, started in the Middle Triassic. The development of the first angular unconformity was coeval with the formation of the Dabieshan orogen. This indicates that the Tongling deformation was triggered and largely controlled by the convergence of the North China block and the Yangtze block. Several angular unconformities are developed between the Middle Triassic (T2d) and Quaternary, representing a complex deformation process (Table 1).

The acid-mediate magmatic rocks intruded during 150–134 Ma and induced wide and intense mineralization (Zhou et al. 2000; Mao et al. 2003; Xie et al. 2009; Deng et al. 2011). The petrological data and geophysical profiles evidenced that a shallow magma chamber was developed in the Mesozoic at about −10 km and overlain by a fault system (Wu et al. 2000; Deng et al. 2006). In terms of geological phenomena, it is proposed that the ore-bearing magma stemmed from the shallow chamber migrated into the caprock via a diking pattern, in which magma with volatiles at its top rapidly ascended along pre-existing structures by a hydrofracturing pattern (Deng et al. 2006, 2007).

The Tongling region mainly comprises five orefields: the Xinqiao, Shizishan, and Tongguanshan orefields in the north-western area, and the Fenghuangshan and Jinlang orefields adjacent to the south-eastern boundary.

**Structural framework and deformation stage**

**Structural framework**

From the enhanced thematic map (ETM) image shown in Figure 2, it is revealed that the Tongling uplift is much different from the surrounding basins in terrain and outcropped strata. These obvious differences suggest that the region may be confined by faults. Based on the ETM image, the region boundaries are delimited. The region boundaries are generally divided into six segments, that is the north-western, northern, south-eastern, southern, north-eastern, and south-western boundaries, which construct an irregular set. Via the deep reflection seismic profiles and geological observations, it is further verified that these boundaries are mostly the large-scale deep faults (Chang et al. 1991; Pan and Dong 1999; Zhai et al. 1999; Deng et al. 2004b, 2010; Lü et al. 2004a, b). The boundary faults divided the Tongling region from the surrounding basins and made it experience a relatively independent deformation (Chang et al. 1991; Pan and Dong 1999; Zhai et al. 1999). The south-eastern boundary fault can be observed on the surface, and it is identified that this boundary fault with high dip angle behaved as a strike-slip fault first, which is deduced to have been formed or re-activated by shear generated by the collision between the North China block and the Yangtze block, and then was reworked by intense compression in the intraplate deformation.

A series of NE–SW-trending S-folds dominate the structural framework. The folds consist of the strata from the Silurian to Middle Triassic Dongmaanshan Formation, as shown in Figure 3, thus it is deduced that the folds were caused by the same tectonic event as that which led to the formation of the angular unconformity upon the T2d.

In addition, in the north-eastern part of the Tongling region, although most strata strike NE–SW, some strata trend NW–SE and dip to the northeast or southwest, constructing small-scale NW–SE-trending anticline and syncline. However, it is difficult to determine whether the Middle Triassic Tongtoujian Formation (T2t) is involved in the NW–SE-trending folds. The NW–SE-trending folds are superimposed upon the NE–SW-trending ones in the north-eastern part of the Tongling region.

Faults in the Tongling region can be generally divided into two types. The first is bedding-parallel faults, which mostly trend NE. The bedding faults, widely developed in
the fold limbs, resulted from the relative movements between the strata with distinct mechanical properties (Figure 3). The second type is strike-slip faults, which are mostly sinistral and trend NW–SE or NNW–SSE, cutting the NE–SW-trending folds. Several large-scale NW–SE or NNW–SSE-trending sinistral strike-slip faults with noticeable displacement developed in the central part are especially remarkable. Near the north-eastern boundary, some strike-slip faults trend NE–SW, cutting the NW–SE-trending folds.

Several structures in the caprock are considered to control the migration of ore-bearing fluids. High-angle reverse faults near the fold cores are proposed as pathways for the fluids. Disharmonic folds are widely spread and contain lots of void spaces, serving as emplacement places for the magmas and ore-bearing fluids. Moreover, multi-layered stratabound skarn or hydrothermal ore bodies are controlled by bedding-parallel faults.

Therefore, it is concluded that the structural framework in the Tongling region is characterized by dominant S-folds and sinistral strike-slip faults in an area confined by several deep faults and with an irregular set of boundaries. In addition, NW–SE-trending slip-strike faults, reverse faults nearby fold cores, and the disharmonic folds indicate a continuing intense NW compression and a complex deformation process.

**Deformation stage**

The NE–SW-trending folds, NW–SE-trending strike-slip fault array near the south-eastern and north-western boundaries both indicate a NW–SE compression. The NW–SE-trending folds and NE–SW-trending strike-slip fault near the north-eastern boundary both suggest a NE–SW compression. Based on the superposition of the folds, two stages, that is, early NW–SE compression, and later weak NE–SW compression, can be identified. The NW–SE compression formed the main framework of the structures at first. And the NE–SW-trending strike-slip faults and NW–SE-trending folds formed in the later stage superimposed on the previous NE–SW-trending folds in the north-eastern part and redeformed the local structural framework to a minor extent.

**Fold geometries**

In Figures 3 and 4, it is shown that the regional first-order NE–SW-trending folds comprise four anticlines and four synclines. And there are also second-order folds developed within the first-order folds, yet their scales are too small to be detected in the 1:50,000 geological map. The synclines are named S-1, S-2, S-3, and S-4 and the anticlines A-1, A-2, A-3, and A-4 from northwest to southeast. The fold geometrics can be clearly recognized in the most parts of the region; nevertheless, the southern part of anticline A-4 is badly altered by the faulting, and the fold geometric elements are barely preserved.

The strata in the core of the anticlines consist of Silurian systems and those of the synclines are Triassic. The strata in the limbs range from Silurian to T2d. In the geological map, it is shown that the cores of the folds A-1 and A-4 in the regional margin are much narrower, indicating a small interlimb angle. The cores of the synclines and anticlines in the central part, including folds S-2, S-3, A-2, and A-3, are wider, showing a larger interlimb angle. The fold cores near the southern and northern boundaries are also wider than those near the north-western and south-eastern boundaries. It is thus shown that the fold geometrical elements near the north-western and south-eastern boundaries are much different to those near the other boundaries and in the central part.

Four NW–SE-trending and nearly parallel sections, named AA′, BB′, CC′, and DD′ from northeast to southwest, are cut in the geological map, and then verified and supplemented
by the fieldworks, to study detailed fold geometric characteristics (Figure 5). The area to the northeast of section BB’ is called the north-eastern part of the Tongling region, and the other area is called the south-western part.

In the sections, the geometric differences of the folds are more obvious. From section AA’, it is seen that the anticline A-4 near the south-eastern boundary is isoclinal and overturned with a SE-dipping axial surface, and the syncline S-4 is elasticus. However, folds A-3 and S-3 in the centre and fold S-2 near the northern boundary are open to gentle, and their axial surfaces are nearly upright. In section BB’, fold A-4 is tight to isoclinal and overturned; nevertheless, folds A-3, S-4, and S-3 in the middle are open to gentle and nearly upright, and A-1 is closed and upright. From the sections AA’ and BB’, it is indicated that the deformation near the south-eastern boundary is most intense in the north-eastern part. In contrast, in sections CC’ and DD’, fold A-1 near the north-western boundary is tight to closed and overturned with a NW-dipping axial surface, and folds A-2, A-3, S-2, and S-3 in the middle become open and inclined to upright. The deformation near the north-western boundary is thus the most intense in the south-western part. The four sections also show that the fold geometric elements also change along hinges. For example, the anticline A-1 is upright in its north-eastern part, whereas it becomes overturned in the south-western part.

Based on fold geometry analysis, it is clearly revealed that the regional deformation intensities are differentiated to a great extent.

**Fault density distribution**

The box dimensions of the faults in the various areas in the Tongling region are calculated and compared to quantify the spatial distribution of fault density.
Figure 5. Composite sections in the Tongling ore cluster region, China (based on the fieldwork and the 1:50,000 geological map accomplished by 321 geological team, Anhui province and verified by the field work).
Definition of box dimension and box-counting method

As the fault system in the surface or a geological map is discrete and irregular, it can be considered as a fractal set. A fractal set has a fractal dimension $D$ greater than the topologic dimension of the objects that constitute the set (Mandelbrot 1983). The fractal dimension $D$ can be obtained by the box-counting method, and thus also called the box dimension (Mandelbrot 1983). The box dimension is a measure of the manner in which the plane is filled by faults, and a higher fractal dimension denotes a greater fault density, it increases with increasing degree of space filling. If the plane is completely filled by faults, $D$ is 2; whereas if there is only a straight line across the map, $D$ is 1. In the case of only a few short faults, $D$ can also be smaller than 1. Thus, the spatial distribution of the faults can be characterized by $0 < D < 2$.

The area for fractal dimension calculation is broken into equally spaced divisions of length $r$, and the number of divisions $N_r$ that contain one or more faults is recorded. After repetition for a range in $r$, the box dimension $D$ is related to $r$ and $N_r$ by

$$D = \frac{d(\ln N_r)}{d(\ln \frac{1}{r})}. \quad (1)$$

If $D$ is a constant between 0 and 2 for a range in $r$, the faults compose a homogeneous fractal set over the range of length scale (Mandelbrot 1983; Wang et al. 2010).

Fractal dimension calculation

The Tongling region is divided into 35 squares with constant side length, the northwest and southeast sides of each square trend NE and generally parallel to the fold hinge. The area of each square is 100 cm$^2$ on the map, representing a 25 km$^2$ area in reality (Figure 4).

Using the box-counting method, the box dimensions of the strike-slip faults and the total faults are calculated for each square. The $N(r)$ is numbered manually as $r$ is selected as 100, 50, 25, 10, or 5 mm. The $\ln N(r)$–$\ln r$ plots show a linear relationship when $r$ ranges from 100 to 5 mm, and the plots are fitted by a straight line via the least squares method (Figure 6). The box dimension is then obtained from the slope of the fitted line. The box dimensions for all squares are listed in Table 2.

Fault density analysis

The spatial distributions of box dimensions of the strike-slip faults and all faults are shown in Figure 7. From this figure, it is shown that the box dimensions of the strike-slip faults in the squares near the south-eastern boundary are generally the highest, suggesting the greatest density of strike-slip fault near this boundary. The dimensions of strike-slip faults in the squares along north-eastern boundary are also comparatively large. And a high box dimension also appears in square 19 near the north-eastern boundary. The dimensions near the northern, southern, and south-western boundaries and in the central part are small, indicating a lower fault density in those parts.

Because of the development of bedding-parallel faults, the dimensions of the squares adjacent to the north-eastern and south-western boundaries are elevated greatly compared
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Figure 6. Fractal models of the fault in typical squares in the Tongling region, China: (a) strike-slip faults; (b) all faults.

Table 2. Box dimensions of the strike-slip fault and total fault in each square in the Tongling ore cluster region, east China.

<table>
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<tr>
<th>Square</th>
<th>NW fault</th>
<th>Total fault</th>
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with those of the strike-slip faults. The dimension distribution of the total faults is similar to that of the strike-slip faults, also displaying relatively high values near the north-western and south-eastern boundaries and low values in the central and near northern and southern boundaries.

**Deformation model and process**

**Deformation model**

Based on the superposition of folds, the Tongling deformation process can be roughly divided into two stages, including an early NW–SE-trending compression and later NE–SW-trending compression.

The strike-slip faults were formed directly by the compression, and nearly independent of the strata folding; hence, they can reflect the compression intensity more accurately than the bedding-parallel fault and the total faults. The distribution of the box dimensions suggests that the area adjacent to the two boundaries suffered intense compression, and was heavily faulted and broken and had a high fault density. Correspondingly, the overturned and close to isoclinal fold shape at the two force boundaries also indicates intense compression. Therefore, the south-eastern and north-western boundaries are considered as force boundaries; and other boundaries as fixed ones during the first stage. In addition, the deformation near the south-eastern boundary is generally more intense than that near the north-western boundary, as is revealed by the fold shape and fault density; thus, the NW–SE-trending compression force on the south-eastern boundary is supposed to be greater, and the compressions at the force boundaries was asymmetric. Moreover, the compressions on the two boundaries were non-coaxial because of the irregular set of the boundaries. The deformation in the early stage was hereby characterized by non-coaxial and asymmetric compression, as illustrated in Figure 8.

The high box dimension of strike-slip faults mostly trending NE–SW, in square 19, represents a NE–SW compression acted on the north-eastern boundary in the later stage, as is consistent with the fold analysis (Figure 7).

The convergence of the North China block and the Yangtze block starting from T₂ controlled the deformation in the first stage in the Tongling region. In the Late Jurassic to Early Cretaceous (~140 to ~125–122 Ma), because of the south-westwards subduction of the Izanagi plate beneath the Eurasian plate, eastern China, was dominated by extension and rifting, resulting in development of a series of NE–SW-trending volcanic basins, for example Luzong, Ningwu, and Fanchang basins in the metallogenic belt of Middle-Lower
Yangtze River. Besides, the subduction also produced a weak southwestward compression acting on the north-eastern boundary of the Tongling region, which was responsible for the fold formation in the later stage. It is shown that the deformation duration in the Tongling region was mainly from the Middle Triassic to Early Cretaceous. Several angular unconformities developed in the region from the Middle Triassic to Early Cretaceous indicating that compression took place in episodes.

Later tectonic events represented by the angular unconformities developed after the Early Cretaceous are considered to have had little influence on the structural framework.

**Deformation process**

By virtue of the non-coaxial and asymmetric compression model, the deformation process in the first stage is constructed (Figure 9). In the early period of the tectonic compression, the strata near the force boundaries were folded with an open interlimb angle and upright axial surface. As the intense compression continued, the folds near the force boundaries transformed into overturned and tight to isoclinal gradually, and then propagated forward. The folds were transferred from the north-western and south-eastern boundaries to the central in the south-western part of the Tongling region, and from the south-eastern boundary to the northern boundary in the north-eastern part.

As the folds propagated along the NW direction, the strikes of the different segments of fold hinges also changed continually with the confinement of the irregular set of region
boundaries. For the folds A-1, A-2, S-2, and S-3, their south-western segments of the hinges were affected by the north-western boundary, however the north-eastern segments of the hinges were confined by the northern boundary; hence the folds turned clockwise integrally, forming the S-folds. Similarly, because of the confinement of the southern boundary, the south-western parts of the folds A-3, A-4, and S-3 turned counterclockwise with respect to their north-eastern parts influenced by the south-western boundary, which was responsible for the formation of S-folds. In addition, in the non-coaxial and asymmetric compression, disharmonic folds developed easily. During the formation of the S-folds, small-scale shears occurred at both the force boundaries and fixed boundaries; and these shears at the boundaries are proposed to have been generated by the compression force.

Because of the non-coaxial compression, the north-eastern part of the region tends to be pushed to the northwest, whereas the south-western part is thrust in the inverse direction. The opposite movements of the two parts induced a large shear in the central and the tear of the strata, which is expressed by the NW-trending sinistral strike-slip fault.

Although the size and shape of the boundary set changed in the deformation process, its irregular features remained invariable, as is proven by the deformation characteristics. It is probably because the boundary faults are mostly deep faults and their orientations are difficult to change (Chang et al. 1991).

Discussion
Comparisons with previous deformation models
Previous deformation models focused on the formation of S-folds. In the model ‘double-lateral compression and shear’ model (Wu et al. 2003), the Tongling region with a rectangle boundary shape suffered a double-lateral coaxial NW–SE compression, forming NE–SW-trending folds with straight hinges; the next sinistral shear at the boundaries changed

Figure 9. Fold evolution in the early stage according to the non-coaxial and asymmetric compression model in the Tongling region, China: (a) fold evolution in section AA’; (b) fold evolution in section CC’.
the folds into S-shaped (Figure 10). According to another ‘one-lateral compression and shear’ model (Deng et al. 2004b), an analogue experiment with a multi-layer structure was performed to reveal the formation process of caprock structure. In the analogue experiment, the S-folds formed by the shear at boundaries (Figure 11). Both models emphasized that the S-folds are formed in a separate shear stage, and ignored the irregular set of the boundaries and the intense shear in the central part.

Based on the combined analyses of the fold shape and fault density, a non-coaxial and asymmetric compression model is established in this article. The new model is very different from the two previous models. The S-folds are considered to be formed in the non-coaxial and asymmetric compression, instead of in a separate simple shear process. The new model concurs with the irregular boundary shape and explains well the development of the sinistral strike-slip faults especially in the central part.

**Indications for fluid transport**

The high fault density near the force boundaries indicates a densely interconnected fault system. According to the pervasive model, as the fault density reaches a threshold, fluid migration in the fault network takes place (Roberts et al. 1998). Thus, ore-bearing magma in the shallow chamber preferred to migrate and emplace into the shallow crust near the force boundaries. In Figure 3, it can be observed that the magmatic rocks are mostly developed in the squares with high fault density near the force boundaries, and barely in the parts near the fixed boundaries.

![Image 10](image10.png)

**Figure 10.** Deformation model proposed by Wu et al. (2003): (a) original model; (b) compression; (c) simple shear forming a series of S-folds.

![Image 11](image11.png)

**Figure 11.** Analogue experiment model performed by Deng et al. (2004b): (a) compression; (b) simple shear forming a series of S-folds.
Conclusions
The Tongling structural framework is characterized by S-folds and sinistral strike-slip faults in an area defined by an irregular set of boundary faults. By analysing the spatial distribution of fold geometry and fault density, we propose a new deformational model for the Tongling region, which can explain the characteristics and formation of the regional structural framework.

The deformation of the Tongling region occurred mainly during the Middle Triassic and the Early Cretaceous, as two compressional stages, that is, early NW–SE-trending contraction and later NE–SW-trending contraction. In the early stage, the shortening, mainly resulted from the collision between the Lower Yangtze block and the North China block, along the south-eastern and north-western boundaries of the Tongling region. The compressional directions were non-coaxial, and their intensities varied, making them asymmetric. With the confinement of the irregular set of region boundaries, the non-coaxial and asymmetric compression resulted in the differentiation of deformation, and induced the formation of NE–SW-trending S-folds and sinistral strike-slip faults. In the later stage, a relatively weaker compression, derived from the southwestward component of subduction of the Izanagi plate beneath the Eurasian plate, impinged on the north-eastern boundary, forming the NW–SE-trending folds, which were superimposed on, and reformed the NE–SW-trending S-folds in the north-eastern part of the region.

Near the stress boundaries, fault density was high, facilitating ore-bearing magma emplacement and the intense mineralization.

Acknowledgements
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A porphyritic copper (gold) ore-forming model for the Shaxi-Changpushan district, Lower Yangtze metallogenic belt, China: geological and geochemical constraints

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Ore-forming P-T-X conditions and the nature of gold occurrence in the Shaxi-Changpushan porphyry copper deposit, central Anhui Province, eastern China, were investigated employing a wide range of geological and geochemical methods. Our results document liquid-vapour conditions and show that abundant fluid inclusions occur in quartz veins accompanied by pyrite-chalcopyrite-gold mineralization. Most economic deposits involved coexisting liquid and gas phases, whereas a few formed in equilibrium with a homogeneous aqueous liquid. The ore-forming temperature lies between 230 and 350°C. Isotope studies show that the $\delta^{34}$S values are between $-0.20$ and $3.00$‰ for most of the sulphides; $\delta^{34}$S values of chalcopyrite are somewhat more homogenous than those of pyrite. Ore-forming fluids and materials were mainly derived from magmatic sources. Meteoric water played a small role in the ore-forming process, judging by the oxygen and hydrogen isotope data for fluid inclusions measured by the explosion method ($\delta^{18}$O values ranging from 3.51 to 5.52‰, and $\delta^D$ ranging from $-59.8$‰ to $-82.4$‰). In the ore deposit, the gold occurs as micro-inclusions heterogeneously distributed in chalcopyrite and pyrite. Gold mineralization is positively correlated with As in chalcopyrite, pyrite, and some Cu-bearing ores.

Igneous rocks and sedimentary rock distributions in the Shaxi-Changpushan ore district were strictly controlled by the regional fault system since the Jurassic period, especially the Tan-Lu fault system in east China. Intrusive bodies comprising porphyritic quartz dioritoid, biotite-quartz dioritoid, and fine-grained dioritoid are ore-bearing, cutting sedimentary rocks of the Upper Jurassic and Middle–Lower Silurian series. Sediments exposed in the ore district consist of Upper Devonian–Middle Silurian clastic rocks, Middle and Lower Jurassic and Upper Cretaceous terrestrial clastic rock series. Petrologic data show that formation of Cu-Au ore bodies was related to adakitic intrusives in the Shaxi-Changpushan area. Based on geochemical exploration and the tectonic background of the southern part of Tan-Lu fault zone, we propose a porphyric copper (gold) ore-forming model for the Lower Yangtze metallogenic belt: ore bodies were controlled by structural shielding in the core of the regional anticline. Combined geological and geochemical evidence suggests that a super-large porphyry (gold) deposit may be present in the region.

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Introduction

The Shaxi porphyry copper (gold) deposit represents one of the important discoveries during the 1970s mineral exploration in the middle-lower reaches of the Yangtze River. The geological survey and exploration work on the Shaxi deposit has been undertaken by several governmental geological institutes as well as mining companies, including No. 327 Geological Team of the Anhui Bureau of Geology and Mineral Resources, which has conducted exploration work in the area for more than 20 years. It has demonstrated that there are 258,500 tons of contained copper (grading >0.4% Cu) and 231,000 tons of copper with lower grade (0.2–0.4% Cu) in this region, belonging to the middle–lower parts of the Yangtze metallogenic belt, where more than 200 polymetal deposits have been discovered, mainly consisting of Cu, Fe, Cu, Pb, and Zn. Scholars have intensively studied the Yangtze metallogenic belt in terms of its geology and geochemistry, and obtained several important conclusions (e.g. Chang et al. 1991; Ren et al. 1991; Pan and Dong 1999; Xu et al. 1999; Wu et al. 2003, 2004; Zang et al. 2004; Mao et al. 2004; Yang and Lee 2005; Yang et al. 2006, 2007a,b; Deng et al. 2006, 2007; Zhang et al. 2006; Lan et al. 2009; Xie et al. 2009; Zhou et al. 2008; Yu et al. 2009). However, the genesis of some Cu-Au deposits is still debated, including the Shaxi-Changpushan porphyry Cu-Au deposit, one of the most important porphyry Cu-Au deposits in the Yangtze metallogenic belt.

This paper focuses on the geochemistry and gold occurrences of the Au-bearing porphyry copper deposit to better understand metallogenic processes and associated intrusive bodies. We discuss genetic models for this Cu-Au deposit and conclude that a large or super-large porphyry Cu-Au deposit is present in the Shaxi-Changpushan region.

Geological settings

The Shaxi-Changpushan porphyry copper (gold) deposit is located in the northwestern Luzong volcanic basin, in the southern part of the Tan-Lu fault belt, one of the largest deep faults in the east Asian continent (Xu et al. 1987). It also belongs to the north of the middle and low part of the Yangtze iron and copper metallogenic zone, the location of multiple faults, where Fanshan–Tongling deep fault and the Tan–Lu fault belt come through the whole mineralization region and resulted in serious rock deformation in the Jurassic (Chang et al. 1991; Yang 1996; Yang et al. 1996, 1998a, 2001). In the southeast is the Luzong volcanic basin, where Jurassic–Cretaceous volcanic activities occurred, with more than 10 deposits or occurrences of Cu, Au, Ag, Pb, and Zn commodities.

Figure 1 shows the regional geologic-tectonic map and the distribution of the granitoid intrusions related to Cu-Au mineralization, such as the Shaxi porphyry, Huangtun diorite intrusion, Anqing diorite intrusion related to massive hydrothermal and skarn Cu-Au deposits, and Tongling granodiorite intrusion and Chuxian diorite intrusion, both associated with skarn Cu-Au deposits. As a comparison, the volcanic rocks in the Jurassic–Cretaceous Luzong volcanic basin are also studied in this contribution, because previous study (Ren et al. 1991) suggests that volcanic rocks may be linked to the formation of the Shaxi intrusion.

The tectonic background in Shaxi has been controlled by the Tan–Lu slip fault system since the formation of Jurassic sedimentary rocks (Chang et al. 1991). The igneous
rocks and the distributions of sedimentary rocks have been strictly controlled by the fault system since the Jurassic period. The sediments exposed in the Shaxi deposit consist of Upper Devonian–Middle Silurian clastic rocks of continental-sea facies, Middle and Lower Jurassic inland clastic rocks of climatic facies, and Cretaceous red sandstone and conglomerate. There is also wide distribution of intrusive rocks of Upper Jurassic to Early Cretaceous series and continental volcanic rocks. Some of the intrusive bodies comprising porphyritic quartz dioritoid, biotite-quartz dioritoid, and fine-grained dioritoid are ore-bearing, cutting the sedimentary rocks of the Upper Jurassic series and the Middle–Lower Silurian series.

From north to south, the Shaxi porphyry copper (gold) deposit is divided into four ore zones based on the morphological units, that is, Qipanshan, Tongquanshan, Shizishan, and Duanlongjing (No. 327 Geological Team 1982). Drilling proved these ore zones to be united, however, controlled by a composite fold trending NNE in this region. The Changpushan prospecting area is located in the southern part of the Shaxi porphyry copper (gold) deposit, which is separated by the Duanlongjing fault; the structural line is slightly declined to the east compared with the Shaxi deposit, suggesting that it may be an independent ore deposit, although it has a close relationship with the structure of the Shaxi deposit in terms of regional geological setting (Figure 2; Yang et al. 2001).
Mineralogy and metallogeny

Ore types
Five types of copper (gold) ore are present, based on field observations: chalcopyrite ore, Cu-bearing pyrite ore, magnetite-chalcopyrite ore, pyrite-bornite-chalcopyrite ore, and chalcopyrite-molybdenite ore. These types of ore are not distributed homogeneously, and vary horizontally and vertically in this ore district. For example, the chalcopyrite-molybdenite ore is only found in the very northern part of the deposit in a small amount. The ore assemblages are characterized by relatively simple ore minerals, such as chalcopyrite, pyrite, pseudomorph haematite, bornite, magnetite, chalcocite, covellite, and arsenopyrite; the ore grade ranges from 0.2 to 0.4% copper; the gangue minerals are quartz, K-feldspar, calcite, gypsum, and anhydrite.

Alteration and mineralized stages
The alteration varies from the interior to outside of the deposit: potassic zone, sericitic zone, and propylitic zone. Generally, the contact between each alteration zone is not clear.

Figure 2. Geological map of the Shaxi–Changpushan porphyry copper (gold) deposit, central Anhui, China. 1, 2, 3, and 4 in the map denote the Qipanshan, Tongquanshan, Shizishan, and Duanlongjing sub-ore districts, respectively.
Alteration zoning is evident in mineralized quartz porphyry and biotite-quartz porphyry dioritoids, where Cu ore is hosted mainly in the potassic alteration zone. The ore contains gold averaging 3.16 ppm.

Detailed observations on the assemblages of alteration minerals and their relationship in the field indicate that three mineralized stages may have been present in the deposit (No. 327 Geological Team 1982): (1) the early biotite-K-feldspar-magnetite stage formed above 400°C, suggested by studies of fluid inclusions in quartz (this is not the main Cu (Au) mineralization stage); (2) the sericite-quartz-sulphide stage, the major Cu mineralization stage, formed at temperatures ranging from 250 to 300°C; and (3) the late quartz-carbonate-sulphide stage comprising carbonate, chlorite, sericite, kaolinite, and albite, which was formed at temperatures of 200–150°C. At this late stage, Cu mineralization is less important compared with the second stage. These three mineralized stages are coherent to one another, which accords with the diagenetic period of the main intrusion – the quartz diorite porphyry in this region. The alteration of the intrusive rocks in the deposit is similar to that of most porphyry copper deposits associated with diorite to granodiorite porphyry elsewhere, such as the Kounrad and Erdentuin porphyry copper deposits in central Asia (Vadim et al. 1993), Peschanka and Bingham porphyry copper deposits in the USA (Lowell and Guilbert 1970). The main mineralized stage, however, is not in the same period as wall-rock alteration. For example, in the Kounrad porphyry copper deposit, the main copper mineralization is related to the medium to late stages of alteration formed at 230–360°C (Vadim et al. 1993).

Table 1 (see supplementary material in the online version of this article at http://www.informaworld.com/tigr) gives the mineral assemblages of the ore deposit, indicating that the ore assemblage is relatively simple, consisting of chalcopyrite, pyrite, pseudomorph magmatite, bornite, magnetite, chalcocite, covellite, and arsenopyrite; the ore grade is 0.2–0.4% Cu.

**Petrography**

The intrusive rocks in the Shaxi–Changpushan porphyry copper (gold) deposit occur as stock, tongue, ethmolith, and dike. The ore deposit is associated with quartz diorite porphyry, biotite-quartz diorite porphyry, and fine- to medium-grained porphyry diorite that exhibit subhedral seriate texture. The porphyritic rocks contain plagioclase and alkali-feldspar phenocrysts, ranging from 8–3 to 5–1.5 mm in size. Some of the feldspars are altered to sericite, chlorite, and kaolinite in alteration zones. The dioritic rock consists of plagioclase, amphibole, quartz, microcline, and biotite, and minor muscovite, apatite, sphene, pyrite, magnetite, and rutile. Some quartz crystals show undulatory extinction and have several generations; most of them contain inclusions of other minerals and needles of some metal minerals. Microcline occurs as subhedral crystals with cross-hatch twinning. Microperthite is also evident. Plagioclase is subhedral with albite twinning; it is mainly andesine (An values ranging from 25 to 45 by EPMA analysis), although oligoclase-albite (An5–An20) is present because of hydrothermal alteration. Amphibole is subhedral, 1.3–0.4 to 0.2–0.1 mm (locally up to 16 mm) in size. It is noted that some diorite porphyries contain up to 15% amphibole. Some amphibole grains are replaced by chlorite at their margins, where muscovite and quartz are present. Biotite grains are commonly subhedral. Ore minerals are scattered among the main rock-forming minerals.

Figure 3 shows the relationship between ore minerals and rock-forming minerals and also the characteristics of fluid inclusions in the Shaxi porphyry Cu (Au) deposit, and Figure 4 shows photomicrographs of ore minerals and mineralized rocks in the Shaxi porphyry Cu (Au) deposit.
Mineralogy of gold-carrier minerals

The porphyry copper ore is commonly associated with fine-grained gold mainly occurring in the surface of pyrite and chalcopyrite crystals (No. 327 Geological Team 1982; Ji et al. 1987; Yang 1996; Yang et al. 1998b, 2002).

Various studies show that gold is mainly hosted in pyrite and chalcopyrite (Ji et al. 1987; Yang 1996; Yang et al. 1998a, 2002). In this study, 16 new samples of pyrite and chalcopyrite were selected for compositional analyses using a JEOL JXA-50A electron microprobe equipped with 5WDS spectrometers and a CAMECA SX50 linked with an EDS system under conditions of 15 kV, 15 nA, and 100 cps. The results are listed in Tables 2 and 3 (see online supplementary material), respectively. It is noted that silver is enriched in these gold-carrier minerals, and arsenic is relatively elevated, too. Figure 5 shows the S-Cu-Fe ternary diagram to illustrate the composition of both pyrite and chalcopyrite, which fall into a small area in the compositional space reflecting the unique source of ore fluids during mineralization.

The relationship between gold and As contents in pyrite and chalcopyrite is shown in Figure 6, revealing a positive correlation between these two trace elements.

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Figure 3. Photomicrographs of granitoids associated with Cu-Au mineralization in the Shaxi-Changpushan porphyry Cu-Au deposit, central Anhui. (All the images were taken with a Leica microscope under polarized light conditions, the scale bar for each of the images is 0.30 mm. Am, Amphibole; Bi, biotite; Chl, chlorite and chloritization; Kf, potassic feldspar; Pl, plagioclase; Py, pyrite; Ser, sericite and sericitization). (a) Amphibole and plagioclase crystals with strong chloritization and sericitization in porphyrite, the vein-type pyrite cutting across plagioclase; (b) plagioclase with strong chloritization and sericitization in the porphyrite, amphibole is totally chloritized resulting in the formation of pyrite; (c) idiomorphic crystal grains of potassic feldspar with sericitization; (d) crystals of plagioclase, amphibole, and biotite with strong sericitization; (e) crystals of potassic feldspar, plagioclase, and amphibole with sericitization in the porphyrite associated with the porphyry Cu-Au deposit; (f) plagioclase and amphibole in the porphyrite with strong sericitization associated with the porphyry Cu-Au deposit; (g) idiomorphic crystal grains of amphibole and plagioclase replaced by sericite and chlorite.
The chemical compositions of the intrusive rocks associated with Cu-Au mineralization are presented in Table 4 (see online supplementary material). This indicates that the Shaxi-Chagpushan intrusive rocks mainly belong to calc-alkaline to high-K calc-alkaline series, and only a few samples are shoshonitic or tholeiitic series (Figure 7). In contrast, samples from both Tongling and the Luzong volcanic basin mainly belong to shoshonitic to high-K calc-alkaline series; samples in Anqing are high-K calc-alkaline series. These data imply different characteristics of sources for these Cu-Au metallogenic districts, reflected also by REE and trace elements data as shown below.

The chemical classification of the TAS diagram shows that most samples from Shaxi-Changpushan fall into the diorite region, similar to those of Tongling and Anqing diorite, whereas the volcanic rocks in Luzong volcanic basin are much different (Figure 8).

**Rare earth elements**

The data of REE and trace elements are listed in Table 5 (see online supplementary material). The intrusive rocks associated with mineralization in the Shaxi-Changpushan district have total REE contents between 66 and 263 ppm, with enriched LREE relative to
heavy REE (HREE) without Eu anomaly (Figure 9). It is not evident for a significant change in REE patterns of the altered intrusive rocks with increasing depth (Figure 9). Compared with the average contents of the continental crust, the REE patterns of the intrusive rocks area are more similar to the lower crust (Taylor and McLennan 1985), although their total REE contents are higher; and fractionation of LREE and HREE is larger. This may be an important indication for Cu mineralization in this region. Furthermore, the light REE patterns of Shaxi, Luzong, Anqing, and Tongling Cu-Au-mineralized intrusive rocks

Figure 5. Isothermal section of a S-Fe-Cu diagram at 300°C from the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui (after Yund and Kullerud 1966). Py, pyrite; Cp, chalcopyrite; Cov, coversite; Bn, bornite; Id, idaite; Cb, cubanite; Cch, chalcocite; Po, pyrrhotite.

Figure 6. The relations between element contents of Au and As in pyrite and chalcopyrite.
are very similar, although their heavy REE distributions are different. It is worth noting that the intrusive rocks associated with Cu (Au) mineralization have similar ages (Cretaceous) and display comparable Sr and Nd isotopic compositions (Chang et al. 1991; Yang 1996; Chen and Jahn 1998). Intriguingly, different styles of Cu (Au) mineralization are
evident in different areas of the region. For example, in Luzong volcanic basin and Anqing high-potassic diorites that are near the Shxi–Changpushan deposit, Cu (Au) mineralization occurs mainly as massive sulphidation, whereas in the Tongling area to the south of the Shaxi–Changpushan deposit, the Cu-Au mineralization is mainly hosted in skarn.

**Trace elements**

The spider diagrams of the intrusive rocks from the Shaxi–Changpushan area compared with those related to Cu-Au mineralization from the Luzong, Anqing, and Tongling areas in Anhui Province of the lower Yangtze metallogenic belt are shown in Figures 10–13, suggesting that the mantle compatible elements (e.g. Sc, Cr, Co, Ni) and some transitional elements (e.g. Ti, V, Mn, Fe, Cu) in these rocks are strongly fractionated relative to the crust rocks (Taylor and McLennan 1985; Thorpe 1976, 1982), with pronounced Cu positive anomalies. This could be an important indication for Cu mineralization in this region. Large ion lithophile elements such as K, Rb, Th, Sr, Ba, and Li are also enriched compared to the average contents of crust rocks, which manifest the regional geochemical anomalies of these elements, which may be a favourable feature for mineralization.

**Age of the Shaxi–Changpushan intrusive complex and its tectonic environment**

**Age of the Shaxi–Changpushan intrusive complex**

The age of the Shaxi–Changpushan intrusive complex has been debated for long time. There is a wide distribution of igneous rocks in this region with characteristics of multiple
Figure 10. Spider diagrams of trace elements in the Shaxi–Changpushan district. (a) Diagram of transitional elements. (b) Diagram of large lithophile elements.

Figure 11. Spider diagrams of trace elements in the Luzong volcanic basin, central Anhui. (a) Diagram of transitional elements. (b) Diagram of large lithophile elements.
magmatic activities that are manifested by field observations; the volcanic rocks overlie the Middle–Upper Jurassic sandstones of the Xiangshan group and have intrusive contact with the Lower Cretaceous red beds. Therefore, the volcanic activities were confined between the Late Jurassic to Early Cretaceous. Earlier dating with the K-Ar method on whole rock samples presented 173–123 Ma (No. 327 Geological Party 1982).

Recently, relatively high-precision dating methods, such as Ar-Ar and SHRIMP, have been used to date the Shaxi–Changpushan intrusive complex and surrounding intrusions. The results of 40Ar/39Ar dating on four monominerals (two biotite and two plagioclase) separated from the Shaxi–Changpushan complex yield ages ranging from 126 to 135 Ma, which are interpreted to represent the age of formation of the intrusion host to the Shaxi Cu-Au deposit (Fu et al. 1997; Yang et al. 2007b). The concordia age of ~131 Ma determined by SHRIMP zircon U-Pb dating on the Huangtun intrusion (see location in Figure 1; Yu et al. 2009) indicates that two intrusions of Shaxi–Changpushan and Huantun in the Shaxi–Luzong area may have occurred in the same magmatic event when the regional porphyry Cu-Au formed.

The two intrusive bodies of Shaxi–Changpushan and Huantun may have been derived from the same magmas sourced from the deep crust (No. 327 Geological Team 1982; Wang et al. 1994), displaying two stages of magmatism in the Shaxi–Changpushan–Huangtun regions. The early stage is an intrusive magmatism associated with variable copper (gold) mineralization, represented by quartz diorite porphyry, biotite quartz diorite porphyry, and the less important amphibole diorite porphyry and brecciated diorite porphyry.

In the Luzong volcanic basin nearby (Figure 1), the volcanic rocks are shoshonitic and have similar ages of 136–124 Ma (Yuan et al. 2008) to the Shaxi–Changpushan complex.
Chemical composition and isotopic data suggest that the intrusive rocks from both Shaxi–Changpushan area and Luzong volcanic basin require a source like enriched mantle (Yang 1996; Yuan et al. 2008).

The late stage of magmatic activity is represented by magma injection accompanied by volcanic explosion and sub-volcano activities of a large amount of basic, intermediate, and intermediate-acid magmas without copper (gold) mineralization.

**The tectonic environment of Shaxi–Changpushan complex**

On the tectonic discrimination diagram of Batchelor and Bowden (1985), the intrusive rocks in the Shaxi–Changpushan area fall in the fields of syn-collision and post-collision uplift environments (Figure 14). In the Nb-Y and Yb-Ta trace element discrimination diagram (Figure 15a,b), the Shaxi–Changpushan intrusive rocks are located in syn-collision or volcanic arc fields. Considering the early Cretaceous age of the Shaxi–Changpushan complex and the tectonic background of east China in the Yanshanian period (Zhou and Li, 2000; Deng and Wu 2001; Sun et al. 2007), the Shaxi–Changpushan intrusive complex is likely to be related to the West Pacific plate subduction under the East China continent.

Where did the collision environment come from? To answer this question, we must first consult the background of east China since the Jurassic. After the completion of subduction of the Yangtze and North China plates, the east part of China jointed together as a single craton. However, this part was soon affected by the subduction of the West Pacific plate...
since the Jurassic (Sun et al. 2007), which almost controlled the igneous activities and their metallogenesis in east China, traditionally called the Yanshanian movement by Chinese geologists. By using the discrimination diagrams, we obtained Figure 16a,b, which can be fully used to interpret the forming environment of these Cretaceous intrusives related to Cu-Au deposits along the Yangtze metallogenic belt. Among them, Shaxi intrusive activity with an age range of 126–135 Ma (Yang et al. 2007b) is a typical Cretaceous magmatism, with distinguished characteristics of adakitic origin (Drummond and Defant 1990a,b). According to the La/Yb vs. Sm/Yb diagram (Figure 17), the Shaxi–Changpushan intrusive engaged a high-middle extent of melting.

From the above discriminations, we inferred that the Shaxi porphyry copper (gold) deposit has some relation to the collision of the plate tectonics.

**Fluid inclusions**

Fluid inclusions in gold-bearing quartz veins from the Shaxi deposit are liquid-gas coexisting inclusions. The composition of representative fluid inclusions together with homogenization temperatures are given in Table 6 (see online supplementary material). The relationship between Na⁺ and Cl⁻/F⁻, Na⁺/K⁺, and Na⁺/(Ca²⁺ + Mg²⁺) ratios is shown in Figure 18, from which two trends can be obtained. One is for Na⁺ to Na⁺/(Ca²⁺ + Mg²⁺) and the other is for Na⁺ to Cl⁻/F⁻ and Na⁺/K⁺. The homogenization temperatures range from 230 to 350°C, similar to most porphyry Cu deposits and some hydrothermal
Cu-Au deposits elsewhere (e.g. Lowell and Guilbert 1970; Kamili and Ohmoto 1977; Barton et al. 1977; Shelton 1983; Shelton and Lofstro 1988; Choi et al. 1997; So et al. 1997).

Stable isotopes

Sulphur isotope

Bulk samples were systematically collected from the different ore bodies in the deposit to examine sulphur isotopes. The samples were crushed to <120 meshes in size, which were used for mineral separation. Pure pyrite and chalcopyrite concentrates were obtained by Rantz magnetic separator, standard heavy liquid, and handpicking, which were analysed.
Figure 16. Discrimination diagram for the origin of intrusive rocks in Shaxi–Changpushan and its adjacent region. (a) Y (ppm) versus Sr/Y diagram (Drummond and Defant, 1990b). The curves represent various models of the partial melting of depleted and altered MORB with an amphibolite or eclogite resi-tilate: 1, eclogite (gt/cpx = 50/50); 2, garnet amphibolite (gt/am = 10/90); 3, amphibolite eclogite (am/gt/cpx = 10/40/50); 4, garnet amphibolite (gt/am = 10/90). Starting compositions for curves 1 and 2: Sr = 141 ppm and Y = 21 ppm; curves 3 and 4: Sr = 264 ppm and Y = 38 ppm, gt, garnet; cpx, clinopyroxene; am, amphibolite. (b) Chondrite-normalized YbN versus (La/Yb)N diagram modified after Jahn et al. (1981), Martin (1986) and Drummond and Defant (1990b). Four partial melting curves are displayed, two of which (amphibolite and 10% garnet amphibolite resi-tite curves) assume a MORB source and the other two partial melting curves (eclogite and 20% horn-blende eclogite curves) assume a MORB source with YbN = 12 and (La/Yb) N = 1. Percent partial melt values are listed on each of the model curves.
Figure 17. La/Yb v.s. Sm/Yb diagram for intrusive rocks in Shaxi–Changpushan and its adjacent region (Martin 1986).

Figure 18. The relation between the Na\(^+\) and ratios of Cl\(^-\)/F\(^-\), Na\(^+\)/K\(^+\) and Na\(^+\)/(Ca\(^{2+}\) + Mg\(^{2+}\)) in fluid inclusions from the Shaxi–Changpushan porphyry Cu-Au deposit.
for sulphur isotopes in the Institute of Coal Science, Xi’an, China. The analytical accuracy is about 0.5‰. All the results are expressed as $\delta^{34}S$ values relative to the Cañon Diablo Troilite sulphur (CDT). Sulphur isotope data in this deposit and those from some typical Cu-deposits in China are summarized in Table 7 (see online supplementary material).

The $\delta^{34}S$ values in the Shaxi–Changpushan porphyry Cu-Au deposit range from −0.01 to 0.30‰, which can be calculated for the total $\delta^{34}S$ values of 0.11‰ based on sulphide assemblages using the method of Pickney (1972). The narrow variation in $\delta^{34}S$ values is similar to those of large to super-large porphyry copper deposits, such as Dexing, Yulong, and Duobaoshan in China (Rui et al. 1984), suggesting similar sulphur sources for these deposits. However, the sulphur isotope compositions in the copper deposits in the Luzong volcanic basin, Anqing, and Tongling areas adjacent to the Shaxi–Changpushan district are remarkably different, which is also reflected by their different styles of mineralization mentioned above. Figure 19 presents the diagram of sulphur isotopic results for regional variations of both pyrite and chalcopyrite in the Shaxi–Changpushan porphyry copper (gold) deposit and other copper deposits in China. It is noted that the sulphur isotopic values of chalcopyrite are relatively narrow compared to pyrite.

**Oxygen and hydrogen isotopes**

Oxygen and hydrogen isotopic data in this deposit and those from some typical Cu-deposits in China are summarized in Table 8 (see online supplementary material), showing that $\delta D$ and $\delta^{18}O$ values of ore fluids range from −71.7 to −82.4‰ and from 4.0 to 4.6‰, respectively, whereas the $\delta^{18}O$ value of post-mineralization fluid is −4.38‰. The $\delta^{18}O$ values of whole rocks range from 8.3 to 11.6‰, appearing to decrease with increasing depth of alteration and mineralization. Figure 20 is the histogram showing the variation of $\delta^{18}O$ values in different minerals of the Shaxi–Changpushan, Dexing, and Yulong porphyry...
copper deposits, and the other three copper-mineralized areas adjacent to the Shaxi–Changpushan district.

Hydrogen and oxygen isotopic data show that ore-forming fluids are composed mainly of magmatic water with minor meteoric water (Figure 21), while post-mineralization fluids are dominated by meteoric water. Thus the ore-forming fluids and materials were mainly derived from magmatic sources, and meteoric water may have played little role in the formation of ore. This is consistent with the result of sulphur isotopes.
Geochemical exploration and ore-forming model

Geochemical exploration

The characteristics of mineralization for different elements in the ore deposit are summarized in Table 9 (see online supplementary material). It can be seen that Mo, Pb, Zn and Co, Au, and Ag anomalies are evidently associated with Cu mineralization; F and Cl are also enriched. Potassium, Rb, Si, Na, and Sr are enriched in the magmatic stage, whereas Ti and Mn are enriched in both magmatic and hydrothermal stages.

Figure 22 shows these chemical variations of the alteration zones, illustrating that the ore bodies are surrounded by anomalous Cu and Co halos. However, Mo and Ag anomalies do not show any relationship to the ore bodies. Zinc and Pb anomalies are evident on the surface of the ore bodies, which may be related to the oxidation of ore bodies.

The element contents in the Cu-Au bearing ores in the Shaxi–Changpushan porphyry Cu-Au deposit are listed in Table 10 (see online supplementary material), the correlation between Au and As, Cu, and S is shown in Figure 23, and two linear trends are evident between Au, Cu, and As, suggesting that they are closely related in ore fluids, consistent with the relationship shown in pyrite and chalcopyrite (see Figure 6).

Table 11 (see online supplementary material) lists results of some major and trace elements from exploration drilling samples from different alteration and mineralization zones. The results are plotted in Figures 24 and 25, showing chemical variations in different alteration zones.

From Figure 24, it can be seen that SiO₂ and Al₂O₃ are enriched in the quartz-sericitization zone and depleted in both potassic alteration and propylitization zones; Fe₂O₃, MgO, and CaO are enriched in both potassic alteration and propylitization zones and depleted in the quartz-sericitization zone. K₂O is elevated in the potassic alteration zone and depleted in the other alteration zones; H₂O is enriched in the propylitization zone. The other major elements do not show significant variation in the different alteration zones.

From Figure 25, it can be seen that Cu, Mo, Ag, Zn, Ba, and Rb are highly enriched in the potassic alteration zone, but relatively depleted in the other alteration zones. Co, Sr, and Ni are depleted in the potassic alteration zone and relatively enriched in the other alteration zones. Cl, S, F, and I show relatively constant contents in the different alteration zones except in Silurian and Jurassic sedimentary rocks.

Ore-forming model for the Shaxi-Changpushan prospecting region

The drilling data reveal that most of the ore bodies have an overturned U-shape, and the porphyry dioritoids are also emplaced in the core of a composite anticline in this region (Figure 26), suggesting that the fold may have controlled the emplacement of the intrusions and associated ore formation. The Upper to Lower Silurian clastic rocks, in particular mudstone and siltstone, may serve as the shielding of the ore bodies and the intrusive rocks, and the distribution of the ore bodies and porphyry dioritoids near the core of the anticline now exposed on surface may result from the denudation of the sediments. This structural analysis suggests that the Changpushan district adjacent to the south of Shaxi porphyry Cu (Au) deposit may have high potential for mineralization, where the Silurian sediments are also exposed and Cu-bearing gossans were discovered during our field work (Figure 27). Three grab samples contain 560 to 1450 ppm Cu (Table 12, see online supplementary material); they also contain relatively high Pb, Zn, Co, S, F, and Cl (Figure 28). Moreover, mineralization occurs in the core of the Shaxi–Changpushan anticline, which provides a favourable setting for the formation of ore deposit.
Figure 22. Distributions of rock facies and element zoning in No. 9 explored line in the Shaxi–Changpushan Cu-Au deposit, central Anhui (after No.327 Geological Team 1982). (a) The distributions of the rock facies by drilling exploration in No. 9 explored line in Shaxi porphyry Cu-Au deposit; (1) Jurassic system; (2) Silurian system; (3) coarse grained porphyry dioritoid; (4) middle grained porphyry dioritoid; (5) hypabyssal porphyry dioritoid; (6) fault; (7) the top boundary line of intrusive facies distinguished by grain size. (b) Element zoning in No. 9 explored line; (1) ore bodies; (2) the oxidation zone; (3) isogram of Cu (in ppm); (4) isogram of Mo (in ppm); (5) isogram of Ag (in ppm). (c) Element zoning in No. 9 explored line; (1) ore bodies; (2) the oxidation zone; (3) isogram of Pb (in ppm); (4) isogram of Zn (in ppm); (5) isogram of Co (in ppm).
The movement of Tan–Lu fault in the Triassic resulted in relatively strong deformation of the Cu-Au-mineralized quartz porphyries and their wall rocks consisting of Silurian and Jurassic clastic sediments (Yang 1996). Barren intrusive rocks exposed in the two limbs of the anticline may be transitional facies of the central intrusion, which are mainly volcanic and subvolcanic rocks (Figure 2).

From the above facts, a model for controlling ore bodies in the core of the anticline, where the hydrothermal fluids and mineralization are concentrated, is illustrated as Figure 29. In the limbs of the anticline, little fluid could be concentrated so that no ore bodies were formed (Yang 1996). The Tan–Lu fault belt had been a larger scale of left translation in the Indo-Sinian period, which caused a series of secondary faults and plumose fractures with NNE direction in the sedimentary rocks. This tectonic process formed the anticline structure in the Shaxi–Changpushan region (Xu et al. 1987; Yang 1996; Yang et al. 1998a,b). The secondary faults and fractures in the sedimentary rocks provide channels for ore fluids that generate mineralization in the core of the anticline and form economic ore bodies.

Discussion

Structural analysis suggests that the Tan–Lu fault belt had played a key role in transporting ore fluids. This deep fault, reaching the mantle, and derivative fault and fracture systems cut sedimentary rocks in the ore district, providing an ideal channel for ore fluids derived from the intrusions. This setting is also present in other large to super-large porphyry copper deposits in China. For example, the Dexing super-large porphyry copper deposit in the middle part of the Yangtze valley is situated in the tip of the waved arc structure, and the Tongchang porphyry copper deposit (also in the middle part of the Yangtze valley) is located in the core of the local anticline (Zhou 1983; Rui et al. 1984). Chang et al. (1991) and Zhai et al. (1996) pointed out that the Eastern Yangtze Craton in central to eastern China is an important Fe-Cu metallogenic province, and metallogenic belts were controlled by faults and aulacogens in the continental plate in the early Yanshan epoch.
(Jurassic); the dominant west-northwest and east-west lithospheric faults control the distributions of Cu (Mo and Au) mineralization.

Geochemical mapping in the China continent (Xie et al. 1997) shows that Cu and Au in the Shaxi and Tongling areas are high, favourable for the formation of Cu and Au deposits. Metals
Figure 25. Trace element migrations during alteration processing in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui (From left to right of the X axial of the diagram, representing the decreasing depth of samples from ore bodies and wall rocks; all the legends are the same as those in Figure 24).
may be derived from the low crust and/or upper mantle, which had undergone extensive fractionation in trace and rare earth elements in particular, which may be important for porphyry copper mineralization. It is likely to form the mineralization of large and super-large porphyry copper deposits in China (Zhou 1983; Wang and Qin 1991). The S, H, and O isotopic data suggest that ore-forming fluids and materials were mainly derived from magmatic sources. Chen and Tang (1993) proposed that tectonic setting and palaeo-sedimentary environment are two main factors for forming large and super-large copper deposits in China. The Yanshanian-Himalayan episodes are the dominant times for development of porphyry copper deposits in China, such that Yulong, Dexing, Jinduigcheng, Deheishan, and Nanihu deposits all occur in this period, where all the large and super-large deposits occur in the earlier stage of geosynclinal regions. The ore-bearing intrusions generally occur as stocks striking obliquely to the strike of the surrounding strata, which display many similarities to those in the Shaxi–Changpushan district (Chang et al. 1991).
After the Indo–Sinian period (Mesozoic–Cenozoic), the great majority of crust in China was in the stage of platform activation-depression (Chen 1982). The thickness of the continental crust increased notably; the activities of fractures were strong. A large number of intermediate-acid rock intrusive bodies and down-faulted basins were formed, and the mainly humid, hot palaeoclimate (Palaeozoic) changed to the mainly dry hot one, that is, indicative of large-scaled red beds in this period. This geological setting was well developed in the Shaxi–Changpushan district with Cu-Au mineralization, which is fertile in the formation of large to super-large porphyry copper deposits (Guo et al. 1978; Rui et al. 1984; Chen 1984; Chen and Tang 1993).

According to the mapping standard of Cu and Au anomalies in the Yangtze metallogenic belt (Xie et al. 1997), several grades of anomalies have been proposed, such as for Cu anomalies, there are six grades with 12.0, 18.0, 25.0, 40.0 and 50.0 ppm, respectively; and for Au anomalies, there are two grades with 3–60 ppb and more than 6 ppb, respectively. Compared to our study, the Cu content is largely variable in the Shaxi porphyry copper deposit, varying from 14.2 up to 9569.0 ppm. In Luzong region nearby, Cu content is variable from 5.1 to 353.6 ppm; in Anqing area, Cu content ranges from 55.1 to 148.0 ppm; in the Tongling area, Cu content is varied from 0 to 182.5 ppm. Au content in

Figure 28. Diagrams showing the relationships between Cu and other elements from samples in Figure 27. (a) The relation between Cu and Pb, Zn Co, Ni, and Cr. (b) The relation between Cu and S, As, F, Cl, and Sr.
the Shaxi and Tongling area range from 3.2 to 93.8 ppb, and 0.7 to 36.1 ppb, respectively (Table 3, see online supplementary material).

In summary, the formation of Shaxi–Changpushan porphyry copper (gold) deposit is mainly controlled by the abundances of ore-forming elements coming from the lower crust or the upper mantle by a large extent of fractionation, the other important factor is the special evolution of the crust in this region, where there is great potential to form a large porphyry copper deposit.

Tectonic environmental discriminations

In recent years, petrologists favoured adakite to trace the Cu-Au mineralization in east China and presented a number of petrochemical proofs (e.g. Zhang et al. 2001; Xu et al. 2002; Chung et al. 2003; Wang et al. 2006).

What is adakite or adakitic rock? According to the definition proposed by scholars (e.g. Drummond and Defant 1990a; Martin 1999), adakites are intermediate to felsic igneous rocks, andesitic to rhyolitic in composition (basaltic members are lacking), which should have trondhjemitic affinities (high-Na$_2$O contents and K$_2$O/Na$_2$O of 0.5) and their Mg no. (0.51), high contents of Ni (20–40 ppm) and Cr (30–50 ppm) contents are higher than in typical calc-alkaline magmas (Martin 1987; Drummond and Defant 1990b). Sr contents in adakite are usually high (>300 ppm, until 2000 ppm) and REE show strongly fractionated patterns with very low HREE contents (Yb $\leq$ 1.8 ppm, Y $\leq$ 18 ppm). These adakatic rocks are depleted in Nb and Ta compared with other igneous rock. The origin of adakites was due to the remelting of young subducted oceanic crust.

However, in a large sense, the tectonic formation of adakites are still disputed at present, the points of views are (1) the melting of young oceanic crust during the subduction; (2) delamination or foundering of dense mafic lower crust rocks (e.g. eclogite and garnet pyroxenite) in mafic lower crust to the mantle during continental orogenesis. Consequently, the Fe-Cu-Mo mineralization is closed related to the formation of adakites.

Figure 4 presents a clue that intrusive rocks in Shaxi porphyry copper (gold) deposit have some relation to the collision of the plate tectonics. But where did the collision environment come from? To answer this question, we must first consult the background of east
China since the Jurassic. After the completion of subduction of the Yangtze and North China plates, the east part of China jointed together as a single craton. Thereafter, this jointed craton was soon affected by subduction of the West Pacific Plate since the Jurassic. By using discrimination diagrams of adakite, we obtained Figures 6 and 7, which can be reasonably used to interpret the forming environment of these Cretaceous intrusives related to Cu-Au deposits along Yangtze metallogenic belt, among them, Shaxi intrusive activities with ages ranging from 126 to 135 Ma are typical Cretaceous magmatism (Yang et al. 2007b), with distinguished characteristics of adakitic rocks (Lan et al. 2009). Recently, Chinese scholars have identified typical high-Mg adakites (131 ± 3 Ma) with lower radiogenic lead in the Dabie UHP orogenic belt north adjacent to the Shaxi–Changpushan region (Huang et al. 2008), which is of significance to understand the adakitic formation and regional crust evolution.

From the above discussion, the adakitic origin is reasonable for an explanation of the formation of Cu-Au related intrusives in Shaxi–Changpushan area, where there is a great possibility to form a large–super-large Cu-Au deposit.

Conclusions
Fluid inclusions in Shaxi–Changpushan quartz veins associated with Cu (Au) mineralization consist dominantly of liquid and gas phases, although some inclusions are composed only of a liquid phase. Ore-forming temperatures were between 230 and 350°C. Sulphur isotope studies show that δ34S values of chalcopyrite are somewhat more homogenous than those of pyrite; the ore-forming fluids and materials were mainly derived from magmatic sources, but meteoric water played a minor role consistent with the results of oxygen and hydrogen isotope study. Gold occurs as micro-inclusions heterogeneously distributed in chalcopyrite and pyrite. Formation of the Shaxi–Changpushan porphyry copper (gold) deposit was mainly controlled by the abundance of ore-forming elements derived from the lower crust or the upper mantle by a high degree of crystal-melt fractionation. The other important factor is the special evolution of the crust in this region (the medium–fine-grained altered diorite complex, good sedimentary bedding, and deep-cutting fault system), provided great potential to form a large porphyry copper deposit. The existence of widespread porphyry Cu-Au mineralization in the Changpushan district adjacent to the Shaxi deposit is significant for this orogenic belt. The metallogenic and tectonic background was controlled by slip along the Tan-Lu fault system, with the Jurassic sedimentary rocks as well as the igneous rocks associated with the Cu (Au) mineralization.

Whatever the ultimate origin, the presence of a giant porphyry Cu-Au deposit in the Shaxi–Changpushan district appears to be highly likely.

Acknowledgements
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Geochemistry of gold deposits in the Zhangbaling Tectonic Belt, Anhui province, China

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The Zhangbaling Tectonic Belt (ZTB) is located in eastern Anhui province, adjacent to the Tan-Lu fault zone to the W and the Lower and Middle Yangtze River metallogenic zone to the E. Two types of gold deposits: (1) altered-tectonite gold and (2) quartz-vein gold are present in the ZTB. Three ranges of homogenization temperatures ($T_h$) were obtained by fluid inclusion investigations of the altered-tectonite gold deposits: 115–165°C, 235–275°C, and 335–395°C; and of the quartz-vein gold deposits: 145–195°C, 205–255°C, and 255–335°C, respectively. $d^18O$ values of the ore-forming fluids range from $−52.2‰$ to $−75.3‰$, and their isotopic compositions calculated from quartz analytical data show negative $\delta^18O$ values ($−6.3–0.1‰$) for the quartz-vein gold deposits. The calculated $\delta^18O$ values of water are evidently lower than magmatic water, and probably were derived from mixtures of magmatic and meteoric water. Although the total rare earth elements (REE) content of the quartz-vein gold ores are much lower than those of the spatially associated granites, their chondrite-normalized patterns are similar, indicating that ore-forming elements in the ZTB quartz-vein gold deposits probably were derived from the plutons. Ores from the altered-tectonite gold deposits show $\delta^{16}O$ values and chondrite-normalized REE patterns similar to those of the granites, indicating that ore-forming elements of the altered-tectonite gold deposits also were sourced in the Yanshanian plutons. The gold deposits in the ZTB are remarkably similar to those in the Jiaodong gold metallogenic province with regard to tectonic settings, mineralization-controlling factors, mineralization ages, and the ore-forming temperatures and the stable isotopic compositions.

**Keywords:** gold deposits; fluid inclusion; hydrogen and oxygen isotopes; REE; Zhangbaling Tectonic Belt; east Anhui province; China

Introduction

The Zhangbaling Tectonic Belt (ZTB) is located in eastern Anhui province, which is adjacent to the Tan-Lu fault zone to the W and the Lower and Middle Yangtze River metallogenic zone to the E. This NNE–SSW-striking belt extends to Susong to the S, then westward to Wudang and Suixian in Hubei province. To the N, it extends to Guanyun in Jiangsu province.
A rift developed in ZTB during the late Proterozoic, with acceptance of extensive marine volcanic rocks and sediments which were modified by the subsequent Triassic blueshist-facies metamorphism (Jin et al. 1991).

Several gold deposits are distributed in the ZTB, which are probably associated with Yanshanian granite (Huang et al. 2000a). Two major types, that is, mineralized tectonic breccias and gold-bearing quartz veins, can be observed in the ZTB, which commonly coexist in their occurrence. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of quartz from gold deposits gave ages between 116.1 ± 0.6 Ma and 118.3 ± 0.5 Ma (Ying and Liu 2002), which shows that the gold mineralization is coeval with or slightly postdate granitoid intrusions. This can be compared with that of the Jiaodong gold province in Shandong in the N along the Tan-Lu fault zone (Chen et al. 2004a) and the Shaxi copper–gold deposits in the adjacent Lower Yangtze metallogenic zone (Yang et al. 2002). The occurrences of all major ore bodies are controlled by the sub-fractures of Tan-Lu fault zone (Zhu et al. 2007), indicating that the granite intrusions and the gold mineralization are closely correlated with the tectonic movement similar to the situation in Jiaodong.

The ZTB is key to connecting two famous metallogenic zones in China: the Lower and Middle Yangtze River and the Jiaodong. The study of the tectonic evolution and mineralization in the ZTB can provide valuable information for further probing into the relationship between tectonic evolution and mineralization in these two famous metallogenic zones. Meanwhile, ZTB is similar to Jiaodong in tectonic settings and mineralization-controlling factors, which shows a potential of gold mineralization in ZTB. However, study on the deposits in Zhangbaling area is still poor. This article presents data of element compositions and fluid inclusions from fresh igneous rocks and altered rocks. Discussion is focused on the origins of the ore-forming fluids and their implications for ore genesis of gold mineralization in ZTB, on the basis of oxygen- and hydrogen-stable isotopes and rare earth elements (REE). Detailed comparison is shown between gold mineralization in ZTB and the Jiaodong peninsula, the largest gold production base in China, which is also controlled by the Tan-Lu fault zone (Zhou et al. 2002).

Figure 1. Tectonic map showing the situation of the Zhangbaling Tectonic Belt (modified from Dong and Huang 1995).
Geologic setting and geology of the deposits

Geologic setting

The ZTB is situated in Anhui province in China, which is adjacent to the Chu-He fault to the E and the Tan-Lu fault zone to the W. The Tan-Lu fault zone comes through the entire mineralization region and results in strong deformation in the Jurassic (Xu et al. 1987; Yang et al. 1998, 2001a). The strata exposed in the ZTB include the Neoproterozoic Zhangbaling group, the Sinian system, the lower Palaeozoic, and the Cretaceous–Palaeogene system (see Figure 2 for distributions). The Zhangbaling group is composed of schists and

Figure 2. Schematic map of the Zhangbaling Tectonic Belt (Modified from BGMR 1987).
phyllites with banded blueschists, which were formed inside late Proterozoic aulacogen (BGMR 1987). Studies show that the metamorphism of the Zhangbaling group took place during the Triassic period (Niu et al. 1993). The lower Sinian system consists of clastic sedimentary rocks and the upper system mainly consists of limestone and siliceous limestone. The lower Palaeozoic unit is a sequence of shallow marine carbonates and clastic sedimentary rocks. The Cretaceous–Palaeogene rocks were dominated by fluvial and lacustrine sandstones and conglomerates with minor volcanic rocks.

The granitoid intrusions are distributed in the western part of the belt, and are adjacent and parallel to the Tan-Lu fault zone, stretched in a NNE–SSW direction (Figure 2). Gold deposits in the ZTB are widely scattered. In the Zhangbaling area, it is conspicuous that the gold mineralization, either from deposit or orebody scale, was controlled by fractures, which are part of the Tan-Lu fault system. The second-order, deep Guandian–Longwangjian fault, characterized by ductile deformation, controls the regional distribution of most gold deposits in this belt (Huang et al. 2000b).

Deposits geology

Quartz-vein gold deposits

The quartz-vein gold deposits in the ZTB are mainly composed of intensive quartz veins with economic gold grade. The quartz vein lodes are confined to fractures in three directions: NNW–SSE, NW–SE, and NNE–SSW. The NNE–SSW-trending lodes usually dip to the NWW in steep angles with thickness of 0.2–1 m. The NW–SE-trending lodes have SW dip with an average thickness of 0.5 m and the NNW–SSE-trending lodes dip to the SWW with thickness of 1–2 m.

Wall-rock alteration associated with gold mineralization is characterized by K-feldspar and silica alteration, sericitization, chloritization, carbonation, and pyritization. The ore is dominated by sulphide-bearing quartz veins. The mineral assemblage of the ore includes quartz, carbonate, albite, pyrite, arsenopyrite, sphalerite, galena, chalcopyrite, magnetite, and traces of other minerals. Gold mainly occurs as microscopic inclusions in arsenopyrite, pyrite, and chalcopyrite.

Paragenetically, the mineralization is divided into three stages: (1) an early Au-poor stage with pyrite-arsenopyrite-quartz assemblage; (2) an Au-rich stage with pyrite-arsenopyrite-chalcopyrite-galena-sphalerite-quartz assemblage; and (3) late-stage quartz-carbonate (Huang et al. 2000a). The fine-grained gold is mainly associated with pyrite or arsenopyrite, which is similar to the Shaxi copper-gold deposits in the adjacent Lower Yangtze metallogenic belt (Yang et al. 2002).

Altered-tectonite gold deposits

Mineralization in this type of gold deposit is disseminated in the altered-tectonite zone inside which structural breccia is developed. The occurrence of the ore body is concordant with and confined to the altered-tectonite zone, which is trending NNE and dipping SEE with a thickness of 2–10 m. Sulphide-bearing quartz veinlets, which formed at late-stage mineralization, can be found inside the altered-tectonite zone.

Wall-rock alteration in association with gold mineralization is intense and shows obvious alteration zoning. According to the mineral assemblages, from the centre of the tectonite zone into the wall rock, the alteration can be divided into three zones: a pyrite-quartz-sericite-chlorite
zone, a sericite-quartz-chlorite zone, and a quartz-potassium feldspar zone. The ore types include altered structural breccia and minor veins inside or adjacent to the structural breccia zone. The sulphide minerals consist mainly of pyrite and arsenopyrite together with scarce amounts of chalcopyrite, sphalerite, and galena.

**Petrochemistry of intrusive rocks and ore deposits**

**Major elements of intrusive rocks**

The chemical compositions of the intrusions associated with gold mineralization in the ZTB are presented in Table 1. Some of the granitic rocks in this region are petrographically classified as quartz monzodiorite, and the others as granodiorite and granite based on the quartz-alkali feldspar-plagioclase (QAP) diagram (Figure 3), which indicates that the intrusions in this belt are mainly composed of granodiorite, quartz monzodiorite, and granite. The chemical classification of the Na₂O + K₂O – SiO₂ (TAS) diagram (Figure 4) shows that most samples from the area belong to subalkaline series, and are characterized by high-K value (Figure 5).

**Rare earth elements of intrusive rocks**

The data of REE and trace elements of intrusive rocks associated with mineralization in the ZTB are listed in Table 2. The total REE contents are between 103 and 233 ppm, with enriched light REE (LREE) relative to heavy REE (HREE) without Eu anomaly (Figure 6). The chondrite-normalized patterns of REE curves of the granitoid samples from different intrusions are similar. The (La/Yb)ₙ ratio varied from 13.79 to 47.18. The total REE contents of granites are slightly higher than those of the granites from Jiaodong in Shandong province (Xu et al. 2002), which may be because of the differences of source rocks of the granites and the degree of partial melting. The total REE contents and the chondrite-normalized patterns are similar to those of the granitoids from the Lower Yangtze metallogenic belt (Yang et al. 2009), which were probably derived from the lower crust (Yang et al. 2009).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rocks</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>FeOT</th>
<th>Fe₂O₃T</th>
<th>MnO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
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<td>D-10</td>
<td>Quartz monzodiorite</td>
<td>60.77</td>
<td>0.73</td>
<td>14.79</td>
<td>1.81</td>
<td>3.58</td>
<td>5.21</td>
<td>5.79</td>
<td>0.09</td>
<td>4.33</td>
</tr>
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<td>0.71</td>
<td>14.73</td>
<td>1.85</td>
<td>3.46</td>
<td>5.12</td>
<td>5.69</td>
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</tr>
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<td>3.74</td>
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<td>1.23</td>
<td>11.86</td>
<td>12.97</td>
<td>14.41</td>
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<td>1.96</td>
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<td>3.06</td>
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<tr>
<td>S-1</td>
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<td>3.43</td>
<td>4.09</td>
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<td>1.21</td>
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<td>ZK53-5</td>
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<td>0.83</td>
<td>0.74</td>
<td>99.71</td>
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</table>

Source: From Li et al. 1985.
To trace the origin of the ore-forming elements of the quartz-vein gold deposits in the ZTB, the ore samples in quartz-vein gold deposits were collected for REE analysis as well (see Table 2). The total REE contents of the ores, both fresh and oxidized, are much lower.

**Figure 3.** The QAP diagram of granitoid intrusions in the Zhangbaling Tectonic Belt. 2, Alkali-feldspar granite; 3, potassium-feldspar granite; 4, monzonitic granite; 5, granodiorite; 6, tonalite; 7, alkali-feldspar quartz syenite; 8, quartz syenite; 9, quartz monzonite; 10, quartz monzodiorite; 11, monzodiorite.

**Figure 4.** Chemical classification of the TAS diagram (Wilson 1989). 1, olive gabbro; 2a, Syenogabbro; 2b, gabbro; 3, gabbro-diorite; 4, diorite; 5, granodiorite; 6, granite; 8, alkali-gabbro; 9, alkali-gabbroicdiorite; 10, syenodiorite; 11, alkali-grnmodirite; 12, syenite; 13, feldspathoid gabbro; 14, feldspathoid monzonite diorite; 15, feldspathoid menzonitic syenite; 16, feldspathoid syenite; 17, foidite pluton; 18, leucite rock.

**Rare earth elements of gold deposits**

**REE of quartz-vein gold deposits**

To trace the origin of the ore-forming elements of the quartz-vein gold deposits in the ZTB, the ore samples in quartz-vein gold deposits were collected for REE analysis as well (see Table 2). The total REE contents of the ores, both fresh and oxidized, are much lower.
than those of granites. This probably indicates that REEs tend to incorporate into granites rather than the ore-forming fluids. However, the chondrite-normalized patterns of REE curves of granites and fresh ores are similar (Figure 7). The (La/Yb)\textsubscript{N} is from 10.45 to 22.92, which shows that the samples are rich in LREEs as seen from the curves. The chondrite-normalized patterns of REE curves of oxidized ores display different patterns from those of granites and fresh ores. The oxidized ores are relatively rich in HREEs, which may be because of the release of LREEs during oxidation, whereas HREEs are relatively stable and tended to remain inside oxidized ores. Therefore, the results of REEs, especially the similar chondrite-normalized patterns of granites and ores, indicate that the ore-forming elements of quartz-vein gold deposits in the Zhangbaling are possibly derived from Yanshanian granites.

**REEs of altered-tectonite gold deposits**

Wall-rock alteration in association with gold mineralization in mineralized altered tectonites is more intense and shows more evident alteration zoning in the study region, which implies that the ore-forming fluid flow is not limited to ore-bearing structural conduits, but instead involves interaction between auriferous fluids and surrounding host rocks. Therefore, it cannot be excluded that the wall rocks supply partly ore-forming elements. To probe into the relationship between wall rock and mineralization, the REEs of granites and ores, as well as altered tectonite and wall rock were analysed (see Table 2). The total REE contents of granite just adjacent to ore, altered wall-rock, tectonite, and ore range between 219.14 and 234.31 ppm. However, the differences of the chondrite-normalized patterns of REE curves between these four types of samples are obvious, especially on the LREE pattern curves and δ\textsubscript{Eu} (Figure 8).

The (Ce/Yb)\textsubscript{N} ratios of granites, ore, altered tectonite, and wall rock are 20.81, 8.90, 5.05, and 4.13, respectively, which display the relative increase in HREEs in the order

![Figure 5. SiO$_2$–K$_2$O diagram for the granitoid rocks in the Zhangbaling area (after Le Maitre et al. 1989; Rickwood 1989).](image-url)
Table 2. The REE and trace element data of granitoids and gold deposits from Zhangbaling.

<table>
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<th>Sample</th>
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<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
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<th>LREE</th>
<th>HREE</th>
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Figure 6. Chondrite-normalized REE distribution patterns of the granitoids in the Zhangbaling.

Figure 7. Chondrite-normalized REE patterns of the granites and ores in quartz-vein gold deposits.
granites > ore > altered tectonite > wall rock. The $\delta$Eu values of granites, ore, altered tectonite, and wall rock are 0.93, 0.86, 0.64, and 0.45, respectively, which display the increase in Eu depletion from granites to ore, altered tectonite, and wall rock. As a whole, the chondrite-normalized patterns of REE curves of granites and ore are similar, which indicates that ore-forming elements of altered-tectonite gold deposits in Zhangbaling are from Yanshanian granites, the same as those of quartz-vein gold deposits. The pattern of the REE curve of altered tectonite is similar to wall rock and tends to approach the curves of ore and granite, which implies that the REEs in altered tectonite mainly inherit from wall rock, and take in partly those from ore-forming fluids originating from granites.

The ore-forming fluids

Temperature and salinity of fluid inclusions

Microthermometric measurements of primary fluid inclusions in quartz samples from the Guodawa, Songweizi, Tonggoucheng, and Xiaomiaoshan were conducted using the Linkam THMSG-600 programmed heating–freezing stage and employing standard procedures (Shepherd et al. 1985) by Yichang Institute of Geology and Resources (Table 3). It can be seen from Table 3 that most of the investigated primary fluid inclusions are composed of two phases (liquid-H$_2$O and vapour-H$_2$O). Three phases (liquid-H$_2$O+vapour-H$_2$O+vapour-CO$_2$) are observed only in two samples, which is different from those from the Linglong gold deposit (Shandong province), where the fluid inclusions are rich in CO$_2$ (Zhang et al. 2007). Generally, in gold deposits associated with intrusions, the early-stage ore fluids are characterized by being CO$_2$-rich and late-stage fluids by being CO$_2$-poor and
the lack of daughter minerals (Yang and Zhou 2000; Yang et al. 2001b; Qiu et al. 2002; Chen et al. 2004b, 2007a). Therefore, the low content of CO$_2$ in the fluid inclusions in the Zhangbaling area may be because most of the studied fluid inclusions are formed at the late stage.

Three ranges of homogenization temperatures ($T_h$) were obtained by fluid inclusion investigations of the altered-tectonite gold deposits: 115–165°C, 235–275°C, and 335–395°C, and of the quartz-vein gold deposits: 145–195°C, 205–255°C, and 255–335°C, respectively (Table 3 and Figure 9), which shows that the two types of gold deposits were formed under similar temperatures except that the former show slightly higher temperature on high-temperature range, and the later are closer to those obtained from Jiaodong in the Shandong province (Chen et al. 2004b, 2007a). The $T_h$ of the fluid inclusions in the samples from quartz-vein gold deposits are similar to most hydrothermal deposits elsewhere (e.g. Shelton and Lofstro 1988; So et al. 1997; Xie et al. 2009).

Table 3. The results of microthermometric measurements of fluid inclusions in quartz from the deposits in Zhangbaling Tectonic Belt.

<table>
<thead>
<tr>
<th>Types of gold deposits</th>
<th>Sample number</th>
<th>Phases</th>
<th>Vapour/liquid ratios</th>
<th>$T_h$ (°C)</th>
<th>Salinity (wt.%)</th>
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<td>LH$_2$O + VH$_2$O</td>
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<td>165–195°C</td>
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<td>20–30%</td>
<td>255–335°C</td>
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<td>LH$_2$O + VH$_2$O</td>
<td>10–15%</td>
<td>145–185°C</td>
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<td>15–20%</td>
<td>215–235°C</td>
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<td>15–20%</td>
<td>205–255°C</td>
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<td>G$_3$</td>
<td>LH$_2$O + VH$_2$O</td>
<td>15–25%</td>
<td>205–275°C</td>
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<td>25–30%</td>
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$H$–$O$ Stable isotopes

Stable isotope analyses ($\delta D$ and $\delta^{18}O$) of minerals and fluids provide valuable insights into fluid sources, hydrothermal processes, and fluid–rock interaction in a wide range of
geological environments (Wilkinson et al. 1995; O’Reilly et al. 1997; Naden et al. 2003). To probe the origin of ore-forming fluids in the gold deposits in the ZTB, five quartz-vein samples associated with gold mineralization are collected from quartz-vein gold deposits. Quartz was crushed into grains with sizes of 0.2–0.4 mm, and then purified more than 99% by hand-picking under a binocular microscope. Oxygen isotope compositions of separated quartz were analysed. $^{18}$O/$^{16}$O ratios were measured with a MAT-261 mass spectrometer in the Isotope Laboratory of Yichang Institute of Geology and Resources of China. Oxygen was extracted from quartz by reaction with BrF$_5$ and converted to CO$_2$ by reaction with heated carbon. The ratios are reported in standard $\delta$-notation in per mil (‰) relative to the V-SMOW standard. The accuracy of analysis is better than ±0.2‰ for $\delta^{18}$O. Two standard quartz samples, National Standard of China GBW-04409 (+11.2‰ for $\delta^{18}$O) and International Standard NBS-28 (+9.6‰ for $\delta^{18}$O), were used for reference in oxygen isotope analysis. All quartz grains used for analyses of $\delta D$ of fluid inclusions were heated under vacuum at 150°C overnight to remove adsorbed atmospheric water. The resultant H$_2$O was reduced to H$_2$ by reaction with zinc metal at 500°C for 15 minutes. The $\delta D$ values of the hydrogen were then measured on a MAT-261 mass spectrometer with internal

Figure 9. Homogenization temperature histograms of fluid inclusions in quartz from the deposits in the Zhangbaling Tectonic Belt.
biotite ($\delta D: -64 \pm 5.0‰$) and kaolinite ($\delta D: -125 \pm 5.0‰$) standards calibrated against the certified international biotite standard NBS-20 ($\delta D: -65‰$). The overall analytical precision for the hydrogen isotope measurements is around $\pm 5.0‰$. All results are reported in standard $\delta$-notation in per mil (‰) relative to the V-SMOW standard.

The analysed $\delta^{18}O$ of quartz ($\delta^{18}O_q$), $\delta D$ of fluid inclusions ($\delta D_{H_2O}$), and the $\delta^{18}O$ values of fluids ($\delta^{18}O_{H_2O}$) calculated by the $\delta^{18}O_q$ using the fractionation equation of Zhang (1989) and average $T_h$ of each sample are shown in Table 4. $\delta D$ values of ore-forming fluids ($\delta D_{H_2O}$) range from $-52.2‰$ to $-75.3‰$, which is similar to the $\delta D$ values of fluids at the early and late stages from Shanggong gold deposit (Henan province), where the ore-forming fluid is relatively poor in $D$, which is due to the large-scale precipitation of sulphides (Chen et al. 2004b). The $\delta^{18}O$ values of quartz range from +6.4‰ to +12.1‰. The isotope compositions of the fluid calculated from the quartz data show negative $\delta^{18}O$ values, ranging from $-6.3‰$ to 0.1‰. The calculated $\delta^{18}O$ values of water are evidently lower than that of fluids originating from magma (+5‰ to +7‰, Sheppard 1986).

On the diagram of $\delta^{18}O_{H_2O}$ versus $\delta D_{H_2O}$, the plots of the samples are far away from the magmatic water and meteoric water (Figure 10). Hydrothermal alteration of the rocks

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<th>Sample</th>
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Note: $\delta^{18}O_q$: $\delta^{18}O$ values of quartz; $\delta D_{H_2O}$: $\delta D$ values of water; $\delta^{18}O_{H_2O}$: $\delta^{18}O$ values of water, calculated from the quartz analyses using the fractionation equation $1000 \ln a_{quartz-water} = 3.306 \times 10^6 T^{-2} - 2.71$ of Zhang (1989) and fluid inclusion homogenization temperatures for each quartz sample.
is widely developed in the gold deposits in the Zhangbaling area, which suggests that the ore-forming fluids of the gold deposits may be affected by water–rock interaction. Therefore, we also modelled the isotope evolution lines of magmatic water and meteoric water through equilibrium of isotopic exchange with the granite at 270°C (about middle \( T_h \) of inclusions) and at 350°C (about the highest \( T_h \)) (Figure 10). However, the plots of the samples are not nearby the evolution lines as well. Considering the close relationship between the gold deposits and the granites in study area, the most reasonable source of ore-forming fluids for samples 1 and 5 is mixture of Mesozoic meteoric water and the evolved magmatic water, whereas the ore-forming fluids of samples 2, 3, and 4 may involve Mesozoic meteoric water, the evolved magmatic water, and initial magmatic water. Therefore, data of oxygen and hydrogen isotopes show that the ore-forming fluids of gold deposits in the ZTB are from at least two sources: Mesozoic meteoric water and magmatic water.

To compare gold deposits in Zhangbaling with those in Jiaodong, we listed some \( \delta^{18}O \) and \( \delta D \) values from Jiaodong gold deposits in Table 4 as well. The oxygen and hydrogen isotope compositions of the ore-forming liquids of Sanshandao and Jiaojia gold deposits are similar to magma-originated water. On the diagram of \( \delta^{18}O_{H_2O} \) versus \( \delta D_{H_2O} \) (Figure 11), the plots are inside or near the scope of magmatic water. However, the \( \delta^{18}O_{H_2O} \) and \( \delta D_{H_2O} \) values of the samples from Linglong, Lingnan, and Dazhuangzi gold deposits are deviated from that of magmatic water. The samples from Linglong and Lingnan...
deposits are near the evolution lines of meteoric water through isotopic exchange with the granite at 270°C or at 350°C (Figure 11), but the plots of the samples from the Dazhuangzi gold deposit are neither inside magmatic water scope nor near the evolution lines of meteoric water. In general, the source and evolution of ore-forming fluids of Linglong, Lingnan, and Dazhuangzi gold deposits are similar to those in the Zhangbaling area to some extent.

Tectonic environment of magmatism in ZTB

Age of intrusive rocks

In the Zhangbaling area, several stages of structural deformation can be identified after the Neoproterozoic (Hou et al. 2004; Mercier et al. 2007). Among these tectonic activities, the Mesozoic fracturing movements, which are dominated by the Tan-Lu fault zone, are directly associated with gold mineralization. It is suggested that the first sinistral displacement of the Tan-Lu fault zone happened in the latest Middle Triassic, from 236.2 ± 0.5 Ma to 238.0 ± 0.4 Ma (Zhang et al. 2008). In the Early Cretaceous (120–130 Ma), the fault zone underwent another sinistral displacement, followed by extensional activities (Zhu et al. 2001a, 2001b). The recent results show that the granites in the ZTB also emplaced during this period. Niu et al. (2008) obtained ages of 126.9 ± 1.0 Ma, 114.8 ± 1.3 Ma, 108.1 ± 1.6 Ma, 103.0 ± 0.9 Ma, and 120.3 ± 0.7 Ma for different granitoids in the Zhangbaling by zircon U-Pb LA-ICP-MS analyses, which is concordant with the results by Liu et al. (2002) and Niu (2006). U-Th-Pb dating of zircons from the Guandian granite obtained an age of 128 Ma (Li et al. 1985). All the dating results indicate that these rocks formed in the Yanshanian period, about 20–30 million years younger than the forming ages of some important Cu-Au deposits such as Shaxi and the Tongling region in the western side of the ZTB (e.g. Mao et al. 2006; Yang et al. 2007; Xie et al. 2009), but coeval with the sinistral displacement of the Tan-Lu fault zone, which may record the subduction of west Pacific plate from northeast to mainland China (Sun et al. 2007; Lan et al. 2009).
Origin of intrusive rocks

The I$_{Sr}$ of the granitoids in the Zhangbaling ranges from 0.70623 to 0.70685, slightly higher than mantle source (Niu et al. 2002). However, the extremely high negative $\varepsilon$Nd (−15.5, Li et al. 1985; −16.8 to −18.1) and the low $^{206}$Pb/$^{204}$Pb (16.504) and $^{207}$Pb/$^{204}$Pb (15.292) ratios (Li et al. 1985) strongly suggested that the granites are from melting of lower crust. The result of trace elements (Figure 12) shows that among the incompatible and middle-incompatible elements, Ba and Sr are enriched evidently but Rb and Nb are relatively depleted. This may be because granitoids originated from the melting of lower-crust source rocks, which is usually rich in Ba and Sr, and relatively poor in Rb and Nb.

Tectonic environment of intrusive rocks

On the Nb–Y trace element discrimination diagram (Figure 13a), the granitoids in the Zhangbaling are located in syn-collision or volcanic arc fields, whereas on the Rb–Y + Nb diagram (Figure 13b), all the samples fall inside volcanic arc scope, which resulted from the low contents of Rb. We suggested that the granitoids in the Zhangbaling area are from melting of lower crust during or post-orogenic process, which is concordant with the conclusion from the result of Nd and Pb data (Li et al. 1985). Considering these rocks distributing in orogen regions associated with continent–continent collision, these high-K calc-alkaline granitoids probably indicate the change of tectonic environment from compression to extension (Xiao et al. 2002), similar to the situation in the Jiaodong.

Discussion of ore genesis

Orogenic gold deposits occurring in metamorphic belts have attracted interest from both researchers and industry globally (Chen et al. 2004b). Many researchers diagnose the orogenic gold deposits according to the sources of metals and fluids based on stable isotope
systems. However, understanding of the sources of the metals and fluids remains ambiguous. Previous studies have suggested different sources of the fluids for the orogenic gold deposits, such as, hydrous fluids liberated by metamorphic dehydration (McCuaig and Kerrich 1998), magmatic-hydrothermal fluids (De Ronde et al. 2000), deeply convecting
meteoric water (Jenkin et al. 1994), CO₂-rich fluids released from the mantle (Colvine 1989), or fluids from an external source (Breeding and Ague 2002). Meanwhile, the orogenic deposits usually display three mineralization stages (Chen et al. 2004c) and the isotopic compositions of the ore-forming fluids are generally variable for these stages (Chen et al. 2004b). Therefore, it is suggested that isotope indicators are not necessarily diagnostic in terms of metamorphic and magmatic sources of fluids and metals (Chen et al. 2004c). In addition to the sources of the metals and fluids, the orogen tectonic setting, structure-control of the orebodies, and CO₂-rich metamorphic fluid system are key markers of orogenic-type gold lodes (Chen et al. 2004c, 2005). Virtually all orogenic gold deposits show a close spatial association with ‘first- and second-order’ structural breaks (Bierlein et al. 2004). All these ‘necessarily diagnostic indicators’ and ‘virtual characters’ are evidently shown in the gold deposits in the ZTB.

Comparison with gold deposits in Jiaodong

Jiaodong gold metallogenic zone is a famous gold-centralized area in China, which is adjacent to the Tan-Lu fault zone to the W, the same as the ZTB. The strata in the belt are composed of the Archaean Jiaodong Group, Proterozoic Jinshan Group, Fenzishan Group, and Penglai Group. The Mesozoic granitoids, such as Linglong granite, Guojiazhai granodiorite, Lanjiahe granite, and Kunlunshan granite, are widely developed in the region. Wang et al. (1998) obtained the zircon SHRIMP dating result of 150–160 Ma from Linglong granite. The 40Ar/39Ar step-heating ages of the biotite from Guojiazhai granodiorite are 124.0 ± 0.4 to 124.5 ± 0.4 Ma (Li et al. 2003). The dating results suggest that Mesozoic granitoids in Jiaodong were emplaced during several thermal events. The identification of inherited zircons coupled with ISr ratios (>0.709) indicate that these granitoids were mainly derived from the continental crust by re-melting or partial melting (Chen et al. 2007a).

The gold deposits in Jiaodong are controlled by fractures mainly in NNE striking, which were considered as derivative structures of the Tan-Lu fault zone (Goldfarb et al. 2001; Zhou et al. 2002). Three types of gold deposits, altered-tectonite gold deposits, quartz-vein gold deposits, and hydrothermal breccia gold deposits, can be identified in the region (Mao et al. 2005). Based on the dating combined with the analysis of previous data, Chen et al. (2004a, 2007b) suggested that in the Jiaodong gold province, mineralization occurred in the Mesozoic, with peak activities between 110 and 130 Ma, coeval with or postdating Mesozoic granitoid intrusions. The ISr values obtained from ores and fluid inclusions are generally higher than 0.709 and slightly higher than those from Mesozoic granitoids, which indicates that both ore fluids and metals were mainly derived from the crust (Chen et al. 2004b, 2007a). The granitoid emplacement and large-scale gold metallogenesis were related to three evolution stages in a collisional orogen, and the most important metallogenic phase occurred at the transition from collisional compression to extension (Chen et al. 2004a, 2007b). From the discussion above, it can be seen that the gold deposits in the ZTB are very similar to those in the Jiaodong gold metallogenic province in the tectonic settings, mineralization-controlling factors, and mineralization ages, as well as in the ore-forming temperature and the oxygen and hydrogen isotopes composition to some extent, which convince us of an orogenic origin for the gold deposit in ZTB.

Comparison with deposits in Xiongershan

Xiaoqinling-Xiong’ershan in East Qinling is another important base of gold and other metals in China. Some of the gold deposits in this area are considered to be orogenic
(Chen et al. 2004c). The Shanggong gold deposit can be taken as the typical representation of orogenic gold deposits in this belt. The Shanggong gold deposit is located in Xiong’ershan terrane, which is in the northern part of Qingling-Dabie orogen. The strata distributing in this terrane mainly include Archaean Taihua Group and Middle Proterozoic Xionger Group. The former mainly consists of gneiss and hornblendite and the later of basalt, basaltic andesite, andesite, dacite, and rhyolite (Chen et al. 2004c). The Mesozoic granitoids, such as Haopinggou granite, Wuzhangshan granodiorite, and Huashan granite, are developed in this region.

The mineralization is controlled by fractures mainly in NE striking, which were considered to have evolved from compressional shear to tensional shear (Chen et al. 2004c). The early-stage veins and minerals are structurally deformed and broken, suggesting that they are formed in a compression or compressional shear setting. The late stage, characterized by developed quartz-carbonate veinlets and comb structure, is likely formed in an extensional tectonic environment (Chen et al. 2004c). The hydrothermal ore-forming process is divided into early, middle, and late stages, characterized by pyrite-ankerite-quartz, polymetallic sulphides, and carbonate-quartz, respectively. The mineralization processes include early, middle, and late stages for both types of deposits. The temperatures of three stages were 115–165°C, 235–275°C, and 335–395°C for altered-tectonite gold deposits, and 145–195°C, 205–255°C, and 255–335°C for quartz-vein gold deposits, respectively. The ore-forming elements of gold deposits were derived mainly from the Yanshanian granites, which originated from melting of the lower crust during or slightly post-orogeny. The gold deposits in the ZTB are remarkably similar to those in the Jiaodong gold metallogenic province and in the Xiong’ershan metallogenic zone with regard to tectonic settings, mineralization-controlling factors, and mineralization ages, as well as the ore-forming temperatures and the O–D
isotopes compositions. We suggest that the gold deposits in the ZTB are probably orogenic gold deposits similar to those in the Jiaodong and the Xiong’ershan. This conclusion suggests that the ZTB is a favourable target for further exploration of gold resources.

Acknowledgements
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Fluid inclusion study of the Tangjiaping Mo deposit, Dabie Shan, Henan Province: implications for the nature of the porphyry systems of post-collisional tectonic settings

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The Tangjiaping porphyry Mo deposit in Shangcheng County is located in the Dabie continental collisional orogenic belt. The hydrothermal alteration and mineralization processes can be divided into three stages: K-feldspar + quartz + pyrite + magnetite + molybdenite in the early stage, quartz + pyrite + molybdenite ± chalcopyrite in the middle stage, and quartz + carbonate ± pyrite veins or carbonate veinlets in the late stage. The middle stage involved important Mo mineralization. Four compositional populations of fluid inclusions (FIs) occur in hydrothermal quartz formed in the early and middle stages, namely: pure CO\textsubscript{2}, CO\textsubscript{2}–H\textsubscript{2}O, daughter mineral-bearing, and NaCl–H\textsubscript{2}O. The late-stage quartz-carbonate ± pyrite veinlets contain only NaCl–H\textsubscript{2}O FIs.

Homogenization temperatures of the early-stage FIs are mainly above 375°C, with salinities up to 62.10 wt.% NaCl equiv. Haematite daughter minerals, which probably represent an oxidizing environment, together with halite, sylvinite, and chalcopyrite, are present in the FIs of this stage. Most of the middle-stage FIs homogenized between 235 and 335°C, with fluid salinities ranging from 1.06 to 45.87 wt.% NaCl equiv. In middle-stage quartz, besides halite and sylvite daughter minerals, abundant chalcopyrite and jamesonite are also present, reflecting a reducing environment. The daughter mineral-bearing FIs coexist with vapour- and liquid-rich FIs with contrasting salinities, and they homogenized in divergent ways at similar temperatures. This feature strongly suggests that fluid boiling occurred during the middle stage, which is well accepted as an important mechanism for the precipitation of ore-forming materials. FIs in late-stage minerals totally homogenized in the range 115–195°C, with low salinities ranging from 1.91 to 9.98 wt.% NaCl equiv.

Combined with the published H–O isotope data, we propose that the initial ore fluids were magmatic in origin and were characterized by high temperature, high salinity, high oxygen fugacity, high levels of metallic elements, and high levels of CO\textsubscript{2}. In the middle stage, the fluids boiled and resulted in CO\textsubscript{2} release, oxygen fugacity decrease, and rapid precipitation of ore-forming materials. The late-stage fluids, characterized by low temperatures, low salinities, and low contents of CO\textsubscript{2}, might have been sourced from meteoric water.

Daughter mineral-bearing CO\textsubscript{2}–H\textsubscript{2}O FIs, especially multiple species daughter mineral-bearing FIs, are regarded as indicators of porphyry ore systems generated in continental collisional settings. This understanding is validated by recent studies of other porphyry ore systems in Chinese collision orogens.

Keywords: Tangjiaping porphyry Mo deposit; ore geology; fluid inclusion study; Dabie Shan; continental collision regime; high-salinity carbonic fluid

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Introduction

Traditional metallogenic theories state that porphyry deposits mainly occurred in oceanic subduction-related magmatic arcs, such as the southwestern Pacific Islands and the Andes (Sillitoe 1972; Pirajno 2009). In recent years, geologists have come to realize that an intra-continental tectonic regime is also favourable for development of porphyry ore systems (Chen and Fu 1992; Chen 1998; Chen et al. 2000, 2007a, 2009). The Lower Yangtze porphyry-skarn ore belt is an intra-continental fault-controlled magmatic belt (Chen et al. 2007a; Xie et al. 2009; Yang and Lee 2011; Yang et al. 2011). The NE Qinling porphyry Mo belt (Chen et al. 2000; Li et al. 2007b; Mao et al. 2008; Zhang et al. 2010), the Mongolia-Hinggan porphyry Cu-Mo ± Au belt (Li et al. 2007a, 2007c; Zhang et al. 2009), the Yulong porphyry copper belt (Chen 1996; Liang et al. 2007, 2009), and the Gangdese porphyry copper belt (Zheng et al. 2002; Hou and Cook 2009) are all examples of metallogenic provinces with porphyry-type deposits formed under a continental collision regime (including syn- and post-collisional settings). Consequently, to understand the genesis of porphyry ore systems in collisional orogens, a tectonic model for collisional orogenesis, petrogenesis, metallogenesis, and fluid flow has been proposed (Chen and Fu 1992; Chen et al. 2000, 2007a) and widely supported (e.g. Zheng et al. 2002; Mao et al. 2008; Pirajno 2009).

The questions remain as to whether porphyry deposits generated in intra-continental settings and magmatic arcs have similar or contrasting geological and geochemical features, and how to distinguish the deposits formed in different tectonic settings. These issues are open to discussion and important for both study of regional mineralization and mineral exploration targeting. Considering the difference in geochemical backgrounds between intra-continental settings and magmatic arcs, Chen et al. (2007b) theoretically inferred that they might have notable differences in petrochemical and geochemical compositions of ore-associated porphyries, mineral assemblage of ores, metallic inventories, wall-rock alteration, as well as fluid inclusion (FI) compositional populations. The daughter mineral-bearing CO$_2$-rich FIs, especially multiple species daughter mineral-bearing FIs, rarely reported in previous publications, are argued to be commonly observed in and employed as an indicator to intra-continental porphyry systems. These inferences need to be validated by numerous case studies because, so far, few intra-continental porphyry systems have been well studied.

The Qinling–Dabie–Sulu belt is a typical inter-continent collisional orogen. The northeastern Qinling orogen is the world’s largest porphyry molybdenum province with five world-class super-large deposits (each has >0.5 million tons of Mo metal) and total resources of more than 5 million tons of Mo metal (Li et al. 2007b). Dabie Shan is the eastern extension of the Qinling orogen, but universally accepted as an ore-barren area due to strong weathering denudation, which is shown by the outcrop of ultra-high-pressure (UHP) eclogites. However, geological investigation in the northern Dabie Shan, Henan Province, resulted in the discovery of Mo deposits and occurrences, of which the Tangjiaping porphyry system is ranked as a large-sized Mo deposit (No. 3 Geological Investigation Team of Henan 2006; Yang et al. 2008 and references therein). This discovery not only ends the ‘barren Dabie Shan’ history, but also provides an ideal case for studying porphyry ore systems in a continental collision regime and ascertaining whether the above inference is correct or not. Therefore, this article reports the results of FI studies of the Tangjiaping Mo deposit and, accordingly, discusses several problems related to mineral systems developed in collisional orogens.
Geological setting

The Dabie Shan is an eastern extension of the Qinling orogen and well known as a Mesozoic continental collision orogen for its widespread UHP eclogites (Li et al. 1992; Hacker et al. 1996). Composed of many terranes with complicated internal structure, it is bounded to the south by the Xiangfan–Guangji fault and to the north by the Luanchuan–Minggang–Gushi fault (Figure 1). The Guishan–Meishan fault is the final suture zone between the North China and Yangtze ancient continents (Figure 1), equivalent to the Shang–Dan fault in Qinling area (Hu 1988; Chen and Fu 1992). To the north of the Guishan–Meishan fault, the Qinling Group (mainly Palaeoproterozoic) and the Erlangping Group (Neoproterozoic–Eopalaeozoic) occur in turn, forming the Caledonian metamorphic accretion belt of the North China Craton. This Caledonian accretion belt is locally overlain by late Palaeozoic strata, such as the Lower Carboniferous Huayuanqiang Group, which is mainly made up of ferruginous sericite-quartz schist, sericite-quartz schist, and carbonaceous quartz schist (Yang 2007a). To the south of the Guishan–Meishan fault, three metamorphic terranes are present: the Xinyang Group, a Hercynian–Indosinian (late Palaeozoic to early Mesozoic) accretionary complex; the Xiaojiamiao Group, a Caledonian accretionary complex; and the Dabie/Tongbai metamorphic complex, with the Tongbai–Shangcheng and Xiaotian–Mozitan faults as their boundaries, respectively. The Xinyang Group is a Neopalaeozoic ophiolitic melange containing Precambrian fragments, which makes the age of the Xinyang Group controversial. The Xiaojiamiao Group consists of muscovite-albite schists, muscovite-quartz schists, two-mica oligoclase schists, and lenticular marble intercalations, which were formed from the Caledonian (early Palaeozoic) metamorphism of a Sinian–Early Ordovician clastic–argillic–carbonate sequence. The Dabie metamorphic complex, accommodating UHP eclogite massifs, is composed of high-grade metamorphosed plutons and supracrustal rocks either of Archaean or of Palaeoproterozoic ages (Henan Bureau of Geology and Mineral Resources 1989), and weakly metamorphosed Jinningian (ca. 1.0 Ga) granitoids and un-metamorphosed Yanshanian granitic intrusions (Figure 1). The strongly metamorphosed plutons include gneissic adamellite, tonalite, and granodiorite rocks, whereas metamorphic supracrustal rocks consist mainly of biotite-plagioclase gneisses, granulites, and amphibolites. The Dabie metamorphic complex is unconformably overlain by a low- to middle-grade metamorphic phosphate-containing sedimentary sequence, i.e. the Hong’an Group. Therefore, the Dabie metamorphic (or Tongbai) complex was interpreted to be the oldest basement in Dabie Shan, analogous to the basement of the South Qinling micro-continent in Qinling orogen (Zhang et al. 1996). The main structures strike NW or WNW, controlling the distribution of the major tectonic units in Dabie Shan. The area south of the Xiaotian–Mozitan fault is in total called southern Dabie Shan, the tectonic units north of the Guishan–Meishan fault are called northern Dabie Shan, and the very complicated belt between these two faults is called the Dabie subduction–collision melange belt or central Dabie Shan.

The above main tectonic belts and their boundary structures are cross-cut by NE- to ENE-trending faults developed since the Jurassic, resulting in a latticed fault system in Dabie Shan. This unique fault system controls the development of Yanshanian intrusions and related mineralization (No. 3 Geological Investigation Team of Henan 2006). The Yanshanian igneous rocks include deeply seated granite batholiths, small-sized porphyries and breccia pipes, as well as volcanic rocks in Cretaceous basins. The Cretaceous volcanic rocks are composed of potassic dacite and rhyolite and are distributed as a NW-trending belt in northern Dabie Shan (Figure 1). The Yanshanian granitic batholiths, such as Lingshan, Xinxian, and Shangcheng, mainly occur along the NW-trending belt in the Dabie Shan.
The smaller granitic stocks, compositionally including intermediate-felsic alkali granite porphyries, granites, quartz porphyries, and granodiorites, outcrop along the latticed fault system and are usually observed between the Cretaceous volcanic belt and Yanshanian batholithic granite belt. The porphyry stocks, such as Tianmushan, Xiaofan, Mushan, Dayinjian, and Tangjiaping, are associated with porphyry-type Mo mineralizations, constituting the Dabie porphyry Mo belt (Yang 2007b).

Ore deposit geology
The Tangjiaping Mo deposit is located in southern Dabie Shan. The ore-associated porphyry intruded into the Dabie Group (Figure 1). Lithologies of the Dabie Group in the deposit area are biotite- and hornblende-plagioclase gneisses, which were partly altered (Figure 2). Structures related to mineralization are faults associated with the porphyry system. Rocks in or close to the fault zones are mostly brecciated, silicified, and kaolinized.

The ore-hosting Tangjiaping granite porphyry is ca. 0.34 km\(^2\) (Figure 2). The porphyry contains 10\% phenocrysts by volume, which consists of K-feldspar (5\%), quartz (3\%), and plagioclase (2\%). The matrix comprises K-feldspar (20–56\%), plagioclase (10–30\%), quartz (10–25\%), and a little bit of biotite and muscovite (Figure 3). The accessory minerals are magnetite, haematite, zircon, titanite, monazite, and rutile. In the porphyry stock, andesite enclave can be observed (Figure 2).

Orebodies are hosted in the granite porphyry and its contact zones. The largest one is lenticular, with a length of 1120 m and width of 960 m. It dips southwestward with an
angle of about 20° (Yang 2007c), containing metal Mo reserve of 0.235 million tons, with an average grade of 0.063% and cut-off of 0.02% metal Mo. However, it is a molybdenum-only deposit, because no other metals can be recovered as by-product.

Major ore minerals include molybdenite, pyrite, magnetite, and haematite. Minor ore minerals are sphalerite, chalcopyrite, and galena. Molybdenite occurs as (1) radial coarse-grained aggregates disseminated in K-feldspar-quartz stockworks, which fill open-space fissures; (2) spotted and scaly, sparsely disseminated in the altered granite porphyry (Figure 3D); and (3) tiny grain aggregates or films associated with quartz and pyrite, forming millimetre-thick, fine-grained, quartz-pyrite-molybdenite stockworks.
The main gangue minerals are quartz, feldspar, sericite, and muscovite (>5 vol.%), with lesser biotite, chlorite, and epidote (0.1–5 vol.%). Limonite can be observed in the weathering zones. Various ore textures were observed, such as flaky, replacement, replacement remnant and embayment, idiomorphic to hypidiomorphic grain, phenocryst, and cataclastic. Ore textures include disseminations, veins, veinlets, stockworks, breccias, and lumps.

Based on petrographic study (Figure 3), the mineralization process can be roughly divided into three stages: early (E), middle (M), and late (L). The early stage is characterized by the assemblage of K-feldspar + quartz + pyrite + magnetite + molybdenite. Sulphides are mostly disseminated. The molybdenite is scaly (Figure 3D), pyrite occurs as hypidiomorphic to idiomorphic cubes (Figure 3C), and most of the quartz crystals are cataclastic. Coeval alteration consists of K-feldspathization, silicification, and weak sericitization. The middle stage, characterized by stockworks of quartz + pyrite + molybdenite...
± chalcopyrite, represents the main mineralizing event. Silicification and phyllic alteration are the most conspicuous in this stage (Figure 3B). The late stage is characterized by quartz + carbonate ± pyrite veins or carbonate veinlets (Figure 3F), which cross-cut the earlier formed veins, stockworks, and altered porphyry blocks.

From the centre towards the periphery of the system, two alteration zones can be recognized as follows: potassic and silica alteration and silicification–sericitization–chloritization (phyllic alteration) zones. The potassic-silica zone is pervasive and extensive, extending to the metamorphic wall rocks. The phyllic alteration, to some extent, is slight to weak and overprinting on the potassic-silica alteration zone.

Re–Os isochron age of molybdenite is 113.1 ± 7.9 Ma (Yang 2007b), indicating that metallogenesis is coeval with the Early Cretaceous post-collisional igneous activity.

Fluid inclusions

Samples and analytical methods

Doubly polished thin sections (<0.30 mm thick) were made from 27 samples, including various kinds of veinlets, altered rock, and quartz phenocrysts (Figure 3A). FIs were carefully observed to identify their genetic and composition types, vapour–liquid ratios, spatial clustering, and the species of daughter minerals. Fifteen samples were selected for microthermometric measurements and laser Raman spectroscopy analyses.

Microthermometric measurements were performed using the Linkam THMSG600 and THMSG1500 programmed heating–freezing stage and employing standard procedures at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). Stage calibration was carried out at −56.6, −10.7, and 0.0°C using synthetic FIs supplied by Fluid Inc. (Denver, CO). The estimated precision of the measurements is ±0.2°C for temperatures lower than 30°C, ±1°C for the interval of 30–300°C, and ±2°C for temperatures higher than 300°C. The freezing point of NaCl–H2O inclusions (Tmice), final melting of clathrate (Tclath), homogenization within CO2 phase (ThCO2), dissolution temperatures of daughter minerals (TmNaCl), and total homogenization temperatures of FIs (Th) were measured. A heating rate of 5°C/min was used during the initial stages of each heating run and reduced to 0.5–1°C/min close to the phase transformation points.

Salinities of CO2–H2O and NaCl–H2O inclusions were calculated using the final melting temperatures of CO2 clathrate (Collins 1979) and ice points (Bodnar 1993), respectively, and expressed as wt.% NaCl equiv. (Table 1). The homogenization temperatures of the CO2-rich phase in inclusions (ThCO2) were used in calculating the CO2 density (Touret 1979; Table 1). Salinities and densities of daughter mineral-bearing FIs were calculated using the dissolution temperatures of daughter minerals (Hall et al. 1988) and together with the homogenization temperatures (Liu 2001), respectively. In addition, the density of NaCl–H2O inclusions was estimated according to the T–W–ρ diagram for NaCl–H2O system (Bodnar 1983).

Laser Raman spectroscopic analyses were performed in the Laboratory of Orogen and Crust Evolution, Peking University. Compositions of individual FIs, including vapour, liquid, and daughter mineral phases were analysed. The laser source was an argon laser with wavelength of 514.5 nm and a source power of 1000 mW. Integration time was 10 s, with 10 accumulations for each spectral line. The spectral resolution was ±2 cm⁻¹ with a beam size of 1 μm. Instrumental settings were kept constant during all analyses.
Table 1. Microthermometric data of fluid inclusions of the Tangjiaping Mo deposit.

<table>
<thead>
<tr>
<th>Metallogenic stage</th>
<th>Type</th>
<th>Number</th>
<th>$T_{\text{mice}}$ (°C) or $T_{\text{mCO}_2}$ (°C)</th>
<th>$T_{\text{clath}}$ (°C)</th>
<th>$T_{\text{hCO}_2}$ (°C)</th>
<th>$T_{\text{mNaCl}}$ (°C)</th>
<th>$T_{\text{h}}$ (°C)</th>
<th>Salinity (wt.% NaCl equiv)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magmatic stage</td>
<td>W</td>
<td>3</td>
<td></td>
<td>466–498</td>
<td>27.5–30.8</td>
<td>477–597</td>
<td>0.58–0.68</td>
<td>0.58–0.68</td>
<td>1.23–1.37</td>
</tr>
<tr>
<td>Magmatic stage</td>
<td>C</td>
<td>11</td>
<td></td>
<td>548–630</td>
<td>548–630</td>
<td>66.58–78.60</td>
<td>1.23–1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magmatic stage</td>
<td>S</td>
<td>8</td>
<td></td>
<td>210–439</td>
<td>548–630</td>
<td>66.58–78.60</td>
<td>1.23–1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early stage</td>
<td>W</td>
<td>11</td>
<td></td>
<td>210–439</td>
<td>548–630</td>
<td>66.58–78.60</td>
<td>1.23–1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early stage</td>
<td>C</td>
<td>19</td>
<td>−58.4 to −56.7</td>
<td>−2.5 to 4.8</td>
<td>24.2–30.6</td>
<td>259–460</td>
<td>9.39–17.75</td>
<td>0.59–0.73</td>
<td></td>
</tr>
<tr>
<td>Early stage</td>
<td>S</td>
<td>12</td>
<td>−58.4 to −56.7</td>
<td>−2.5 to 4.8</td>
<td>24.2–30.6</td>
<td>259–460</td>
<td>9.39–17.75</td>
<td>0.59–0.73</td>
<td></td>
</tr>
<tr>
<td>Middle stage</td>
<td>W</td>
<td>70</td>
<td>−0.6 to −12.7</td>
<td>173–383</td>
<td>227–380</td>
<td>4.32–19.16</td>
<td>0.61–0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle stage</td>
<td>C</td>
<td>50</td>
<td>−57.8 to −56.6</td>
<td>−4.7 to 7.8</td>
<td>16.6–30.2</td>
<td>227–380</td>
<td>4.32–19.16</td>
<td>0.61–0.81</td>
<td></td>
</tr>
<tr>
<td>Middle stage</td>
<td>S</td>
<td>24</td>
<td>−57.8 to −56.6</td>
<td>−4.7 to 7.8</td>
<td>16.6–30.2</td>
<td>227–380</td>
<td>4.32–19.16</td>
<td>0.61–0.81</td>
<td></td>
</tr>
<tr>
<td>Late stage</td>
<td>W</td>
<td>20</td>
<td>−6.6 to −1.1</td>
<td>116–234</td>
<td>191–9.98</td>
<td>1.91–9.98</td>
<td>0.82–0.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Types of fluid inclusions**

FL types were identified based on their phases at room (21°C) and subzero temperatures, with phase transitions observed during heating and cooling (−196 to +600°C) and laser Raman spectroscopy. Four composition types of FLs designated as PC-, C-, S-, and W-types were identified in this study and are briefly described below.

(1) **PC-type**: Pure CO₂ or carbonic FLs. They have irregular to ellipsoidal and negative crystal shapes (Figure 4A) with size ranging from <2 to 20 μm; appear as one (liquid CO₂) or two phases (liquid CO₂ + vapour CO₂) at room temperature, with a transparent centre and a black rim; and form clusters commonly coexisting with C-type FLs.

(2) **C-type**: CO₂–H₂O FLs, composed of H₂O and CO₂ phases, with the CO₂ phase accounting for 5–95% volume. It is the most abundant type of FL observed in the middle-stage quartz of the Tangjiaping deposit, and classified into C1-subtype (vapour CO₂ + liquid CO₂ + liquid H₂O) (Figure 4B) and C2-subtype (liquid CO₂ + liquid H₂O) according to the number of phases at room temperature, but the C1-subtype is in the majority. Vapour CO₂ can be also observed in C2-subtype FLs during cooling to 0°C. The C-type FLs appear irregular, ellipsoid, and rarely as perfect negative crystal in shape, with size ranging from 4 to 18 μm. In middle-stage quartz, the C-type FLs with contrasting volumetric percentages of CO₂ are homogenized in divergent ways at similar temperatures, suggesting fluid boiling (Fan et al. 2003; Lu et al. 2004; Hu et al. 2007).

(3) **S-type**: Daughter mineral-bearing FLs or polyphase FLs. The S-type FLs consist of one or more daughter minerals and fluid with one to three phases. They are irregular to elliptical in shape and 2–10 μm in size. The most common opaque daughter minerals are haematite (Figure 4E), chalcopyrite (Figure 4H), and jamesonite, identified by laser Raman spectroscopy. Transparent daughter minerals are mainly cubic halite (Figure 4F and H) and round sylvite (Figure 4D), and occasionally anhydrite. The number of daughter minerals in S-type FLs in the Tangjiaping ore system is up to 4 (Figure 4H), which is similar to those in other porphyry deposits in the world. Daughter minerals in the early-stage quartz are mainly haematite and chalcopyrite, while in the middle-stage quartz they are chalcopyrite and jamesonite, possibly suggesting conditions changing to reducing. In terms of phase compositions, the S-type FLs can be distinguished between the S1-subtype, which is daughter mineral-bearing NaCl–H₂O solution (Figure 4D) and S2-subtype, which is daughter mineral-bearing CO₂–H₂O inclusions (Figure 4E and F). They occur mainly in isolation and clusters, and occasionally in sharp trails that are interpreted to be secondary or pseudo-secondary FLs.

(4) **W-type**: Aqueous FLs or NaCl–H₂O solution. They usually appear as two-phase (liquid water and vapour water) FLs at room temperature (Figure 4H), with size ranging from 2 to 8 μm and vapour volume accounting for 5–20% of the total FLs. Trace content of CO₂ can still be identified in the vapour bubbles by laser Raman spectroscopy, although no visible CO₂ phase appears during heating or cooling runs. The secondary W-type FLs can be observed as trails in early-stage quartz.

Not all of the types of FLs described above can be observed in each thin section. In the magma-crystallized quartz phenocrysts, the FLs are dominated by PC- and C-types. Quartz formed in early-stage hydrothermal alteration and mineralization mainly contains PC- and
Figure 4. Microphotographs of fluid inclusions of the Tangjiaping Mo deposit. (A) PC-type FIs; (B) coexistence of chalcopyrite-containing S2-subtype and C-type FIs; (C) coexistence of C-type FIs with contrasting CO$_2$/H$_2$O ratios, which is a fluid-inclusion population trapped from boiling fluids; (D) coexistence of C-type inclusion and S1-subtype inclusion, which contains halite and sylvite daughter minerals; (E) haematite- and halite-containing S2-subtype FI; (F) halite-containing S2-subtype FI; (G) coexisting FIs of C-, PC-, S-, and W-types in middle-stage quartz; (H) coexistence of C-type and W-type FIs in middle-stage quartz. Abbreviations: Cp, chalcopyrite; H, halite; K, sylvite; Hem, haematite; l, liquid; g, gas.
C-types of FIs, followed by S-type FIs and few W-type FIs. The FIs in the middle-stage quartz are mostly of S- and C-types and to a lesser extent of W-type. On the contrary, only the W-type FIs can be observed in late-stage quartz or carbonate. This may imply an evolutionary sequence of the ore-forming fluid system.

Microthermometry

The microthermometric data of FIs of the Tangjiaping deposit are summarized in Table 1 and Figures 5 and 6, which show that the homogenization temperatures of FIs vary in a very wide range from 116 to 630°C. This makes it possible and necessary to understand the details of the ore-forming processes and their linkage with specific mineral assemblages, and to decipher physico-chemical conditions of each metallogenic stage.

Quartz phenocrysts contain four types of FIs with a frequency sequence of PC > C > S >> W, showing the characteristic of the transition from magmatic to hydrothermal fluids. The PC-type FIs with size ranging from 2 to 20 μm form clusters with the C-type inclusions and do not show coexistence with the W-type inclusions. The C-type FIs are irregular to round and ellipsoidal in shape and 6–15 μm (a few up to 20 μm) in size, with carbonic phase volume ranging from 20 to 95% and homogenization temperatures (L + V to V, rarely to L) ranging from 477 to 597°C. The S-type FIs are usually round, ellipsoidal, and rarely irregular in shape, 3–12 μm in size, and contain daughter minerals including halite, sylvite, chalcopyrite, and haematite. When heated, halite in S-type FIs was dissolved after disappearance of vapour bubbles. Total homogenization (L + V + S to L) occurred at temperatures ranging from 548 to 630°C, yielding salinities of 66.58–78.60 wt.% NaCl equiv. The density of S-type FIs varies in the range between 1.23 and 1.37 g/cm³.

In the early-stage quartz, main FIs are PC-, C-, and S-types, followed by W-type. The C-type FIs are the most abundant. They are 5–12 μm in size and irregular, ellipsoidal, and round in shape, with variable volume proportion of the carbonic phase (10–90%). The melting temperatures of solid CO₂ \( T_{\text{mCO}_2} \) are clustered in the range of −58.4 to −56.7°C, below the triple-phase point (−56.6°C) of CO₂, suggesting minor amounts of dissolved components in the carbonic phase (Lu et al. 2004). The clathrate melting \( T_{\text{clath}} \) occurs in the interval of −2.5 to 4.8°C, indicating that the salinities are between 9.39 and 17.75 wt.% NaCl equiv. The carbonic phase \( T_h\text{CO}_2 \) is partially homogenized to liquid at temperatures ranging from 24.2 to 30.6°C. Total homogenization \( T_h \) of the carbonic and aqueous phases (L + V to L, few L + V to V) is observed at temperatures ranging from 259 to 460°C. The C-type FIs with >50 vol.% CO₂ generally decrepitated prior to total homogenization, and the decrepitated temperatures vary from 270 to 413°C. The S-type FIs are small-sized (2–6 μm) and mainly ellipsoidal in shape. Their vapour bubbles disappear at temperatures of 122–471°C, and daughter minerals dissolve at temperatures 326–517°C, yielding salinities of 35.33–62.10 wt.% NaCl equiv. The total homogenization temperatures and densities of S-type FIs range from 326 to 517°C and from 1.04 to 1.18 g/cm³, respectively. Halite daughter minerals in four of the 12 studied S-type FIs dissolve before the disappearance of vapour bubbles, and those in the other eight S-type FIs dissolve after the disappearance of vapour bubbles. The divergent homogenization temperatures show that the S-type FIs were trapped mainly from oversaturated solutions, and to a lesser extent from unsaturated solutions. The opaque and apparent daughter minerals are haematite and chalcopyrite, and sylvite and halite, respectively. The S2-subtype FIs are very abundant and usually show four phases (vapour CO₂ + liquid CO₂ + liquid H₂O + daughter mineral) at room temperature. The least common W-type FIs are 2–6 μm in size and ellipsoidal and irregular in shape, with the vapour bubbles accounting for 10–20% of the
Figure 5. Histogram of homogenization temperatures of FIs in quartz of different stages (A, B).
total volume. Three W-type FIs are homogenized at temperatures below 255°C (Figure 5) and the others homogenized in two temperature ranges of 315–375°C and 395–455°C. Considering the hydrothermal influence in the middle and late stages, the W-type FIs with homogenization temperatures of 395–455°C, 315–375°C, and <255°C may be interpreted as primary, pseudo-secondary, and secondary, respectively, although there is no clear petrographic evidence. The W-type inclusions are too small to measure the freezing point, making salinity calculations impossible.

The middle-stage quartz contains abundant C- and W-type FIs, followed by S-type and a few PC-type FIs. The C-type FIs are irregular to ellipsoidal in shape and 2–15 μm in size, mostly 4–10 μm. Their CO₂ phase (L + V) takes 10–90% of the FIs in volume. Melting temperatures of solid CO₂ ($T_{mCO₂}$) are close to −56.6°C, with some lower than −57.8°C, suggesting that a few of the CO₂ phases contain small amounts of other gases. Clathrate dissociation temperatures ($T_{clath}$) range from −4.7 to 7.8°C, giving the corresponding fluid (CO₂–H₂O–NaCl system) salinities of 4.32 to 19.16 wt.% NaCl equiv. The carbonic phases are partially homogenized to liquid at temperatures ($T_{hCO₂}$) of 16.6–30.2°C. The densities of CO₂ phase are calculated between 0.61 and 0.81 g/cm³. Most C-type FIs homogenized (L + V to L or L + V to V) in the range of 227–380°C, but some FIs decrepitated at the temperatures of 264–351°C prior to total homogenization due to high inner pressure. The divergence of homogenization depends on the CO₂/H₂O ratios; generally, the FIs with CO₂ phase above 50 vol.% are homogenized from L + V to V, whereas the others are from L + V to L. The homogenization divergence of FIs at similar temperatures, usually with contrasting salinities, can be observed in a small part of the sections, indicating fluid boiling. The W-type FIs are round to ellipsoidal in shape, 2–8 μm in size, and composed of vapour and liquid with ratios from 5 to 25 vol.%. Their freezing points vary from −12.7 to −0.6°C, from which the fluid salinities were calculated from 1.06 to 16.62 wt.% NaCl equiv.; and homogenization temperatures ($T_h$) range from 173 to 383°C, suggesting fluid densities ranging from 0.81 to 0.90 g/cm³. The S-type FIs, oblate spheroid to irregular in shape and 2–8 μm in size, usually contain one or two daughter minerals, such as halite, sylvite, chalcopyrite, jamesonite, and, occasionally, haematite. Some S-type FIs are rich in
CO₂ (Figure 4F). The total homogenization temperatures of S-type FIs are between 326 and 517°C, with partial homogenization temperatures of vapour phases ranging from 103 to 277°C and halite melting temperature ranging from 214 to 385°C. The densities of S-type FIs vary from 1.03 to 1.12 g/cm³. When heated, the vapour of some S-type FIs disappeared before halite dissolution, while the others acted in the opposite way. This phenomenon shows that some S-type FIs were entrapped from oversaturated solutions and the others from unsaturated solutions; in other words, the middle-stage fluid system is somewhat heterogeneous, which might be caused by fluid boiling (Lu et al. 2004). In middle-stage quartz, abundant sulphide-bearing S-type FIs reflect a reducing environment.

Only the W-type FIs can be observed in late quartz-carbonate veinlets. They are diverse in shape, 2–6 μm in size, with the vapour H₂O ranging from 5 to 10 vol.%, and homogenized at temperatures between 116 and 234°C. Their freezing points range from −6.6 to −1.1°C, salinities from 1.91 to 9.98 wt.% NaCl equiv., and densities from 0.82 to 0.97 g/cm³. Figure 5A and B and Table 1 summarize individual measurements. They, together with the discussions above, show that the fluid system evolved from hypothermal NaCl–CO₂–H₂O early to epithermal NaCl–H₂O late. The salinities of FIs decrease from 9.39–62.10 wt.% NaCl equiv. early, through 1.06–45.87 wt.% NaCl equiv. middle and through to 1.91–9.98 wt.% NaCl equiv. late, although they are generally high in early and middle stages (Figure 6). Histograms of homogenization temperatures of FIs in the early-stage quartzes show two peaks with temperature ranges of >375°C and 315–355°C (Figure 5A), respectively. The left peak is within the range of homogenization temperatures of FIs in the middle-stage quartz, indicating the influence of middle-stage hydrothermal process (Figure 5A). Four homogenization temperatures are obviously lower than the majority and interpreted to be obtained from secondary FIs. Homogenization temperatures of FIs in middle-stage quartz range from 175 to 395°C, with the majority falling in the range of 235–335°C (Figure 5B). Four FIs in middle-stage quartz yield homogenization temperatures similar to the majority of those for the early stage, suggesting that a few of the middle-stage crystals might grow from an early-stage quartz core. Similarly, the FIs with homogenization temperatures less than 235°C can be regarded as the influence of late-stage hydrothermal activity.

**Laser Raman spectroscopy analysis**

To constrain the compositions of FIs, representative FIs were identified using laser Raman microspectroscopy. The data show that the vapour and liquid phases of the W-type FIs are dominated by H₂O (Figure 7A), but the vapour bubbles of a few W-type FIs also contain a small amount of CO₂, as shown by small CO₂ peaks on the spectrum (Figure 7B). As anticipated, the spectra of C-type FIs only have obvious peaks of CO₂ (Figure 7C). Although the CO₂ peaks appear on the spectra for vapour bubbles of the Cl-subtype (V₃CO₂ + L₃CO₂ + L₃H₂O) and few W-type FIs, the CO₂ peaks of Cl-subtype FIs are much higher than those of W-type FIs. The liquid CO₂ phase of C2-subtype (L₃CO₂ + L₃H₂O) FIs usually shows the existence of CO₃²⁻ (Figure 7D).

Opaque daughter minerals in S-type FIs were also identified by laser Raman spectroscopy. Red haematite, a common daughter mineral, shows a peak of 1323 cm⁻¹ (Figure 7G). The mineral with triangle or round shapes shows peaks of 287–289 cm⁻¹, characterized by chalcopyrite (Figure 7E). The laser Raman spectra also indicate the existence of jamesonite as daughter mineral in middle-stage FIs (Figure 7F). It should be pointed out that more haematite-bearing FIs were observed in early-stage quartz than in middle-stage minerals, indicating that the early-stage fluids were more oxidized.
Figure 7. Laser Raman analyses of different types of FIs of the Tangjiaping Mo deposit. (A) Spectrum of the W-type FIs in late-stage quartz showing no notable peaks of CO$_2$, but a huge H$_2$O-peak; (B) spectrum of early-stage W-type FIs showing huge H$_2$O-peak and small CO$_2$-peaks; (C) CO$_2$-spectrum of the PC-type FIs; (D) spectrum showing existence of CO$_3^{2-}$ in liquid CO$_2$-phase of the C2-subtype FIs; (E) chalcopyrite (Cp) contained in S-type FIs; Qz, quartz; (F) jamesonite (Jm) contained in S-type FIs; (G) haematite (Hem) contained in S-type FIs; and (H) CO$_2$-spectrum of C-type FIs.
Discussion

Nature, origin, and evolution of fluid system

FI is the ‘fossil’ of ancient fluid systems. Among the FIs trapped in minerals of multistage hydrothermal system, only the primary FIs in the earliest-stage minerals can represent the nature and genesis of the original fluid (Chen et al. 2007b). The Tangjiaping Mo deposit was formed with various types of FIs, which can be used to reveal the nature and origin of ore-forming fluids. Four types of FIs, with a frequency sequence of PC > C > S >> W, were observed in quartz phenocrysts and early-stage quartz, strongly suggesting that an initial high-salinity carbonic fluid system originated from intra-continental magmatism (Chen and Li 2009). Occurrence of haematite-bearing S-type FIs and abundant magnetite in early-stage quartz veinlets indicate that the early-stage fluids were oxidizing and rich in ore metals. Most homogenization temperatures of FIs in early-stage quartz are higher than 375°C, which, together with numerous S-type FIs, is taken as representing a signature of an intrusion-related hypothermal fluid system (Zhang and Zhang 2001; Chen et al. 2007b). The similarity of FIs between early-stage and quartz phenocrysts suggests that the early-stage fluids are extracted from magma. This understanding can be also supported by the H–O isotope systematics of the Tangjiaping deposit (Yang 2007c). Hence, we conclude that the initial ore-forming fluids were derived from a magma and characterized by high temperature, high salinity, high oxygen fugacity, CO2-richness, and fertilized with metals such as Mo.

Compared with the early stage, the homogenization temperatures and salinities of the FIs in middle-stage quartz decreased to some extent, and the PC-type FIs became fewer, suggesting escape of CO2 from the fluid system. Chalcopyrite and jamesonite daughter minerals are more commonly observed in S-type FIs, indicating a decrease in oxygen fugacity of the fluid system. Absence of PC-, C-, and S-type FIs in late-stage minerals implies that the late-stage fluid system was poor in CO2, diluted, and meteoric in origin, which is supported by documented H–O isotope data (Yang 2007c). Therefore, the fluid system evolved from magmatic to meteoric in origin.

Fluid boiling and mineralization

As is well known, fluid boiling is one of the most important mechanisms for ore-metal precipitation (Lu et al. 2004; Ni et al. 2005; Chen et al. 2007b). Fluid boiling is recognized as an important ore-forming process for porphyry systems, such as Grasberg Cu–Au deposit, Indonesia (Lu 2000); Bajo de la Alumbrera Cu–Au deposit, Argentina (Ulrich et al. 2002); Shaxi Cu–Au deposit, Anhui (Yang et al. 2007, 2011); Wunugetushan Cu–Mo deposit, Inner Mongolia (Li et al. 2007a); Baogutu Cu deposit, Xinjiang (Song et al. 2007); Yulong Cu–Mo deposit, Tibet (Liang et al. 2009); Jinduicheng Mo deposit, Shaanxi (Yang et al. 2009a); Nannihu Mo–W deposit, Henan (Yang et al. 2009b); Duobao-oshan Cu–Mo, Heilongjiang (Wu et al. 2009); Jinchang Au system, Heilongjiang (Zhang et al. 2008); and Pulang Cu deposit, Yunnan (Wang et al. 2007).

Our research data show that the Tangjiaping Mo deposit was formed in multistage fluid-boiling processes, which is supported by the following: (1) various types of FIs with similar homogenization temperatures and contrasting vapour/liquid ratios coexisting in quartz crystals formed in the early and middle stages (Lu et al. 2004); (2) C-type FIs with contrasting CO2/H2O ratios and salinities homogenized to liquid and vapour at similar temperatures, indicating that they were trapped from a phase-separating fluid system; (3) in S-type FIs, some vapour bubbles disappeared before daughter minerals, and others in the opposite sequence during the heating process, implying that they were trapped from
oversaturated (bubbles disappear before daughter minerals) and unsaturated (bubbles disappear after daughter minerals) solutions; and (4) late-stage minerals that do not contain C-type FIs, indicating that the CO₂ in a CO₂-rich fluid system escaped rapidly at the middle or early stage, and that the rapid release of voluminous CO₂ must be a phenomenon caused by fluid boiling.

Fluid boiling was extensive and intense during the mineralization, especially in the middle stage, of the Tangjiaping deposit. Boiling caused CO₂ release, and, consequently, fluid condensation, pH increase, and oxygen fugacity decrease, and then the precipitation of MoS₂ and other ore minerals.

**Daughter mineral-bearing CO₂-rich FIs: unique feature of intracontinental porphyry deposits**

The Tangjiaping Mo deposit has the common characteristics of porphyry deposits, such as magmatic initial ore-forming fluids, fluid boiling, and wall-rock alteration patterns. However, the porphyry systems of magmatic arcs mainly contain only the W-type (H₂O–NaCl solution) and S1-subtype (daughter mineral-bearing H₂O–NaCl solution) FIs as, for example, at Batu Hijau (Akira and Yuki 2009) and Grasberg (Lu 2000; Lu et al. 2004) porphyry Cu–Au deposits, Indonesia; Rosario (Collahuasi) porphyry Cu–Mo (Masterman et al. 2005) and El Teniente porphyry Cu–Au (Klemm et al. 2007) ore systems, Chile; Bajo de la Alumbrera porphyry Cu–Au deposit Argentina (Ulrich et al. 2002); and Butte porphyry Cu–Mo (Rusk et al. 2008) and Questa porphyry Mo (Klemm et al. 2008), USA. By contrast, the Tangjiaping porphyry Mo deposit, in addition to the W-type and S1-subtype FIs, also contains numerous C-type (CO₂–H₂O), PC-type (pure CO₂), and S2-subtype (daughter mineral-bearing CO₂–H₂O) FIs, indicating that the ore-forming fluid system is unique for being CO₂-rich, especially for daughter mineral-bearing CO₂-rich FIs.

What causes the Tangjiaping Mo deposit to possess a unique ore-forming fluid system? The porphyry deposits poor in CO₂ generally form in oceanic subduction-related magmatic arcs, whereas the Tangjiaping Mo deposit was formed in a post-collisional tectonic setting. According to Chen et al. (2007b), the ore-forming fluids of magmatic arcs were mainly derived from the metamorphic dehydration of subducted oceanic slabs, which can be roughly regarded as ‘altered oceanic basalt’ (NaCl-brine or seawater-bearing oceanic crust), and, thereby, rich in H₂O, Na, and Cl, and poor in CO₂ (or carbonate), K, and F. Consequently, the porphyry ore systems of magmatic arcs, directly (dehydration-melting of subducted slab) or indirectly (melting of ‘enriched’ lithospheric mantle wedge), are sourced from ‘altered oceanic basalt’, and are characterized by abundant NaCl–H₂O FIs with or without daughter minerals and by a dearth of CO₂-rich FIs with or without daughter minerals. On the other hand, porphyry ore systems formed in syn- or/and post-collisional settings must be sourced from the thinned lower continental crust or lithospheric mantle. Compared to the oceanic slab, both the lower continental crust and lithospheric mantle are poor in H₂O and NaCl, and relatively rich in CO₂ (high CO₂/H₂O), K (high K/Na), and F (high F/Cl), in particular, considering the possibility of carbonate graveyards being preserved in the lithosphere. Hence it is proposed that the porphyry ore systems formed during continental collision regimes must be characterized by CO₂-rich FIs with or without daughter minerals and high K/Na and F/Cl ratios, and associated with strong potassic alteration, fluoritization, and carbonation. The above features are supported in a brief review (Chen and Li 2009) and by recent individual deposit studies such as Wunugetushan Cu–Mo deposit (Li et al. 2007a), Taipinggou Mo deposit (Wang et al. 2009), Baogutu Cu deposit (Song et al. 2007), Yulong Cu–Mo deposit (Liang et al. 2009),
Jinduicheng Mo deposit (Yang et al. 2009a), Nannihu Mo–W deposit (Yang et al. 2009b), Shangfanggou Mo–W deposit (Yang et al. 2009c), Duobaoshan Cu–Mo deposit (Wu et al. 2009), Pulang Cu deposit (Wang et al. 2007), Qiyugou Au deposit (Chen et al. 2009; Fan et al. 2011), Jinchang Au system (Zhang et al. 2008), and Aolunhua Cu–Mo deposit (Shu et al. 2009). Therefore, because the Tangjiaping ore-forming fluid system contains CO2-rich and daughter mineral-bearing FIs, especially daughter mineral-bearing CO2-rich FIs, it can be considered as diagnostic of porphyry deposits of intra-continental and/or post-collisional settings.

Conclusions

(1) The Tangjiaping Mo deposit is a porphyry ore system located in the Dabie collision orogen. Its hydrothermal alteration and mineralization processes can be divided into three stages, defined by the mineral assemblages: early-stage K-feldspar + quartz + pyrite + magnetite + molybdenite, middle-stage quartz + pyrite + molybdenite ± chalcopyrite, and late-stage quartz + carbonate ± pyrite veins or carbonate veinlets. The main ore-forming event occurred during the middle stage.

(2) FIs observed in hydrothermal quartz are classified into four types: pure CO2 (PC-type), CO2–H2O (C-type), daughter mineral-bearing (S-type), and NaCl–H2O (W-type). Quartz formed in early and middle stages contains FIs of all four types, but in late-stage minerals, only the W-type FIs are present.

(3) The ore-forming fluids were initially high salinity, hypothermal, and CO2-rich or carbonic, and originated from granitic magma; these fluids evolved to lower temperature, lower salinity, CO2-poor and meteoric water-dominated fluids. During the evolution, multistage boiling, CO2 escape, and ore metal precipitation occurred, with a decrease in temperature.

(4) The porphyry ore systems of magmatic arcs are directly or indirectly sourced from the oceanic slab (‘altered oceanic basalt’) and are characterized by NaCl–H2O FIs with or without daughter minerals, and by a dearth of CO2-rich FIs with or without daughter minerals; in contrast, those formed in a continental collision regime were sourced from continental crust or lithosphere and developed both NaCl–H2O FIs with or without daughter minerals and CO2-rich FIs with or without daughter minerals. The Tangjiaping Mo deposit appears to be a representative of porphyry ore systems formed in continental collisional and post-collisional settings.

(5) The daughter mineral-bearing CO2-rich FIs may be utilized as indicators of porphyry ore systems generated in continental collisional and/or intra-continental settings.

Acknowledgements

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References


Lead isotope systematics of the Weishancheng Au-Ag belt, Tongbai Mountains, central China: implication for ore genesis

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The Weishancheng ore belt in the Tongbai Mountains consists of the Yindongpo large gold deposit, the Poshan and the Yindongling large silver deposits, and several other, smaller, ore deposits. All these ore deposits are stratabound within the Neoproterozoic Waitoushan Group, and are characterized by relative uniform lead isotope compositions: $^{206}\text{Pb}/^{204}\text{Pb} = 16.7529$–$17.2163$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4166$–$15.6380$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.2505$–$39.0500$. These lead isotopic values are close to those of common lithologies of the Waitoushan Group, and quite different from other lithologic units or granitic batholiths in the Tongbai region. The lead isotope systematics of the Weishancheng ore belt suggests that the ores originated from the Waitoushan Group through metamorphic devolatilization. Based on the regional tectonic evolution, we propose that the ore-forming process occurred during the continental collision between the Yangtze and North China blocks; attendant metamorphic devolatilization of under-thrust slabs induced the development of ore-forming fluids. Subsequently, intense water–rock interaction allowed the ore materials contained in the Waitoushan Group to be extracted, migrated, and enriched in the host carbonaceous sericite schist. We conclude that the Weishancheng Au-Ag ore belt can be classified as a stratabound, orogenic-style metallogenic system.

Keywords: lead isotopic systematics; Weishancheng Au-Ag belt; stratabound orogenic-style mineral systems; Tongbai Mountains; Henan province; China

Introduction

The concept of orogenic-type gold deposits was first introduced by Bohlke (1982) and then thoroughly addressed by Groves \textit{et al.} (1998), Kerrich \textit{et al.} (2000), and Goldfarb \textit{et al.} (2001) to summarize a class of structurally controlled gold deposits formed by fluids, assumed to have originated mainly from syn- to post-orogenic metamorphic devolatilization. Thereafter, several structurally controlled lode gold deposits in China have been assigned to the class of orogenic gold deposits (Chen \textit{et al.} 2000, 2001, 2004a, 2005a, 2006, 2008; Kerrich \textit{et al.} 2000; Hart \textit{et al.} 2002; Mao \textit{et al.} 2002; Rui \textit{et al.} 2002; Zhou \textit{et al.} 2002; Fan \textit{et al.} 2003; Zhang \textit{et al.} 2009b) and interpreted to have mainly formed in continental collision fold belts. Consequently, a tectonic model for collisional orogeny, metallogeny, and fluid flow (CMF model) was established to interpret the metallogenic
mechanism and space–time patterns of various genetic types including orogenic gold lodes (Chen 1998; Chen et al. 2004b; Pirajno 2009). Meanwhile, many structurally controlled Ag±Pb-Zn, Pb-Zn±Ag, Cu, and Mo lodes were identified to be of orogenic type (Chen 2006), as exemplified by the Tieluping and Yindonggou Ag deposits in Henan province (Sui et al. 2000; Chen et al. 2004b, 2005b; Zhang et al. 2009a), the Gaojiabaozi Ag deposit in Liaoning province (Wang et al. 2008; Yu et al. 2009), the Lengshuibeigou, Xigou, and Wangpingxigou Pb-Zn±Ag deposits in Henan province (Qi et al. 2007, 2009; Yao et al. 2008), the Bainaimiao Cu±Au deposit in Inner Mongolia (Li et al. 2007, 2008b), and the Zhifang Mo (Deng et al. 2008) and the Dahu Mo-Au (Li et al. 2008a; Ni et al. 2008, 2009) deposits in Henan province. Significant advances have not only improved the understanding of ore genesis and exploration target in orogenic belts but also introduced several new problems. One of them is whether the orogenic-type deposit can occur as stratabound style; if not, how to clarify the genetic type of deposits formed by metamorphic ore-forming fluids which focused in a unique lithologic layer, for example, carbonaceous beds, banded iron-formation beds, and stratigraphic unconformities; and what are the geochemical signatures and metal sources of these stratabound orogenic-type deposits. Gold deposits, such as Muruntau in Uzbekistan, Kumtor in Kyrgyzstan, Sukhoi Log in Russia, Homestake in the USA (Bierlein and Maher 2001; Goldfarb et al. 2001; Groves et al. 2003), Sawayardun in Xinjiang (Chen et al. 2004a, 2007a), Yangshan in Gansu (Yang et al. 2006, 2009; Qin and Zhou 2009), and Yindongpo in Henan (Chen 1995; Zhou et al. 2002), show stratabound characteristics and have been recognized as orogenic type. Thus, economic stratabound style, orogenic-type Ag, Pb-Zn, and other similar ore deposits may be recognized in the future.

The Weishancheng Au-Ag belt, located in the Tongbai Mountains of Henan province, China, consists of the Yindongpo large gold deposit, the Poshan giant silver deposit, and the Yindongling large silver-dominated polymetallic deposit, as well as numerous small ore occurrences (Figure 1). All these deposits occur in low-grade metamorphic carbonaceous beds of the Neoproterozoic Waitoushan Group, which is located north of the late Palaeozoic–Triassic Shang-Dan (Shangnan-Danfeng) fault zone suturing the North China and Yangtze plates or cratons. Their apparent stratabound characteristics and economic potentials attracted the interest of geologists in the study of the metallogenic type, mechanism, and distribution. The individual deposit has been well studied since the discovery of the Weishancheng ore belt in the 1970s (Chen and Fu 1992; Luo 1992; Chen 1995; Xu et al. 1995; Zhang et al. 1999b, 2008). However, an integrated study on the whole ore belt is not available and no paper has been published in English language journals. Therefore, this article will introduce the lead isotope systematics of the Weishancheng ore belt; discuss ore-metal source, metallogenic mechanism; and propose that the mineral systems of this belt are stratabound orogenic.

**Regional ore geology**

The Tongbai Mountains, located in the southern Henan province, are part of the Central Orogen, that is Qinling–Dabie Orogen (Figure 1). Main faults in the area include the Tongbai (F5), Shang-Dan (SF1), Zhu-Xia (F4), Waxuezi (F3), and Duanzhuang (F6) (Figure 1A and B). Northward from the Tongbai fault, the Xinyang Group, Qinling Group, Erlangping Group (consisting of the Liushanyan Formation, Zhangjiadiazhuang Formation, and Dalishu Formation), Waitoushan Group, and Kuanping Group are developed sequentially at the southern margin of the North China Craton (Figure 1B). In the Phanerozoic, the area experienced two significant geodynamic events. The earlier
event was the Silurian-Devonian (Caledonian) collision between the central Qinling magmatic arc (mainly of the Qinling Group) and the North China craton, resulting in the closure of the Erlangping back-arc basin and greenschist to amphibolite facies metamorphism of the Waitoushan and Erlangping groups (Hu et al. 1988; Xiang et al. 2009). The second and younger event, part of the Yanshanian tectono-thermal activity that affected large areas of eastern China, was the Triassic–Jurassic intercontinental collision between the Yangtze and North China continents. This collision caused a series of northward A-type subducations, such as those along the Shang-Dan, Zhu-Xia, and Waxuezi faults (Hu et al. 1988; Zhang et al. 2001, 2002; Chen et al. 2004b), as well as large-scale (Yanshanian) mineralization and granitic magmatism (Chen and Fu 1992), including the Weishancheng Au-Ag belt and its coeval granitoids (Figure 1B; Zhang et al. 2002, 2008).

The Weishancheng Au-Ag ore belt, about 20 km in length and 1 km in width, is located in the Erlangping early Palaeozoic back-arc basin, north of the Zhu-Xia fault (F4 in Figure 1B). Its eastern and western extensions are covered by Wucheng and Nanyang Cenozoic basins, respectively. The Heqianzhuang anticline is the main fold and strikes 90°–120° (Figure 2), comprising the Waitoushan Group and Dalishu Formation of the Erlangping Group. The anticline is tilted to the east and dips towards the west. The Waitoushan Group outcrops along the axis of the anticline, whereas the Dalishu Formation forms its southern limb. The anticline was further deformed and intruded by granitic
batholiths, such as the Taoyuan Palaeozoic biotite plagiogranite pluton and Liangwan (Yanshanian) adamellite–granodiorite pluton (Figures 1 and 2). In the mining districts of Poshan and Yindongling, lamprophyre dikes of Yanshanian age are present.

The ore deposits and occurrences are mainly sited in the collapsed position of the axis and along the two limbs of the anticline (Figure 2), including, from W to E, the Xialaozhuang Au-Ag occurrence, Poshan giant Ag deposit, Guolaozhuang Ag occurrence, Yindongpo large Au deposit, Zhangzhuang Au occurrence, Luanjiachong Ag occurrence, Jiangzhuang Ag occurrence, Weigou Ag occurrence, Yindongling large Ag-dominated polymetal deposit, Nanxiaogou Ag occurrence, and Zhuzhuang Au occurrence (Figure 2). All these deposits and occurrences are hosted in the Neoproterozoic Waitoushan Group (Figures 1 and 2), which consists of mica schist, mica-quartz schist, and lesser plagioclase-amphibole schist, marble, and quartzite (Table 1). In the Tongbai Mountains, the Waitoushan Group is unique for its high abundance of organic carbon, Au, Ag, and other metallic elements (Chen and Fu 1992; Zhang et al. 1999b). The Waitoushan Group is divided into three formations, namely, upper Waitoushan, middle Waitoushan, and lower Waitoushan Formation, each containing several members. The Poshan Ag deposit occurs in the second member of the Upper Waitoushan Formation, the Yindongpo Au deposit occurs in the second member of the Middle Waitoushan Formation, and the Yindongling Ag deposit occurs in the fifth and sixth members of the Lower Waitoushan Formation (Zhang et al. 2008).

Ore bodies of the Poshan, Yindongpo, and Yindongling deposits are hosted by carbonaceous mica-quartz schists and occur in the Heqianzhuang anticline (Figure 3A), and have stratiform or saddle shapes, with obvious stratabound characteristics. Ores occur mainly as intensively altered tectonite (Figure 3B), breccia, silicic replacement, veinlet-disseminated replacement, silicified muscovite-quartz, and carbonaceous sericite-quartz schists. The main ore minerals are galena, sphalerite, argentite, and native silver at Poshan and Yindongling silver deposits, whereas in the Yindongpo gold deposit they are pyrite, electrum, native gold, and galena. Common wall-rock alteration includes silification, sericitization, and secondarily carbonation and chloritization. The ore-forming process can be divided into three stages. The early stage is characterized by grey and milky quartz
veinlets spotted with pyrite, where the quartz is deformed and crashed (Figure 3C). The middle stage is characterized by grey or smoky, grey quartz stockworks, containing large amounts of pyrite, galena, sphalerite, chalcopyrite, native gold, and electrum (Figure 3D). The late stage is characterized by white quartz or carbonate veinlets (Figure 3E), which cut earlier quartz veins.

The Weishancheng ore belt is widely considered to have formed during the Yanshanian (Mesozoic) tectono-thermal event, but detailed ore-forming age is still controversial. Table 2 lists isotope ages, which can be divided into two ranges: 363–378 Ma and 103–172 Ma. The 363–378 Ma range of ages is interpreted to represent the metamorphism of the Waitoushan Group, which was caused by Caledonian arc-continent collision. The 103–172 Ma range is coeval with the Yanshanian large-scale mineralization and magmatism temporally associated

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Poshan Ag deposit</th>
<th>Yindongpo Au deposit</th>
<th>Yindongling Ag-dominated polymetal deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale</td>
<td>Super-large</td>
<td>Large</td>
<td>Large</td>
</tr>
<tr>
<td>Reserves</td>
<td>Ag: 2662t</td>
<td>32.337 t (332 + 333)</td>
<td>Ag: 1914.22 t (332 + 333 + 3341), Pb + Zn: 33.16 × 10^4 t</td>
</tr>
<tr>
<td>Average grade</td>
<td>Ag: 278 g/t</td>
<td>7.61 g/t</td>
<td>Ag: 295.87 g/t, Pb + Zn: 1.58%</td>
</tr>
<tr>
<td>Mater lode</td>
<td>A1: 1900 m in length, 530 m in depth, and average 5.38 m in thickness</td>
<td>No. 1#: 1600 m in length, 600 m in depth, and 7.6 m in thickness</td>
<td>A1: 1320 m in length, 280 m in depth, and average 2.12 m in thickness</td>
</tr>
<tr>
<td>Host stratum</td>
<td>Second member of upper Waitoushan Formation</td>
<td>Second member of mid-Waitoushan Formation</td>
<td>Fifth member of lower Waitoushan Formation</td>
</tr>
<tr>
<td>Host rock</td>
<td>Carbonaceous sericite–quartz schist; plagioclase-amphibole schist (only for A10 orebody)</td>
<td>Silicification sericite–quartz schist, carbonaceous sericite–quartz schist, lepyntite</td>
<td>Silicification muscovite–quartz schist, lepyntite, and cataclastic marble</td>
</tr>
<tr>
<td>Ore-controlled structure</td>
<td>The intra-layer fault in southern limb of Heqianzhuang anticline</td>
<td>Axial collapse of Heqianzhuang anticline</td>
<td>The intra-layer fault in northern limb of Heqianzhuang anticline</td>
</tr>
<tr>
<td>Occurrence of ore body</td>
<td>Stratiform and lens in shape</td>
<td>Saddle, stratiform and lens in shape</td>
<td>Stratiform in shape</td>
</tr>
<tr>
<td>Wall-rock alteration</td>
<td>Silicification, sericitization, carbonation, chloritization, argillic alteration</td>
<td>Silicification, sericitization, carbonation, chloritization</td>
<td>Silicification, sericitization, carbonation, chloritization, argillic alteration</td>
</tr>
<tr>
<td>Ore type</td>
<td>Intensive altered tectonite</td>
<td>Intensive altered tectonite</td>
<td>Breccia ore, veinlet-disseminated ore</td>
</tr>
<tr>
<td>Ore minerals</td>
<td>Argentite, native silver, freibergite, pyrargyrite</td>
<td>Native gold, electrum</td>
<td>Argentite, native silver</td>
</tr>
<tr>
<td></td>
<td>Galena, sphalerite, pyrite</td>
<td>Pyrite, galena, sphalerite</td>
<td>Pyrite, galena, sphalerite, chalcopyrite</td>
</tr>
<tr>
<td>Gange minerals</td>
<td>Calcite, quartz, plagioclase, sericite, muscovite</td>
<td>Quartz, sericite</td>
<td>Quartz, sericite, muscovite, calcite</td>
</tr>
<tr>
<td>References</td>
<td>This article and No. 3 Geology Team of Henan (1984)</td>
<td>This article and Chu et al. (2000)</td>
<td>This article, Wan (2005), Wu and Ren (2005)</td>
</tr>
</tbody>
</table>
with the Yangtze–North China continental collision. Muscovites from the wall rock (sample TB06) of the Yindongpo deposit yield a larger Ar-Ar plateau age of 361.34 ± 7.07 Ma (80.3% Ar-release) and a smaller plateau age of 142.59 ± 19.43 Ma (2.5% Ar-release), which is interpreted to record the hydrothermal event. Sericite separate from ore (99H32) of the Yindongpo deposit does not yield Ar-Ar plateau age, but the apparent step-ages range from 140 to 250 Ma, suggesting that the mineralization occurred during the Mesozoic collisional orogeny. To calculate the isotope ratios (see Discussion, Table 5, and Figure 4), in this article we take 150 Ma as the mineralization age, although this may need further constraining.
Samples and analytical techniques

Sulphide samples collected from ore deposits and occurrences were separated by hand-picking for purification under a binocular microscope, whereas rock samples collected from different strata were directly powdered in an agate mill under 200 meshes.

Sulphide samples from the Yindongpo gold deposit and the Poshan silver deposit were analysed at the Open Laboratory of Isotopic Geochemistry, Chinese Academy of Geological Sciences, whereas sulphide samples from the Yindongling deposit and other occurrences and whole rock samples of strata from the Tongbai region were analysed at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The U, Th, and Pb contents of whole rock were measured on a Finnigan MAT ICP-MS and were normalized to the values of GSR1, GSR2, and GSR3 at the State Key Laboratory of Lithospheric Evolution.

For lead sulphide samples, approximately 10–50 mg minerals were first leached in acetone to remove surface contamination and then washed with distilled water and dried at 60°C in an oven. Washed sulphides were dissolved in a dilute solution of nitric acid and hydrofluoric acid. Following ion-exchange chemistry, the lead in the solution was loaded onto rhenium filaments using a phosphoric acid-silica gel emitter. The Pb isotopic compositions were measured on a MAT261 thermal ionization mass spectrometer. All ratios were normalized to the values of NBS 981. Estimated precision for the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are about 0.1, 0.09, and 0.30% at the 2σ level, respectively.

For whole rock samples, the powder was totally dissolved in hydrofluoric acid (2% HNO$_3$) under high temperature and high pressure and evaporated to almost dry fluoride. Then the fluoride was dissolved in 6N HCl and evaporated to dryness that was dissolved in 0.6N HBr subsequently. The separate and purified lead was extracted through anionic exchange resins, and then loaded onto rhenium filaments with silica gel and phosphoric acid-silica gel emitters.

### Table 2. Isotope ages for the Weishancheng ore belt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Geology of analysed sample</th>
<th>Method and age (Ma)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>99H23</td>
<td>Sericite form ore, Yindongpo</td>
<td>K-Ar: 119.5 ± 3.6</td>
<td>Chen (2010)</td>
</tr>
<tr>
<td>99H32</td>
<td>Sericite form ore, Yindongpo</td>
<td>K-Ar: 171.8 ± 4.9</td>
<td>Chen (2010)</td>
</tr>
<tr>
<td>TB06</td>
<td>Muscovite from wall rock, Yindongpo</td>
<td>$^{40}\text{Ar}-^{39}\text{Ar}$ plateau: 361.3 ± 7.07; 142.59 ± 7.07</td>
<td>Chen (2010)</td>
</tr>
<tr>
<td>TB06</td>
<td>Muscovite from wall rock, Yindongpo</td>
<td>K-Ar: 331.3 ± 6.1</td>
<td>Chen (2010)</td>
</tr>
<tr>
<td>TB02</td>
<td>Muscovite from wall rock, Yindongpo</td>
<td>K-Ar: 370.9 ± 11.0</td>
<td>Chen (2010)</td>
</tr>
<tr>
<td>YDP1</td>
<td>Sericite from quartz vein, Yindongpo</td>
<td>$^{40}\text{Ar}-^{39}\text{Ar}$ plateau: 373.8±3.2; $^{40}\text{Ar}-^{39}\text{Ar}$ isochron: 373 ± 13</td>
<td>Jiang et al. (2009)</td>
</tr>
<tr>
<td>99H72</td>
<td>Sericite from ore, Poshan – Bulk minette, Poshan</td>
<td>K-Ar: 103.6 ± 4.5; K-Ar: 134</td>
<td>Chen (2010); HIGMR (1985)</td>
</tr>
<tr>
<td>PS3</td>
<td>Biotite from altered lamprophyre, Poshan</td>
<td>$^{40}\text{Ar}-^{39}\text{Ar}$ plateau: 129.0 ± 1.1; $^{40}\text{Ar}-^{39}\text{Ar}$ isochron: 128.4 ± 3.5</td>
<td>Jiang et al. (2009)</td>
</tr>
<tr>
<td>YDL1</td>
<td>Sericite-altered wall rock, Yindongling</td>
<td>$^{40}\text{Ar}-^{39}\text{Ar}$ plateau: 377.4 ± 2.6; $^{40}\text{Ar}-^{39}\text{Ar}$ isochron: 377.8 ± 5.7</td>
<td>Jiang et al. (2009)</td>
</tr>
</tbody>
</table>
acid. The Pb isotopic compositions were measured on a German Finnigan MAT262 thermal ionization mass spectrometer under the temperature of $1300^\circ$C. All ratios were normalized to the values of NBS 981 by applying a mass discrimination factor of 0.1% per atomic mass unit.

**Results**

Lead isotope analyses of sulphides are presented in Table 3. Eight samples of the Poshan silver deposit show little variation in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ with narrow ranges of 16.970–17.124, 15.430–15.638, and 38.356–39.050, respectively. Fourteen samples from the Yindongpo gold deposit yield $^{206}\text{Pb}/^{204}\text{Pb}$ values of 16.990–17.216, $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.419–15.612, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 38.251–38.861; and 13 samples from the Yindongling silver-dominated polymetallic deposit give $^{206}\text{Pb}/^{204}\text{Pb}$ of 16.753–17.216, $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.417–15.521, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 38.683–38.868. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of five sulphide samples from other gold-silver occurrences are 16.912–17.109, 15.439–15.468, and 38.290–38.499, respectively. As a whole, lead isotope compositions of sulphides from the Weishancheng ore belt are less variable and poor in U-radiogenic Pb and rich in Th-radiogenic Pb.

Table 4 lists lead isotope analyses of whole rocks from the Tongbai Mountains lithologies. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 15 samples from the Waitoushan Group range 17.047–18.539, 15.394–15.614, and 38.074–39.426, respectively, showing the lowest $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (Uranium radiogenic Pb) among the lithologic units in the studied area. Of the Erlangping Group, the Dalishu Formation ($n=9$) yields $^{206}\text{Pb}/^{204}\text{Pb} = 17.360–18.789$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.366–15.823$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.894–39.035$; the Zhangjiadazhuang Formation ($n=4$) $^{206}\text{Pb}/^{204}\text{Pb} = 18.105–19.204$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.510–15.749$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.804–39.047$; and the Liushanyan Formation ($n=12$) $^{206}\text{Pb}/^{204}\text{Pb} = 17.848–19.166$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.457–15.633$, and $^{208}\text{Pb}/^{204}\text{Pb} = 37.818–39.739$. The Qinling Group ($n=5$) yield $^{206}\text{Pb}/^{204}\text{Pb} = 17.548–19.134$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.430–15.633$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.966–38.564$. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios ($n=8$) of the Xinyang Group are 18.016–19.490, 15.312–15.747, and 37.408–39.278, respectively. The ratios ($n=11$) of the Tongbai complex are 17.130–17.499, 15.331–15.392, and 37.420–38.188, respectively. As for the Liangwan granite pluton, four analyses yield $^{206}\text{Pb}/^{204}\text{Pb}$ of 17.552–17.812, $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.368–15.394, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 37.837–38.168. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (five samples) of the Taoyuan pluton span are 17.576–19.257, 15.415–15.638, and 38.255–39.856, respectively.

**Discussion**

**Source of ore-forming metals**

All sulphides of the Weishancheng ore belt have narrow ranges of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios and coincident $\mu$ values (9.31–9.77). In the $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot (Figure 4), ore samples show an approximate linear distribution and present a single-stage evolved normal lead composition, suggesting that the source U-Th-Pb system neither separated from each other nor mixed intensively with other U-Th-Pb systems, and that the model ages of the ores can be calculated using the Holmes–Houtermans formula. Calculated model ages of ores vary from 913 to 1182 Ma, which are roughly consistent.
with the geologically estimated age of the Wai toushan Group, that is the early Neoproterozoic (1050–800 Ma) (Hu et al. 1988; Chen and Fu 1992).

The $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of sulphides are relatively variable (Figure 4), implying that the content of Th-radiogenic Pb ($^{208}\text{Pb}$) is variable, caused by a variable and high content of Th, compared with U. The Th/U ratios of sulphides change from 4.60 to 5.13,

Table 3. Lead isotope composition of ore minerals from the Weishancheng ore belt.

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<th>$^{207}$Pb/$^{204}$Pb</th>
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<td>TB35</td>
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(Continued)
relatively rich in Th-radiogenic Pb, and analogous to those of low-grade metamorphic rocks (Zhu 1998), but different from those of chemical sediments, granites, or high-grade metamorphic rocks. This feature coincides, in both lithology and geochemistry, with the Waitoushan Group occurring as a low-grade metamorphic suite consisting of sericite schists and sericite-quartz schists, with Th/U values of 2.19–11.72, mainly in 3–8 (Table 5).

The calculated $\omega$ values of sulphides range 44.34–50.80, higher than those of the normal lead (35.55 ± 0.59), indicating that the ore-forming Pb source is highly matured. This is also matched with the nature of the Waitoushan Group mainly composed of metasediments.

Sulphide samples scatter on the $^{207}$Pb/$^{204}$Pb–$^{206}$Pb/$^{204}$Pb plot (Figure 4), indicating that the ore-forming Pb came from an old U-Th-Pb system. This Pb signature suggests that the Pb source of the ore material is likely to be either from the Waitoushan, Erlangping, Qinling, Xinyang groups or a mixing thereof, but not from young magmatic intrusions.
such as the Taoyuan and Liangwan granite batholiths. Figures 4A and B also show that the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of ores are close to or slightly lower than those of the present Waitoushan Group, whereas the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of ores are lower than those of the present Waitoushan Group. This also suggests that the ore-forming lead might be mainly sourced from the Waitoushan Group, considering that post-ore accumulation of radiogenic Pb can occur in source rocks but not in sulphides that constitute ores, because source rocks usually contain much U and Th, but sulphides have lower or even no U and Th (Chen et al. 2004b). Given that these sulphides formed at about 150 Ma, lead isotope...
Table 5. U, Th, Pb mass fractions and the calculated initial Pb isotopic ratios of the strata in Tongbai area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t/Ma</th>
<th>U/10^{-6}</th>
<th>Th/10^{-6}</th>
<th>Pb/10^{-6}</th>
<th>Th/U</th>
<th>(^{238}\text{U}/^{204}\text{Pb})</th>
<th>(^{232}\text{Th}/^{204}\text{Pb})</th>
<th>(^{206}\text{Pb}/^{204}\text{Pb})_t</th>
<th>(^{207}\text{Pb}/^{204}\text{Pb})_t</th>
<th>(^{208}\text{Pb}/^{204}\text{Pb})_t</th>
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<tr>
<td>W3-1</td>
<td>150</td>
<td>1.29</td>
<td>4.47</td>
<td>44.9</td>
<td>3.47</td>
<td>1.93</td>
<td>6.73</td>
<td>17.095</td>
<td>15.496</td>
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<td>7.48</td>
<td>27.8</td>
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<td>8.22</td>
<td>18.18</td>
<td>17.428</td>
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<td>150</td>
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<td>11.00</td>
<td>171.0</td>
<td>3.63</td>
<td>1.19</td>
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<td>17.345</td>
<td>15.499</td>
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<td>W2-5</td>
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<td>6.87</td>
<td>67.5</td>
<td>3.80</td>
<td>1.80</td>
<td>6.87</td>
<td>17.070</td>
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<td>0.45</td>
<td>2.4</td>
<td>3.75</td>
<td>3.39</td>
<td>12.47</td>
<td>18.051</td>
<td>15.562</td>
<td>38.216</td>
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<td>DLS-4</td>
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<td>4.26</td>
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<tr>
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<td>9.02</td>
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<td>LSY-15</td>
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<td>7.21</td>
<td>77.3</td>
<td>8.58</td>
<td>0.73</td>
<td>6.31</td>
<td>18.039</td>
<td>15.577</td>
<td>38.262</td>
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Notes: 
- The lithologic characteristics of each sample are listed in Table 4. 
- Supposing the t is 150 Ma according to the ages of metallogenesis. The values of \(^{206}\text{Pb}/^{204}\text{Pb}\)_t, \(^{207}\text{Pb}/^{204}\text{Pb}\)_t, and \(^{208}\text{Pb}/^{204}\text{Pb}\)_t, are calculated according the tested data in Tables 4 and 5.
compositions of the Waitoushan Group at 150 Ma should accord with those of ores if the ore lead were really sourced from the Waitoushan Group. Remarkably, this expected scenario is shown in Figure 4A and B, that is the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of sulphides are plotted in the 150 Ma lead isotope domain of the Waitoushan Group. Thus, lead isotope compositions of the Waitoushan Group can match those of the Weishancheng ore belt, supporting our conjecture.

Besides the ore-hosting Waitoushan Group, other lithologic or tectonostratigraphic units in the studied area need to be checked if they too served as metal sources for the Weishancheng ore belt. Sulphides from the Weishancheng ore belt have obvious contrasting lead isotope ratios to both the present and 150 Ma lead isotope compositions of the Erlangping and Qinling groups (Figure 4C and D), which are the two most major tectonostratigraphic terranes in northern Qinling Orogen. For example, sulphides' $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are lower than the present and 150 Ma $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the Erlangping and Qinling groups. This means that the radiogenic $^{206}\text{Pb}$ in sulphides is too poor to be mainly provided by either the Erlangping and Qinling groups, or their combinations thereof. Therefore, the Qinling and Erlangping groups could hardly be the Pb source of the Weishancheng ore belt. In the same way, lead isotope compositions of the Xinyang Group and the Tongbai complex in southern Qinling Orogen are observably different from those of these sulphides (Figure 4E and F), indicating that they could not be the main source of ore-forming materials.

In conclusion, the Waitoushan Group exclusively is the ideal, main source of ore-forming materials for the Weishancheng ore belt.

**Tectonic setting and metallogenic mechanism**

The lead isotope compositions show that ore-forming materials of the Weishancheng ore belt were mainly sourced from the Waitoushan Group. Furthermore, studies on fluid inclusions (Yang 2008) and C-H-O-S isotope systematics (Zhang et al. 2008) confirmed that ore-forming fluids were sourced from the metamorphic devolatilization of the Waitoushan Group, and that the fluids mixed with circulating meteoric water in the middle and late metallogenic stages. Thus, it is clear that both ore-forming metals and fluids were genetically related to the Waitoushan Group. To understand the metallogenic mechanism, we must clarify the Yanshanian tectonic setting.

In this article, we subscribe to the first viewpoint, because of the following: (1) Triassic ophiolite belt and island arc volcanic rocks have been recognized along and north of the Mianxian-Lueyang fault, respectively (Zhang et al. 2001), indicating that the final closure of the oceanic basin could not have been earlier than the Late Triassic; (2) inboard orogenic A-type subduction, deformation (Xu et al. 1986; Hu et al. 1988), and foreland folding-and-thrusting onset occurred since the end of the Triassic (Li et al. 1999), in which the Late Triassic flyschoids unites were involved (Yang et al. 2006); (3) two Indosinian (220–200 Ma) granite belts occur in Qinling Orogen, that is a southern belt consisting of collision-type calc-alkaline granitoids south of the Shang-Dan fault and a northern belt comprising alkaline granitoids locally associated with carbonatites (Chen et al. 2009), which are
interpreted to be derived from thickened continental crust (Liu et al. 2008; Zhang et al. 2009b) and a mantle graveyard of subducted oceanic crust (Ni et al. 2009; Xu et al. 2009), respectively; (4) collision-type granite magmatism occurred during 160–126 Ma, with peak age of 140 Ma (Chen and Fu 1992); (5) the facies of Mesozoic-Cenozoic sedimentary rocks show that the Qinling Mountains were uplifted to their highest in the Jurassic, followed by widespread Cretaceous basins with red beds (Chen and Fu 1992); (6) palaeogeomagnetic studies suggest that Yangtze and North China plates were not joined before the Triassic, and that their relative positions have not changed since the mid-Cretaceous, suggesting that crustal shortening, detachment, and landmass rotation occurred in the period of Triassic–Early Cretaceous (Zhu et al. 1998); (7) collisional P-T-t paths show that the collisional orogenesis, metallogenesis and fluid flow (CMF) should occur most intensely in the decompression-geotherm increasing stage, corresponding to the period from the Jurassic to the Cretaceous in Qinling Orogen (Chen et al. 2004b); and (8) rapid uplift of the orogenic belt ended at about 130 Ma (Chen et al. 2009).

The K-Ar and Ar-Ar isotope ages constrain the formation time of the Weishancheng ore belt in the bracket of 172–103 Ma (Table 2). This shows that metallogenesis occurred in the transition from compression to extension during the intercontinental collision tectonic regime. Integrating evidence from geological setting, lithology, magmatism, metamorphism, ore-forming fluids, and other factors, the ore-forming mechanisms and processes of the Weishancheng ore belt can be reasonably deduced (Figure 5). During the continent–continent collision of Yangtze Block and North China Block in the Mesozoic, the southern Qinling terrane subducted northward beneath the northern Qinling terranes along the Shang-Dan geosuture, which is marked by a mélange zone composed of the Xinyang Group and Qinling Group (Figures 1 and 5). In terms of the CMF model (for details see Chen et al. 2004b and Pirajno 2009), the underthrust slabs (e.g. Qinling Group) would be metamorphosed, devolatilized, and even partially melted, thus providing ore-fluids for ore-forming systems of the Weishancheng ore belt. During migration, circulation, and interaction with country rocks, fluids continuously extracted ore-forming elements from the Waitoushan Group, and then transported them to the locales favourable for ore deposition (e.g. the Heqianzhuang anticline or intra-layer fault zone along carbonaceous strata).
In this process, the sulphides inherited the isotopic characteristics of the Waitoushan Group, especially the lead isotopic signature of low $^{206}\text{Pb}/^{204}\text{Pb}$ ratio and high $^{208}\text{Pb}/^{204}\text{Pb}$ ratio. Therefore, early-stage ore-fluids originated from metamorphic dehydration. When the tectonic setting changed from compression to extension, ductile structures would expand and become brittle and open thereby, becoming more favourable for the circulation of fluids and for ore-metal precipitation. The opening of these structures also facilitated phase separation or fluid boiling and mixing with circulating meteoric water, resulting in rapid precipitation of ore metals. In this way, the ore-forming fluid system changed from metamorphic to meteoric. In support of the above interpretation, the Liangwan granite pluton north of the Weishancheng ore belt was evidenced to have originated from the partial melting of the northward A-type subducted slab, that is of the basement of southern Qinling orogenic belt (Zhang et al. 1999a, 2000).

**Ore genesis**

The above discussion makes it clear that the Weishancheng ore belt was formed in a Mesozoic intercontinental collision regime. Further comparisons of the geological and geochemical characteristics show that the Weishancheng ore belt has similar features of typical orogenic-type deposit (Kerrich et al. 2000; Chen 2006 and references therein). (1) The metallogenesis of Weishancheng ore belt occurred in the transition period from collisional compression to extension after the peak period of continental collision orogenesis of the Qinling Mountains, that is the metallogenic system formed a little later than orogenesis. (2) Study of geological characteristics of the ore belt (Zhang et al. 2008) indicates that widespread and intensive silification has close relationship with mineralization, mostly by the way of metasomatism, and silicification increased the $\text{SiO}_2$ content in wall rocks, changed their composition, structure and texture, and finally formed the massive quartz-replacement rocks. In this case, the boundary between ore body and wall rocks is unclear. (3) The ore-forming fluid of the Weishancheng Au-Ag ore belt is of low salinity (<10 wt.% NaCl equivalent) and CO$_2$-rich (4–15 mol.%) (Figure 3F), which is characteristic of orogenic-type deposits (Chen et al. 2007b).

The Weishancheng ore belt is already recognized as a typical stratabound gold-silver belt (Chen and Fu 1992; Wu et al. 1994; Chu et al. 2000) based on the following evidence: (1) the ore bodies are controlled by the Waitoushan Group in the Heqianzhuang anticline and bedded, tabular, saddle, and lens-like shapes, and the ores are dominated by altered tectonites; (2) the Waitoushan Group has higher contents of Au, Ag, Pb, Zn, Cu, and other metallic elements than the Clark values of other lithologies in the studied area by some orders of magnitude, providing the necessary ore-forming materials to the metallogenetic systems; (3) the C-S-Pb isotopic data indicate that the ore-forming materials were mainly sourced from the Waitoushan Group, and the H-O-C isotopic studies show that ore-forming fluids were mostly originated from metamorphic water in early and middle stages, but were mixed with meteoric water in late stage because of metallogenic system opening; and (4) ore bodies and their foot walls and hanging walls are rich in organic carbon, suggesting that carbonaceous layers acted as sealing units to prevent the upward rise of fluids, allowing deeper downward circulation of meteoric water, and thus gather fluid and ore-metal. Also, the carbonaceous layers can reduce the $[\text{SO}_4]^{2-}$ and Au$^+$ or Au$^{3+}$ in high-$\nu$/O$_2$ fluids, which were once detected rich in K$^+$ and $[\text{SO}_4]^{2-}$ (Zhang et al. 2009a), into Au$^0$ and S$^{2-}$ or S$^{-}$ to form native gold and sulphides including pyrite, respectively.
In other words, deposits in the Weishancheng ore belt belong to orogenic-type metallogenic system with stratabound characteristics, and the Yindongpo and Poshan are the representatives of gold and silver, respectively.

Conclusions

(1) The Weishancheng ore belt consists of the Poshan giant silver deposit, the Yindongpo large gold deposit, the Yindongling large silver-dominated polymetallic deposit, and several small deposits or occurrences. All these ore deposits are stratabound and hosted in the Neoproterozoic Waitoushan Group, particularly, in carbonaceous sericite schist beds.

(2) Lead isotopic ratios of ores, with \(^{206}\text{Pb}/^{204}\text{Pb} = 16.7529–17.2163\), \(^{207}\text{Pb}/^{204}\text{Pb} = 15.4166–15.6380\), and \(^{208}\text{Pb}/^{204}\text{Pb} = 38.2505–39.0500\), respectively, are consistent with those of the Waitoushan Group, but different from those of the other tectonostratigraphic units and magmatic rocks in the Tongbai region, strongly suggesting that the ore-forming materials of the Weishancheng ore belt were sourced from the Waitoushan Group.

(3) The Weishancheng ore belt can be considered as stratabound orogenic-type metallogenic system. The ore-forming process occurred during the continental collision between the Yangtze and North China blocks. The metamorphic devolatilization of underthrust slabs induced the development of metallogenic system. Through fluid–rock interaction, ore metals were extracted out from the Waitoushan Group, and transported to and discharged in the carbonaceous sericite schist beds by the circulating fluids.

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He and Ar isotopic compositions and genetic implications for the giant Shizhuyuan W–Sn–Bi–Mo deposit, Hunan Province, South China

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The Shizhuyuan ore deposit in southern Hunan Province is a world-class W–Sn–Bi–Mo occurrence hosted by Devonian limestone in the thermal aureole of the Qianlishan granite. Mineralization coincided with intrusion of the granite pluton during Mesozoic crustal extension in South China. We present new He and Ar isotope data for volatiles released from pyrite in the Shizhuyuan deposit. Concentrations of \( ^{40}\text{Ar} \) range from \( 0.21 \text{ to } 2.38 \times 10^{-6} \text{ cm}^3 \text{ STP } \text{ cm}^3 \text{ Ar}\)/g, and \( ^{4}\text{He} \) concentrations range from 0.8 to 65.1 \( \times 10^{-6} \text{ cm}^3 \text{ STP } \text{ cm}^3 \text{ He}\)/g. \( ^{3}\text{He} / ^{4}\text{He} \) ratios vary from 0.06 to 1.66 \( \text{Ra} \) (where \( \text{Ra} \) is the \( ^{3}\text{He} / ^{4}\text{He} \) ratio of air = \( 1.39 \times 10^{-6} \)) and \( ^{40}\text{Ar} / ^{38}\text{Ar} \) ratios range from 293 to 1072. The isotopic compositions of He and Ar indicate that the ore-forming fluids were mantle-derived, modified by air-saturated crustal fluids. Shallow-level boiling increased \( ^{3}\text{He} \) concentrations, whereas crustal contamination decreased \( ^{3}\text{He} / ^{4}\text{He} \) ratios in the magmatic fluids. The occurrence of mantle-derived components in the magmatic fluid indicates that the associated Qianlishan granite is not a typical S-type pluton that formed entirely by crustal melting. We propose that the mineralization was related to mantle upwelling and Mesozoic lithosphere extension of the South China Block.

**Keywords:** He and Ar isotopes; Shizhuyuan W–Sn–Bi–Mo deposit; Qianlishan granite; crust–mantle interaction; Hunan Province, China

Introduction

The Shizhuyuan W–Sn–Bi–Mo deposit, located 15 km SE of Chenzhou City, Hunan Province, China, is one of the largest polymetallic ore deposits in the world. It contains 800,000 tons of tungsten, 500,000 tons of tin, 200,000 tons of bismuth, 100,000 tons of molybdenum, and abundant fluorine (Mao et al. 1998). Many researchers have studied the geology (Wang et al. 1987; Mao et al. 1998), petrogenesis and mineralization (Mao et al. 1994; Liu et al. 1995; Mao et al. 1996; Zhao et al. 2001), geochronology (Li et al. 1996, 2004), and geochemistry (Zhang 1989; Xu et al. 2002). However, the origin of the ore-forming fluids is still debated.

He and Ar isotopes are sensitive tracers of volatiles derived from the crust versus the mantle (Ballentine and Burnard 2002a). Simmons et al. (1987) successfully used these isotopes to study the origin of hydrothermal fluids in the Casapalca and Pasto Bueno polymetallic deposits, Peru, about three decades ago. Subsequently, numerous similar studies

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were published (Stuart et al. 1995; Hu et al. 1998; Burnard et al. 1999; Ballentine et al. 2002; Kendrick et al. 2002; Burnard and Polya 2004; Hu et al. 2004; Li et al. 2006; Sun et al. 2006). This article presents He and Ar isotopic compositions of volatiles in hydrothermal minerals in the Shizhuyuan W–Sn–Bi–Mo deposit. We use these data to evaluate the origin of the ore-forming fluids.

Geological background

The Shizhuyuan deposit occurs along the northern edge of Dongpo-Yuemei synclinorium, in the South China fold belt of the South China Block. About 30 km NW from the deposit is the prominent Chaling-Linwu deep fault (Figure 1). The deposit covers an area of 1200 × 600 m², with a thickness of 200–300 m. The styles of mineralization (Figure 2) include veinlet Sn–Be ore in marbles (type I), massive W–Sn–Bi–Mo ore in skarn (type II), W–Sn–Bi–Mo–F ore in greisen-stockwork-skarn (type III), and massive W–Sn–Mo–Bi ore in greisen (type IV) (Wang et al. 1987; Lu et al. 2003). Numerous faults with different strikes transect the area. The NE and NW faults host the stockwork mineralization in the Shizhuyuan mine. The most intense mineralization occurs in deformed skarns and marbles intersected by the major faults.

The sedimentary strata in the ore field include Sinian–Cambrian metasandstone, Middle and Upper Devonian clastic and carbonate rocks, Lower Carboniferous sedimentary rocks, Jurassic and Cretaceous sedimentary rocks. The Middle Devonian was subdivided into the Tiaomajian and Qiziqiao groups, and the Upper Devonian was subdivided into Xikuangshan and Shetianqiao groups. The Devonian Shetianqiao and Qiziqiao groups are most important country rocks (Figure 2). Extensive hydrothermal activity resulted in intensive wall-rock alterations such as skarnization, greisenization, K-feldsparization, albitization, fluoritization, siliconization, and marmarization.

The Shizhuyuan polymetallic deposit occurs in the contact zone between the Qianlishan granite and the Devonian limestone. The Yanshanian Qianlishan granite pluton (∼10 km²) is composed of three intrusive phases: pseudoporphyritic biotite granite, equigranular biotite granite, and granite porphyry (Mao and Li 1995). Strong alteration of skarn and greisen that formed in the contact zone between the first and second phases of granite intrusions and Devonian limestone is responsible for the polymetallic mineralization. The igneous rocks have zircon SHRIMP U–Pb ages of 152 ± 2 million years (Li et al. 2004). The age of mineralization varies from 151 ± 3.5 (Re–Os isochron; Li et al. 1996), 149 ± 2 (Sm–Nd isochron; Li et al. 2004) to 148.2 ± 1.1 million years (mica ⁴⁰Ar–³⁶Ar; Peng et al. 2006), similar to the age of the Qianlishan granite. For decades, the Qianlishan granite has been regarded as the product of crustal remelting and thus classified as of S-type (Xu et al. 1984; Wang et al. 1987; Zhang 1989). However, the occurrence of abundant mafic microgranular enclaves (MME) in the granite (Ma et al. 2005) and the low initial ⁸⁷Sr/⁸⁶Sr ratios of the pluton (0.703–0.729) suggest mixing between crust- and mantle-derived materials (Zhao et al. 2001).

Fluid inclusions in quartz associated with mineralization are dominantly small (5–20 μm in diameter; Figure 3), with low to high salinity (1.2–32.0 wt.% NaCl eq.) and homogenization temperatures of 156–450°C. Fluid inclusion data suggest that at least two types of fluids were associated with mineralization: one with high salinity and a high homogenization temperature, and the other with low salinity and a low homogenization temperature. The occurrence of coexisting saline fluid and vapour inclusions suggests boiling during mineralization (Figure 3).
Figure 1. Regional geologic map of southern Hunan Province, China (after Lu et al. 2003).

**Sampling and experimental methods**

All pyrite samples used in this study were collected from the underground mining cuts at the levels of 358, 490, 536, and 620 m in the Shizhuyuan mine. They are from three types of ore: W–Bi–Mo–Sn massive skarn ore (type II), W–Sn–Mo–Bi–F stockwork ore (type III), and W–Sn–Mo–Bi massive greisen (type IV). In these samples, pyrite occurs as vein or mesh-vein structure, massive aggregates, and disseminated assemblages (Figure 4). All pyrite crystals selected for this study are not deformed, with grain sizes varying from 0.1 to 5 mm in diameter.

The samples were first crushed and then hand-picked under a binocular microscope. He and Ar isotopic compositions of volatiles released from the samples were measured with a VG 5400 inert gas mass spectrometer at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The mass spectrometer was regularly calibrated against $1.32 \times 10^{-7}$ cm$^3$ STP Ar with air $^{40}$Ar/$^{36}$Ar, and $5.6 \times 10^{-7}$ cm$^3$ STP He with $^{3}$He/$^{4}$He = $1.4 \times 10^{-6}$. The volatile extraction and analytical procedures are similar to those of Stuart et al. (1994a). The pyrite samples were
ultrasonically cleaned with acetone for 20 min before loading into the online in vacuo crushing devices. Approximately 0.5–1 g of sample was loaded into a screw-type crusher. The samples were heated at 120–150°C in vacuum for 24 h to remove adhered atmospheric contaminants. The samples were then crushed to release volatiles from fluid inclusions in pyrite. The released gases were purified to remove reactive gas species. Ar and Xe were kept in a cold trap whereas He and Ne were released to the online analytical system. Ar was released at −78°C for isotope determination.

Results
The noble gas compositions of volatiles released from pyrite crystals from the Shizhuyuan deposit are listed in Table 1 and Figure 5. The concentrations of 40Ar range from 0.21 to 2.38 × 10^{-6} cm^3 STP 40Ar/g, and 4He concentrations are 0.8–65.1 × 10^{-6} cm^3 STP 4He/g. The large variations in the noble gas isotopic concentrations may reflect variable fluid inclusion abundance in the sample. The 3He/4He ratios vary from 0.06 to 1.66 Ra (Ra represents the 3He/4He ratio of air, 1.39 × 10^{-6}). The 40Ar/36Ar ratios vary between 293 and 1072.
Discussion

Pyrite is known to be a suitable trap for noble gases (Stuart et al. 1994b; Baptiste and Fouquet 1996; Hu et al. 1998; Burnard et al. 1999). Inclusion-trapped He and Ar are unlikely to be extensively lost within 100 million years (Burnard et al. 1999). Even though the trapped He and Ar are partially lost, the ratios of \(^{3}\text{He}/^{4}\text{He}\) and \(^{40}\text{Ar}/^{36}\text{Ar}\) can still remain unchanged (Baptiste and Fouquet 1996; Hu et al. 1997; Ballentine and Burnard 2002b; Hu et al. 2004). Because the pyrite samples used in this study are from underground workings, cosmogenic \(^{3}\text{He}\) can be ruled out (Simmons et al. 1987; Stuart et al. 1995). The measured He is not the product of nuclear decay of lithium because pyrite is not a Li-bearing mineral (Ballentine and Burnard 2002b). The in situ produced \(^{40}\text{Ar}\) from mineral lattice and fluid inclusions are thought to be negligible due to low diffusivity of Ar in pyrite (York et al. 1982; Smith et al. 2001) and the extremely low K concentration in pyrite (York et al. 1982). The amount of radiogenic \(^{4}\text{He}\) produced from the decay of U and Th is within the analytical errors. In addition, the fluid inclusions in quartz and fluorite coexisting with pyrite are all primary (Figure 3). Therefore, the measured values of He and Ar abundances and isotopic compositions of the pyrite samples likely represent the characteristics of primary fluid inclusions of ore-forming fluids of the deposit.

Hydrothermal fluids contain noble gases from three ultimate sources (Burnard et al. 1999; Ballentine et al. 2002): (1) air-saturated (i.e. meteoric) water; (2) mantle-derived fluids; and (3) He and Ar produced in the crust. Air-saturated water has He and Ar isotopic
compositions of $^{3}\text{He}/^{4}\text{He} = 1.39 \times 10^{-6}$ (1 Ra), and $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$, similar to the atmosphere values, because air-saturated water is isotopically in equilibrium with the atmosphere. The upper oceanic mantle has $^{3}\text{He}/^{4}\text{He}$ ratio of $1-1.3 \times 10^{-5}$ (7-9 Ra), and the subcontinental lithospheric mantle (SCLM) has $^{3}\text{He}/^{4}\text{He}$ ratio of $0.8-1 \times 10^{-5}$ (6-7 Ra) (Porcelli et al. 1992; Patterson et al. 1994; Dunai and Baur 1995; Reid and Graham 1996; Gautheron and Moreira 2002). Mantle-derived Ar has $^{40}\text{Ar}/^{36}\text{Ar}$ ratios > 40,000. Crustal lithophile elements can produce abundant radiogenic and nucleogenic Ar and He. As a result, fluids reacted with crustal rocks will eventually have He and Ar isotopic compositions similar to that of the crust that has $^{40}\text{Ar}/^{36}\text{Ar}$ ratios $\geq 1000$ (Drescher et al. 1998) and $^{3}\text{He}/^{4}\text{He}$ ratios of 0.01-0.05 Ra (Tolstikhin 1978; Stuart et al. 1995).

The proportion of atmospheric He can be calculated using the $F^{4}\text{He}$ values, which are defined as the $^{4}\text{He}/^{36}\text{Ar}$ ratio of the sample relative to the atmospheric $^{4}\text{He}/^{36}\text{Ar}$ value of 0.1655. A sample containing 100% atmospheric He will have an $F$ value of unity. The $F^{4}\text{He}$ values for all the samples studied by us are much greater than 1 (Table 1), indicating that the volatiles released from pyrite contain negligible atmospheric He. Mantle-derived He and radiogenic He produced in the crust are more important in our samples (Turner et al. 1993). As shown in Figure 3, the $^{3}\text{He}/^{4}\text{He}$ ratios of the volatiles released from pyrite crystals of the Shizhuyuan deposit are similar to or higher than the crust values but lower than the subcontinental mantle values, indicating that the volatiles are dominated significantly by crustal-derived fluid with minor mantle-derived fluid. The correlation between He and Ar isotopic compositions (Figures 6 and 7) indicates mixing between two fluids, one with

![Figure 4. Photographs of the Shizhuyuan pyrite samples. (A) Pyrite occurs as a small veinlet in massive skarn. (B) Massive pyrite in greisen. (C) Cubic pyrite associated with colourless fluorite and bismuthinite. (D) Disseminated pyrite and bismuthinite associated with violet fluorite.](image-url)
Table 1. He and Ar isotopic compositions of volatiles released from pyrite in the Shizhuyuan deposit.

<table>
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<th>Sample</th>
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<th>Mineralization type</th>
<th>Sample description</th>
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<th>$^4\text{He}^b$ (cm$^3$STP)</th>
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Notes: a) Sample weights are the fraction of crushed pyrite that passes through a 100-μm diameter sieve. b) Uncertainties in noble gas concentrations are ≈5%; quoted errors of isotope ratios are for 1σ. c) $^{40}\text{Ar}^*$ refers to the excess Ar. d) Not analysed.

Figure 5. Helium isotopes of volatiles released from pyrite in the Shizhuyuan W–Sn–Bi–Mo deposit. (A), (B), and (C) are from Mamyin and Tolstikhin (1984).

high $^{3}\text{He}/^{4}\text{He}$, high $^{40}\text{Ar}/^{36}\text{Ar}$ and the other with low $^{3}\text{He}/^{4}\text{He}$ and near-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$. This is consistent with the presence of two types of fluid inclusions in quartz in the deposit. One type of fluid inclusions has salinity from 26 to 41 wt.% NaCl eq., and the other has salinity from 1 to 21 wt.% NaCl eq. (Lu et al. 2003). The high $^{3}\text{He}/^{4}\text{He}$, high $^{40}\text{Ar}/^{36}\text{Ar}$ fluid was most likely derived from a magmatic source whereas the low $^{3}\text{He}/^{4}\text{He}$, near-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ fluid was undoubtedly surface-derived or ‘modified air-saturated water’ (MASW).
Figure 6. Plot of $^{40}\text{Ar} / ^{36}\text{Ar}$ versus $^3\text{He} / ^4\text{He}$ except the sample SZY-107, a remarkable mixing line exists for two fluids.

Figure 7. Plots of $^3\text{He} / ^{36}\text{Ar}$ versus $^4\text{He} / ^{36}\text{Ar}$ (top) and $^3\text{He} / ^{36}\text{Ar}$ versus $^{40}\text{Ar} / ^{36}\text{Ar}$ (bottom). Least-square fitting to the data gives the equations: $^4\text{He} / ^{36}\text{Ar} = (8.21 \times 10^5) \cdot ^3\text{He} / ^{36}\text{Ar} + 1311$, $r^2 = 0.72$; $^{40}\text{Ar} / ^{36}\text{Ar} = (3.09 \times 10^4) \cdot ^3\text{He} / ^{36}\text{Ar} + 330.87$, $r^2 = 0.88$.

Modified air-saturated water

The crustal component in the volatiles released from pyrite crystals probably contains radiogenic $^4\text{He}$ and (to a lesser extent) radiogenic $^{40}\text{Ar}$. In contrast, the $^3\text{He} / ^{36}\text{Ar}$ of the MASW is unlikely to be changed because both $^3\text{He}$ and $^{36}\text{Ar}$ are not radiogenic. Therefore, it is possible to estimate the $^{40}\text{Ar} / ^{36}\text{Ar}$ for the MASW endmember by extrapolating the trends in Figure 7 to the $^3\text{He} / ^{36}\text{Ar}$ value of PASW (pure air-saturated water, $5 \times 10^5$; Hu
et al. 2004). The estimated \(^{40}\text{Ar}/^{36}\text{Ar}\) for the MASW endmember is 331, which is close to the Ar isotopic composition of PASW \((^{40}\text{Ar}/^{36}\text{Ar} \approx 295.5\), Turner et al. 1993; Stuart et al. 1995; Burnard et al. 1999\) plus minor radiogenic \(^{40}\text{Ar}\) derived either from crustal rocks (Stuart et al. 1995) or from \(^{40}\text{Ar}\) produced by in situ decay of \(^{40}\text{K}\). Similarly, the \(^{3}\text{He}/^{4}\text{He}\) for the MASW endmember is estimated to be 0.08 Ra by extrapolating the trends in Figure 8 to \(^{40}\text{Ar}^{*}/^{4}\text{He}\) value of 0. This value is much lower than the value of PASW \((^{3}\text{He}/^{4}\text{He} = 1\) Ra\), but close to the crustal value, indicating the presence of radiogenic \(^{4}\text{He}\) derived from crustal rocks or from \(^{4}\text{He}\) produced by in situ decay of U and Th.

A \(^{40}\text{Ar}^{*}/^{4}\text{He}\) ratio of 0.1 is obtained from the correlation (albeit poor) between \(^{3}\text{He}/^{4}\text{He}\) and \(^{40}\text{Ar}^{*}/^{4}\text{He}\) (Figure 8), similar to but slightly lower than the estimated value for the crust \((\approx 0.2)\) (Torgersen et al. 1989; Ballentine and Burnard 2002b). The low \(^{40}\text{Ar}^{*}/^{4}\text{He}\) ratios of MASW are attributed to preferential acquisition of \(^{4}\text{He}\) over \(^{40}\text{Ar}\) from aquifer rocks (Torgersen et al. 1989), due to the higher closure temperature of \(^{40}\text{Ar}\) relative to \(^{4}\text{He}\) (Torgersen et al. 1989; Ballentine and Burnard 2002b). \(^{40}\text{Ar}\) is quantitatively retained in most minerals at 250°C, whereas the closure temperature of \(^{4}\text{He}\) is usually less than 200°C (Lippolt and Weigel 1988; McDougall and Harrison 1988; Elliot et al. 1993). The MASW trapped in these samples acquired not only \(^{4}\text{He}\) but also \(^{40}\text{Ar}\) from crustal rocks, implying that it was a relatively high-temperature fluid \(\geq 200^\circ\text{C}\), which is consistent with the homogenization temperatures \(156-450^\circ\text{C}\) of fluid inclusions in coexisting quartz.

The proportion of \(^{40}\text{Ar}^{*}\) can be estimated by the measured \(^{40}\text{Ar}/^{36}\text{Ar}\) values according to the following equation (Kendrick et al. 2001):

\[
^{40}\text{Ar}^{*}\% = \frac{(^{40}\text{Ar}/^{36}\text{Ar})_{\text{sample}} - 295.5}{(^{40}\text{Ar}/^{36}\text{Ar})_{\text{sample}}} \times 100
\]

The estimated concentrations of \(^{40}\text{Ar}^{*}\) range from 0.2 to 72.4%, and the proportion of air-derived \(^{40}\text{Ar}\) is as high as 27.6–99.8% (72.6% average).

Figure 8. Plot of \(^{40}\text{Ar}^{*}/^{4}\text{He}\) versus \(\text{R}/\text{Ra}\). Least square fitting to the data gives the equation: \(^{3}\text{He}/^{4}\text{He} = 8.7856 \times ^{40}\text{Ar}^{*}/^{4}\text{He} + 0.0805, r^2 = 0.37\).
Magmatic fluid
High $^{40}$Ar/$^{36}$Ar ratios and high $^3$He values are unique for the mantle (Stuart et al. 1995). Therefore, the inferred endmember with high $^{40}$Ar/$^{36}$Ar and high $^3$He (Figure 6) is most likely mantle derived. Using a value of 6 Ra to represent the mantle He, and 0.03 Ra for crustal fluid, the proportion of mantle He is estimated to be between 0.6 and 27.3% (mainly in the range of 1–10%), indicating a small quantity of mantle-derived fluid in our samples.

The concentrations of $^3$He in our samples are extremely high ($0.4–6.8 \times 10^{-12}$ cm$^3$ STP g$^{-1}$), higher than in basaltic phenocrysts and most xenoliths in basalts, but lower than in some basaltic glasses (Burnard and Polya 2004). The concentration of $^3$He in the fluid ($[^3\text{He}]_{\text{fluid}}$) may be estimated by assuming that the measured $^{36}$Ar is entirely derived from air-saturated water. The $^3$He/$^{36}$Ar ratios of our samples are in the range 0.0001–0.0198, corresponding $[^3\text{He}]_{\text{fluid}}$ from $5.4 \times 10^{-12}$ to $1.5 \times 10^{-8}$ cc STP g$^{-1}$ H$_2$O assuming $[^{36}\text{Ar}]_{\text{fluid}} = 7.65 \times 10^{-7}$ cc STP g$^{-1}$ H$_2$O. The estimated $[^3\text{He}]_{\text{fluid}}$ values are very high, which may have resulted from boiling and selective sampling of the vapour phase (Ballentine et al. 2002). The characteristics of fluid inclusions in coexisting quartz suggest that boiling may have indeed occurred during mineralization.

The $^3$He/$^4$He ratio of mantle-derived fluid is estimated to be 2.28 Ra by extrapolating the trend in Figure 8 to the $^{40}$Ar$^\ast$/$^4$He ratio of 0.25. The estimated value is much lower than that of the subcontinental lithospheric mantle. This probably resulted from crustal anatexis due to underplating of mantle-derived magma or addition of radiogenic $^4$He produced by decay of U and Th. However, assuming U $2.7 \times 10^{-6}$ (which is possibly much higher than the true value), Th/U = 0 (Th solubility in hydrothermal fluid is extremely low), and age of 160 million years, the amount of radiogenic $^4$He ingrowth is within the analytical uncertainty. Therefore, the low $^3$He/$^4$He ratio in the mantle-derived fluid endmember most probably resulted from mixing between mantle-derived magma and melts produced by crustal anatexis.

Genetic implications
The ore-forming fluids of the Shizhuyuan deposit are thought to be mainly derived from the Qianlishan granitic magma (Zhang 1989; Xu et al. 2002). Our He and Ar isotopes show that mantle-derived fluid is present in the volatiles trapped in pyrite in the contact zone of the granite, suggesting mantle-derived materials were involved in the formation of the Qianlishan granite pluton. This is consistent with Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr} = 0.703–0.729$, Mao et al. 1995) of the Qianlishan granite pluton. In addition, the studies of MME in the Middle–Late Jurassic granite in the middle segment of the Nanling Mountains also show that the Qianlishan granite is formed by crust–mantle interaction (Ma et al. 2005). Therefore, we do not believe that the Qianlishan granite is typical S-type.

The origin of the Qianlishan granite pluton and the Shizhuyuan deposit is most likely related to mantle upwelling and lithospheric extension in South China during the Mesozoic. Mantle-derived magma ascended to mid-lower crust, providing heating and inducing crustal anatexis. Mixing between them formed hybrid magma. Such hybrid magma continued to ascend to shallow crust at levels and continued to provide heating. The emplacement of the hybrid magma triggered large-scale fluid convection in the region, producing mineralization along the contact zones as well as in the nearly fault systems. Similar condition was made previously by Li et al. (2006) who studied the Furong Sn ore deposit in the region.
Conclusions
(1) $^{3}$He/$^{4}$He and $^{40}$Ar/$^{36}$Ar ratios of volatiles released from pyrite in the Shizhuyuan W–Sn–Bi–Mo polymetallic deposit range from 0.06 to 1.66 Ra and from 293 to 1072, respectively. The measured He and Ar isotopic compositions of the fluid inclusion samples are considered to represent the primary ore-forming fluids.

(2) We infer that the ore-forming fluids in the Shizhuyuan deposit formed by mixing of high $^{3}$He/$^{4}$He and high $^{40}$Ar/$^{36}$Ar magmatic fluid, and low $^{3}$He/$^{4}$He and low $^{40}$Ar/$^{36}$Ar meteoric water. The meteoric water experienced an intensive interaction with crustal rocks, gaining crustal He and near-atmospheric Ar isotopic signatures. The magmatic fluid was contaminated by MASW with crustal $^{3}$He/$^{4}$He and near-atmospheric $^{40}$Ar/$^{36}$Ar. The magmatic fluid was derived from the Qianlishan granite pluton. This igneous body has He and Ar isotopes consistent with mantle derivation as well as a crustal melt. This suggests that the Qianlishan granite is not a typical S-type pluton. We conclude that the pluton and the associated Shizhuyuan deposit are related to mantle upwelling and lithospheric extension in South China during Mesozoic time.

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References


The genetic association of adakites and Cu–Au ore deposits

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Adakites may form by partial melting of either the subducting oceanic lithosphere or the lower part of the continental crust. These two magma types can be discriminated geochemically using a combination of La/Yb, Sr/Y ratios, MgO and Na\textsubscript{2}O contents, and Sr–Nd isotopes. Given that the basaltic crust has Cu concentrations more than two times higher than the lower continental crust and the mantle wedge, ‘primitive’ adakites produced by oceanic slab melting should contain significantly higher Cu contents than adakites derived from the continental crust, as well as normal arc andesites. A globally compiled dataset shows that Cu concentrations in adakites are generally lower than that in normal arc rocks. We attribute this low copper content to loss of magmatic fluids as a result of sulphate reduction during adakitic magma differentiation, in turn induced by the crystallization of Fe–Ti oxides, essential to mineralization. Therefore, the underflow of oceanic-slab-derived adakites that can release larger amounts of Cu (presumably Au as well) by crystal fractionation leads to higher potential for Cu–Au mineralization along convergent margins, usually associated with ridge subduction. Such basaltic slab melts initially have considerably higher Cu contents and thus play a crucial role particularly in the relatively closed magma system responsible for generating porphyry Cu deposits.

Keywords: adakite; Cu–Au ore deposit; slab melting; subduction

Introduction

A dakite is a rare rock type in the modern arc system. It was originally named to represent magmas with components derived from partial melting of subducted oceanic slab (Defant and Drummond 1990). Later on, it was believed that adakite could also be formed by partial melting of thickened lower crust or fractional crystallization (Defant et al. 2002; Kay and Kay 2002; Chung et al. 2003; Castillo 2006; Wen et al. 2008; Goss and Kay 2009). A close relationship between adakites and epithermal/porphyry ore deposits (Au, Ag, Cu, Mo) was proposed by previous authors (e.g. Thieblemont et al. 1997; Zhang et al. 2001a), who argued that most of the deposits they studied worldwide were closely associated with, and often hosted by, adakites. This notion has been supported by numerous later studies, such as those on porphyry Cu and epithermal Au deposits in the Philippines (Sajona and

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Maury 1998), epithermal Au deposits in Ecuador (Beate et al. 2001), porphyry Cu deposit in Mongolia (Morozumi 2003) and Chile (Kay et al. 1999; Oyarzun et al. 2001, 2002; Kay and MPodozis 2002; Reich et al. 2003), porphyry Cu-Au deposits in China (Hou et al. 2004, 2007b; Wang et al. 2004, 2006a, 2006b, 2007b; Xie et al. 2008, 2009), and Au deposits in Mexico (Gonzalez-Partida et al. 2003; Levresse and Gonzalez-Partida 2003; Levresse et al. 2004). The close association between adakites and porphyry deposits was attributed to high oxygen fugacity induced by adakitic magmas (Mungall 2002). Some researchers even proposed that the occurrence of adakites may be a useful indicator for Cu deposits (Zhang et al. 2004). The proposed connection between adakite and Cu deposits has also been seriously criticized by Rabbia et al. (2002), Richards (2002), and Richards and Kerrich (2007), who argued that the geochemical signatures of adakites can be generated in normal asthenosphere-derived tholeiitic to calc-alkaline arc magmas by common crustal interaction and fractionation processes (Richards 2002; Richards and Kerrich 2007) or by melting of thickened crust (Rabbia et al. 2002), and do not require slab melting. These arguments, however, do not have any constraints on the relationship between adakite and mineralization.

In fact, adakites and Cu (Au) ore deposits are not always bounded together. For example, some adakitic rocks do not have any deposits (Chiaradia et al. 2004; Huang et al. 2008), whereas some rocks without clear adakitic geochemical features are ore-bearing, for example some porphyry Cu and epithermal Au deposits in Ecuador (Chiaradia et al. 2004) and small porphyry Cu deposits in the western Luzon (Imai 2002); in both cases calc-alkaline andesites are the host rocks. Therefore, it has been argued that high oxygen fugacity, rather than adakitic magma composition, is essential to the formation of porphyry Cu deposits (Imai 2002; Bissig et al. 2003).

Adakite is defined by geochemical characteristics (e.g. SiO$_2$ $\geq$ 56 wt.%, Al$_2$O$_3$ $\geq$ 15 wt.%, Y $\leq$ 18 ppm, Yb $\leq$ 1.9 ppm and Sr $\geq$ 400 ppm; Defant and Drummond 1990). Given that the geochemical characteristics of adakite can seemingly be produced by many geological processes with the presence of garnet (low Y) and absence of plagioclase (high Sr and Sr/Y), several other mechanisms have been proposed in addition to the original slab melting model, for example partial melting of either thickened crust (Petford and Atherton 1996; Zhang et al. 2001b), forearc crust carried down by subduction-erosion (Kay and Kay 2002), delaminated lower continental crust (e.g. Xu et al. 2002; Gao et al. 2004), high-pressure fractional crystallization of mineral assemblages with garnet (Castillo 2006; Macpherson et al. 2006), or even pure amphibole of normal arc magmas (Richards and Kerrich 2007); and polybaric fractional crystallization from exceptionally water-rich parent magmas (Rodriguez et al. 2007). Consequently, crustal processes have been proposed to play a key role in the metal enrichments of some porphyry Cu deposits (Richards and Kerrich 2007).

In this article, we used compiled data from the GEOROC dataset to conduct geochemical modelling that enables us to evaluate the above debates with emphasis on the relationship between adakites and Cu (Au) ore deposits.

**Copper in adakites**

**Compiled GEOROC dataset**

The compiled GEOROC dataset for Cu and SiO$_2$ contents of arc volcanic rocks are plotted in Figure 1. Given the fact that high-quality Au data are rare and that Au and Cu behave similarly during magma differentiation for arc volcanic rocks (Sun et al. 2004),
Figure 1. Diagram of Cu versus SiO$_2$ for adakites and normal arc rocks indicating Cu loss in evolved magmas. Data source: GEOROC. The two zones confined by dashed lines are modified after Sun et al. (2004), representing values of eastern Manus basin volcanic glasses for comparison. Cu concentration increases at the early stage of magma fractionation and then drops suddenly as a result of magnetite crystallization, which reduces sulphate, scavenging Cu, Au out of the magmas in the form of hydrosulphide complexes (Sun et al. 2004).

we will focus on Cu in the following discussion. We did not change the classification of the GEOROC dataset, except to exclude data published before 1991, as the term ‘adakite’ was first proposed in 1990 (Defant and Drummond 1990). Some rocks that were classified as adakites by the original authors were excluded from the compiled normal arc andesite dataset.

Compared to normal arc volcanic rocks, adakites have systematically lower Cu concentration (Figure 1). To most people, this phenomenon does not lend any support to a genetic link of Cu (Au) deposits with adakites. It is probably one of the main reasons many geologists do not believe the association between Cu deposits and adakites. Figure 1, however, cannot be used to rule out a possible association. This is because Cu and Au concentrations may drop quickly when magmas evolve to higher SiO$_2$ contents (∼58 wt.%.) because of the oxygen fugacity fluctuation induced by crystallization of Fe–Ti oxides and subsequent sulphate reduction that scavenges Cu, Au into magmatic fluids (Sun et al. 2003a, 2004; Liang et al. 2006, 2009). These Cu-rich fluids/gases released during magma evolution are important for the transportation and mineralization of Cu (Heinrich et al. 1999, 2004; Seedorff et al. 2005).

Although the compiled Cu data for normal arc rocks do not drop abruptly as SiO$_2$ increases, they show a Cu peak at SiO$_2$ of ∼55-60 wt.%. This is likely because the dataset is not representative of samples from a single magma chamber, but a large collection from the convergent margins worldwide. Nevertheless, the Cu peak is consistent with the notion that there is a major change in Cu behaviour during magma differentiation (Sun et al. 2004). For adakites, in contrast, Cu concentrations drop continuously with increasing
SiO₂ contents without any changes in Cu behaviour (Figure 1). This is probably because Fe–Ti oxides may start crystallizing at the very beginning stage of the magma evolution of adakites that have relatively higher SiO₂ (Defant and Drummond 1990) and arguably higher oxygen fugacity (Mungall 2002) than normal arc lavas, and thus may have released more Cu for mineralization.

The speculation is supported by plots of FeO and TiO₂ versus SiO₂ (Figure 2), in which FeO and TiO₂ of normal arc rocks are both peaked at SiO₂ of ~55–60 wt.%, whereas those of adakites decrease continuously. The message of these diagrams (Figures 1 and 2) is that crystallization of Fe–Ti oxides indeed removes Cu dramatically from adakites and also some evolved normal arc rocks, most likely by sulphate reduction as previously proposed (Sun et al. 2004). Therefore, Cu concentrations cannot be used directly as a geochemical parameter to prove or disprove the link between adakites and Cu (Au) deposits. Also, these diagrams tell us that adakites have given away Cu during magmatic processes, most likely to fluids (Sun et al. 2004). Therefore, in the case that adakites originally contain higher Cu concentrations than normal arc rocks, they have a higher potential of causing Cu mineralization. An immediate question, then, is whether ‘primitive’ adakitic magmas have high Cu contents.

**Modelling results**

Copper concentration in ‘primitive’ adakites depends heavily on the source composition and oxygen fugacity. As stated above, there are three types of petrogenetic models proposed.

![Figure 2](image-url)  
Figure 2. Diagrams of FeO and TiO₂ versus SiO₂ for adakites and normal arc rocks. Symbols are the same as Figure 1. FeO, TiO₂ losses are in phase with Cu loss in Figure 1. Data source: GEOROC.
for adakite formation: slab melting, thickened lower continental crust melting, and fractional crystallization. The continental crust and lower continental crust have Cu abundance estimated as low as 26–27 ppm (Rudnick and Gao 2003), much lower than the oceanic crust represented by MORB that contains 60–120 ppm (e.g. 74.4 ppm in average) of Cu (Hofmann 1988; Sun et al. 2003b).

The partition coefficients for Cu vary dramatically as shown by experimental data and natural samples (GERM 2009), possibly because of its chalcophile characteristics. Nevertheless, it is moderately incompatible in natural samples ranging from MORB to arc volcanic rocks, similar to Re (Sun et al. 2003a, 2003b, 2004). Therefore, partial melting of either the lower continental crust or subducted slab would produce magmas with Cu considerably higher than the corresponding sources. The partition coefficients chosen in our modelling are 0.05 for amphibole, 0.5 for plagioclase (Dostal et al. 1983), 0.5 for garnet, 0.2 for plagioclase and 1 for rutile. The partition coefficients for Sr, Y are from Rollinson (1993) for plagioclase and Xiong et al. (2006) for other minerals (Table 1).

In a Sr/Y versus Cu diagram (Figure 3), melts modelled for partial melting of MORB have Cu (114–245 ppm, using an average Cu of 74 ppm) levels much higher than that of the lower crust (40–85 ppm, using an abundance of 27 ppm). The modelling results indicate that, while the Cu-enriched slab melts are likely to be closely associated with Cu ore formation, melts of the lower continental crust that show significantly lower Cu contents may have no connection to Cu mineralization at all. This explains the positive correlation between tonnages of Cu ores and the mantle components identified in large Chinese porphyry deposits (Hou et al. 2007a), because mantle components identified by

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Note: Mineral compositions are A: amphibole 55%, garnet 4.3%, clinopyroxene 30%, plagioclase 10%, rutile 0.7%; B: amphibole 40%, garnet 19.3%, clinopyroxene 35%, plagioclase 5%, rutile 0.7%; C: amphibole 10%, garnet 39.3%, clinopyroxene 50%, plagioclase 0%, rutile 0.7%; D: amphibole 0%, garnet 39.3%, clinopyroxene 60%, plagioclase 0%, rutile 0.7%. The compositions of lower crust were from Rudnick and Gao (2003), whereas those of M ORB are from Hofmann (1988) for Cu and the average values of Sun et al. (2008) for other elements.
isotopic composition are likely related to slab melts, which usually have isotopic compositions identical to mantle rocks (e.g. Sun and McDonough 1989; Hacker 1991). From this point of view, the association of adakitic rocks with Cu ore deposits might be indicative of a magma origin by slab melting.

**Discussion**

**Slab melting versus lower continental crust melting**

A adakite was originally defined as rocks with slab melts (Defant and Drummond 1990). The geochemical characteristics of adakites, however, can be created through three ways: slab melting, melting of thickened crust, and fractional crystallization (Defant et al. 2002; Kay and Kay 2002). Both melting of thickened crust and fractional crystallization have been proposed as key factors that control Cu mineralization (Bissig et al. 2003; Hollings et al. 2005). Our modelling results, however, show that adakites formed by slab melting tend to have higher initial Cu concentrations that could facilitate Cu mineralization. On the other hand, those formed by partial melting of the lower continental crust have considerably lower Cu, and thus poor opportunities in ore formation because of the lower Cu in the source and lower oxygen fugacity. Therefore, in terms of Cu deposit exploration, it is important to distinguish slab melts from lower crust melts using certain petrogenetic indicators.

Isotope is arguably the most powerful discrimination parameter. In general, slab melting produces magmas with isotope compositions close to MORB values, which are usually similar to that of the depleted mantle whereas partial melting of the lower continental crust usually forms magmas with enriched isotope signatures (Wang et al. 2006a, 2007b; Huang et al. 2008; Wen et al. 2008). Therefore, isotopes are often used to constrain the sources of adakites (e.g. Dreher et al. 2005; Mapherson et al. 2006; Wang et al. 2007a). However, the isotope ratios of adakites may be modified by magmatic processes, for example crust
contamination (Davidson and Desilva 1995; Mori et al. 2007; Ling et al. 2009) and sediment contributions (Kay et al. 1978; Sajona et al. 2000). Therefore, it could be problematic to rely solely on isotopic constraints.

La/Y, Sr/Y, ratios are another useful parameter. The lower continental crust is more enriched in La, Sr and depleted in Y, Yb than average MORB (Hofmann 1988; Sun and McDonough 1989; Rudnick and Gao 2003); thus, lower continental crust melts should contain higher La/Yb, Sr/Y at given Y, Yb than slab melts. The La/Yb, Sr/Y ratios of adakites, however, are highly varied (Defant and Drummond 1990), depending heavily on the partial melting conditions. In the case that the lower continental crust was melted in the presence of plagioclase and/or absence of garnet, the resultant magmas may have Sr/Y ratios comparable to slab melts. Therefore, Sr/Y values are not always conclusive, either. La/Yb is less affected by plagioclase, such that lower continental crust melts may have distinctively higher La/Yb than slab melts.

MgO and Mg# may also be different in slab and lower continental crust melts. In general, melts from a subducting slab would interact with the overlying mantle wedge during magma ascent and thus gain considerable amounts of MgO that raise Mg# numbers (Kilian and Stern 2002; Xiong et al. 2006; Gomez-Tuena et al. 2008). In contrast, lower continental crust melts presumably stay mainly in the crust and have lower MgO. These scenarios, however, are not always right, either. For example, flat subduction may squeeze or erase the mantle wedge, forming low-Mg adakites by slab melting. In addition, when the lower continental crust is melted through the addition of upwelling mantle materials, for example asthenosphere or mantle plume, the MgO contents can be elevated.

Na2O of adakites produced by slab melting are systematically lower than that of experimental results, a feature that has also been attributed to mantle interaction of slab melts (Xiong et al. 2001). In contrast, melts from the lower continental crust have higher Na2O (Xiong et al. 2001). The systematically lower Na2O contents in slab melts compared to lower continental crust melts may also be ascribed to the presence of omphacite in the slab melting residue, as omphacite is a Na-clinopyroxene that could hold back a large portion of Na. Nevertheless, Na2O contents of adakites may be significantly changed during magma differentiation, such that using only this constraint would not be conclusive either.

Consequently, there seems to be no easy solution for discriminating oceanic slab melts from lower continental crust melts. Even so, the more the above criteria match, the better one may constrain the source and origin of adakites. It is also worth mentioning that slab melts may well be contaminated by the lower continental crust through assimilation, especially in places where thick crust exists (Ling et al. 2009). Moreover, there is nearly no magma that can be well preserved from fractional crystallization and assimilation, both of which can dramatically change the composition of the magma. Many adakitic magmas can easily change to no-adakitic characteristics after plagioclase crystallization. In this case, the association of adakites with or without Cu (Au) deposits may provide an additional constraint on the tectonic setting and/or petrogenesis.

Tectonic settings are probably more important than geochemical characteristics for identifying slab melts. Ridge subduction and flat subduction are the most favourable tectonic settings for slab melting. In fact, most of the large porphyry Cu deposits in Chile and Peru are spatially associated with ridge subduction (Cooke et al. 2005; Sun et al. 2010). This strongly supports our model because ridge subduction is the most favourable process for the formation of adakite.
Ore formation related to normal arc rocks

To confirm the close association between slab-derived adakites and Cu (Au) ore deposits, we take a look at normal arc rocks in terms of Cu concentrations. Copper is a moderately incompatible element in the presence of sulphur (Sun et al. 2003a, 2004). The mantle wedge is fairly depleted in incompatible elements, so its Cu abundance is mainly controlled by the addition of Cu from the subducting slab. It has been suggested that aqueous fluids liberated by the subducting slab at the blueschist to eclogite facies transition are dilute, containing only moderate amounts of large-ion lithophile elements, Sr, and Pb and do not transport significant amounts of key elements (Hermann et al. 2006). If this is true for Cu, the mantle wedge should have Cu lower than the primitive mantle (30 ppm) (McDonough and Sun 1995), and therefore normal arc magmas should contain Cu much lower than slab melts.

In Figure 1, normal arc rocks from the compiled data of GEOROC appear to have fairly high Cu concentration. Many of these arc rocks, however, have high enough Sr/Y ratios that they can safely be classified as adakitic rocks; in particular, those samples with Cu >150 ppm are actually adakites as constrained by their very high Sr/Y ratios (Figure 3). Moreover, nearly all the arc rocks, including those that are actually adakites, experienced different degrees of plagioclase crystallization; therefore, some of the arc rocks that have high Cu concentrations (Figures 1 and 3) might be originally of adakitic compositions. On the other hand, it has been proposed that an adakite-type slab melt component may be present in the magmatic source throughout the arc system (Yogodzinski and Kelemen 1998). In that case, slab-released fluids cannot transport much Cu, so the proportion of the slab melt component may determine the Cu concentration in arc magmas.

As shown in Figures 1 and 3, normal arc rocks also lose significant amounts of Cu during magma differentiation, and thus likely contributed to Cu mineralization at the convergent margins, in particular for ore formation in epithermal deposit systems. Precipitation of metals depends on many factors, including temperature, acidity, and iron and sulphide availability (Seedorff et al. 2005; Liang et al. 2009). For a closed magma system (e.g. porphyry), instead specific processes are required to elevate the Cu concentration from 4000 ppm. It is much easier to accomplish this elevation by slab melts that originally contain higher Cu. This, if true, provides a plausible explanation for the observed association between Cu (Au) deposits and slab-derived adakites (e.g. Thieblemont et al. 1997; Sajona and Maury 1998; Wang et al. 2006a, 2006b).

Conclusions

Primitive adakites derived by partial melting of oceanic lithosphere should have systematically higher Cu contents than those from the lower parts of thickened continental crust because Cu concentrations in the former are much higher than those in the latter. The incompatible characteristics of Cu suggests that concentration of this element in the mantle wedge is also likely to be lower than that in the oceanic crust, unless subduction-released fluids have a very high capacity of transporting Cu to the mantle wedge.

Both adakites and normal arc rocks evidently release Cu and presumably also Au during magma differentiation, so they both may contribute to ore mineralization, especially epithermal deposits. The higher Cu abundance in primitive adakites formed by oceanic slab melting implies that more Cu can be released from such magmas, which are thus favourable for ore mineralization, supporting the close relationship of slab-derived adakites with Cu ± Au ore deposits. For a closed magma system, adakites generated from melting of the oceanic lithosphere have a better chance at mineralization because of their higher Cu concentrations.
Adakites from the lower continental crust apparently possess lower initial Cu contents, thus offering fewer prospects for extensive mineralization. This type of adakite may be discriminated from basaltic slab melts using a combination of Sr/Y and La/Yb ratios, MgO and Na2O contents, and Sr–Nd isotopes. For magmas consisting of both slab and lower continental crust components, the level of Cu mineralization may provide an additional constraint on their origin. These are supported by the close association of ridge subduction with large Cu deposits, reflecting the most favourable tectonic setting for slab melting.

Acknowledgements
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References


Mesozoic large magmatic events and mineralization in SE China: oblique subduction of the Pacific plate

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SE China is well known for its Mesozoic large-scale granitoid plutons and ore deposits. In SE China, igneous rocks with intrusion ages between 180 and 125 Ma generally become progressively younger towards the NE. More specifically, 180–160 Ma igneous rocks are distributed throughout a broad area, with mineralization ranging from Cu–Au and Pb–Zn–Ag to W–Sn; 160–150 Ma plutons are present mainly in the Nanling region and are associated with the large-scale W–Sn mineralization; younger igneous rocks occur in the NE area that has many fewer deposits. These can be plausibly interpreted as reflecting a southwestward subduction followed by a northeastward rollback of a subducted oceanic slab, in rough agreement with contemporaneous drift of the Pacific plate. Consistent with this scenario, SE China contains three Jurassic metallogenic belts distributed systematically from NE to SW: (1) a Cu–(Au) metallogenic belt in the NE corner of the South China Block, represented by the Dexing porphyry Cu deposits; (2) a Pb–Zn–Ag metallogenic belt in the middle, represented by the Lengshuikeng Ag and Shuikoushan Pb–Zn deposits; and (3) the famous Nanling W–Sn metallogenic belt in the SW. The distribution of these metallogenic belts is analogous to those in South America where Fe deposits are distributed close to the subduction zone, followed by porphyry Cu–Au deposits and Pb–Zn–Ag deposits in a medial zone, and Sn–W deposits distant from the trench. Inasmuch as quite a few late Mesozoic Fe deposits occur in the Lower Yangtze River Belt to the NE of the Cu–Au deposits in SE China, the distribution of late Mesozoic deposit belts in SE China is identical to that in South America. Therefore, southwestward subduction of the Pacific plate and the corresponding slab rollback are proposed here to explain the distributions of the late Mesozoic (180–125 Ma) magmatism and the associated metallogenic belts in SE China.

Keywords: SE China; late Mesozoic ore deposits; magmatism; metallogenic belt; Pacific plate subduction; slab rollback

Introduction

SE China is well known for its large-scale Mesozoic magmatism and mineralization, with the densest distribution of metal deposits in China (0.1 mine/km²) (Pei et al. 2007). Thus,
this region has been the subject of intensive study since the 1940s (e.g. Hsu 1943; Gilder et al. 1991; Zhou and Li 2000; Zhou et al. 2006; Li and Li 2007; Zhang et al. 2007a; Chen et al. 2008). Several tectonic models have been postulated to explain the Mesozoic evolution of SE China (Hsü et al. 1990; Gilder et al. 1991; Li 2000; Zhou and Li 2000; Wang et al. 2003; Zhou et al. 2006; Li and Li 2007; Chen et al. 2008; Wong et al. 2009). Most models can be classified into one of two types: an active continental margin related to the northwestward subduction of the Pacific plate in the Mesozoic (Jahn et al. 1990; Zhou and Li 2000; Zhou et al. 2006; Li and Li 2007; Chen et al. 2008); or an intraplate lithospheric event, for example, a result of the closure of an oceanic basin in the SE China interior (Hsü et al. 1990; Li 1998). Other models, such as wrench faulting and/or continental rifting and extension (Gilder et al. 1991; Li 2000; Wang et al. 2003, 2005c), have also been proposed based on the intracontinental lithospheric extension and thinning since the early Mesozoic (Wang et al. 2006). A few papers have even proposed Mesozoic mantle plume activities in South China (Xie et al. 1996; Xie et al. 2001; Deng et al. 2004a).

Recently, scenarios emphasizing the effects on eastern China of Mesozoic Pacific plate subduction have become more prevalent. In these models, Mesozoic magmatic rocks in SE China have been interpreted as products of continental arc/back-arc activities and/or foundering of a subducted oceanic plateau. The most famous models are the low-angle subduction model (Zhou and Li 2000; Zhou et al. 2006) and the flat-slab subduction model (Li and Li 2007).

Based on detailed studies of Mesozoic granitoids and volcanic rocks in SE China, Zhou et al. proposed that SE China experienced two tectonic regimes: continent–continent collision of the Indosinian (257–205 Ma) orogeny, with a broad Tethyan orogenic domain in the early Mesozoic, giving way to a broad extension setting as a result of the Yanshanian (180–70 Ma) orogeny genetically associated with the northwest-to westnorthwestward subduction of the Pacific oceanic lithosphere in the late Mesozoic (Zhou et al. 2006). This low-angle subduction model explains the overall southeastward migration of magmatism. The drifting direction of the Pacific plate, however, changed several times, with a major transition at approximately 125 Ma (Sun et al. 2007a); therefore, late Mesozoic magmas should be separated into two groups, before and after 125 Ma, when discussing the temporal–spatial distribution of these igneous events in SE China.

A northwestward flat-slab subduction model has also been proposed to interpret the distribution of magmatism in SE China (Li and Li 2007). According to this model, the subducting oceanic slab was flattened most likely due to the underflow of an oceanic plateau of about 1000 km diameter, which migrated far into the South China Block, followed by slab foundering. It can feasibly explain the 1300 km-wide igneous lithologic belt and the series of other geological events in SE China (Li and Li 2007). This model, however, also cannot fully account for the temporal–spatial distributions of the magmatism and mineralization between 180 and 125 Ma. Moreover, it cannot feasibly explain the distribution and chemical changes of the different rock types.

Advances in isotopic dating technologies, particularly the application of sensitive high-resolution ion microprobe (SHRIMP), Cameca 1280, and LA-ICP-MS analyses in China, have promoted a dramatic accumulation of high-precision geochronological data for igneous rocks and ore deposits in SE China during the past few years, providing clearer information on Mesozoic magmatism and metallogenic formation in SE China. In this contribution, we synthesize the existing results to show that the late Mesozoic (180–125 Ma)
igneous activity and the associated mineralization can be best explained by southwestward subduction of the Pacific plate and subsequent slab rollback.

**Geological setting**

The South China Block is bounded in the N by the Qinling-Dabie orogenic belt, in the W and SW by the Tibetan and Indochina blocks, and in the NW by the Longmenshan belt (Chen and Wilson 1996; Li et al. 2000; Zhou et al. 2006; Li and Li 2007). It consists of two cratonic blocks: the Yangtze Block and the Cathaysia Block, which are separated by the Jiang–Shao (Jiangshan–Shaoxing) fault zone, which is generally taken as a major Neoproterozoic tectonic suture zone (Li et al. 1997; Chen and Jahn 1998; Li et al. 2002; Zhou et al. 2002) (Figure 1A). Geological, petrological, and geochronological studies have confirmed that the Yangtze and Cathaysia blocks have been a single amalgamated terrane since their Neoproterozoic collision (Li et al. 1997; Chen and Jahn 1998; Li et al. 2002; Zhou et al. 2002). The crust of the Yangtze Block is mainly composed of Proterozoic metamorphic rocks, which include the Banxi–Sibao Group in NW Yangtze Block, the Shuangqiaoshan–Shangxi Group (1400 Ma) in SE Yangtze Block, and the Shuangxiwu Group (∼1000–875 Ma) near the boundary between the Yangtze and Cathaysia blocks (Chen and Jahn 1998). Most of the rocks of the Shuangxiwu Group (SE of the Yangtze Block) were formed in an arc setting in the Neoproterozoic, consisting of metamorphosed arc volcanic rocks (978–875 Ma) and metasediments (Li et al. 2002; Zhou et al. 2002). The formations overlying the Proterozoic metamorphic basement in the Yangtze Block are sedimentary strata of Neoproterozoic (Sinian) to Triassic ages. Consensus is that South China experienced a Triassic compressional event, probably caused by the collision between the Indochina and South China blocks (Zhou and Li 2000; Zhou et al. 2006), between the South China and North China blocks (Li and Rao 1993), a combination of both (Wang et al. 2007), or related to a flat subduction event (Li and Li 2007). Since the Cretaceous, the South China Block has been a stable continental platform characterized by redbed sedimentation (Chen and Jahn 1998; Shu et al. 2009).

SE China refers to the southeastern part of the South China Block, which includes most of the Cathaysia Block and the eastern part of the Yangtze Block. Volcanic and intrusive rocks are widely exposed in SE China, distributing mostly in Zhejiang, Fujian, Jiangxi, Guangdong, and Hunan provinces with a total outcrop area of nearly 240,000 km² (Figure 1B) (Zhou et al. 2006). Four major periods have been identified from the early Palaeozoic to the late Mesozoic: the early Palaeozoic (Caledonian), the late Palaeozoic (Hercynian), the early Mesozoic (Indosinian), and the late Mesozoic (Yanshanian) periods, respectively. Caledonian granites are mainly distributed in Jiangxi and Hunan provinces, whereas Hercynian granites are rare and scattered through the whole region. The Mesozoic magmatism is widely dispersed in SE China, which covers almost 90% of magmatism therein (Zhou et al. 2006).

SE China is rich in mineral resources with a wide diversity of deposit types, that is, porphyry/skarn Cu–(Au), stratabound/skarn Pb–Zn–Ag, greisen/quartz-vein W–Sn, U, Nb-Ta, REE, Sb, and Hg, etc. (Chen et al. 1992; Pei et al. 1999; Jin et al. 2002; Hua et al. 2003; Li et al. 2004b; Jiang et al. 2006b; Peng et al. 2006; Wang et al. 2006; Li and Sasaki 2007; Li et al. 2007a, 2007d; Yao et al. 2007; Yuan et al. 2007; Zaw et al. 2007). Most of these deposits formed in the late Mesozoic related to the Yanshanian (Jurassic to Cretaceous) magmatism, which is generally attributed to the subduction of the
Figure 1. (A) Sketched map of the South China Block. The South China Block is surrounded by the North China Block in the north and the Songpan-Ganzi Block and Indochina Block in the west. It is divided by Jiang-Shao Fault into the Yangtze and Cathaysia blocks. (B) Distribution of the late Mesozoic igneous rocks in SE China (modified after Zhou et al. 2006). Four time interval belts are marked with different colours and become younger from the southwest towards the NE. B-1, 180–160 Ma magmatic belt in SE China including Dexing porphyry. Dexing porphyry is adakitic, related to melting of the subduction oceanic plate. B-2, 160–150 Ma (blue) and 150–140 Ma (red) magmatic belts in SE China. 180–160 Ma magmatic belt is shown as a black dotted line. B-3, 140–125 Ma magmatic belt in SE China. The black dotted line represents the 180–160 Ma belt; the blue dotted line represents the 160–150 Ma belt; and the red dotted line represents the 150–140 Ma belt.

Pacific plate (Zhou et al. 2006; Li and Li 2007; Zaw et al. 2007). Furthermore, Mesozoic-Cenozoic basins were well developed in SE China (Shu et al. 1998; Shu et al. 2004; Deng et al. 2004b); they include more than 100 of different sizes, with a total basinal area of >50,000 km² in SE China (Shu et al. 2007; Shu et al. 2009).

Mesozoic igneous rocks in SE China

Mesozoic igneous rocks are abundant in SE China with increasing density towards the ocean (Table 1). Most of the igneous rocks are granites. Early Mesozoic granites are distributed in Hunan, Guangdong, Hainan, and parts of Jiangxi and Fujian provinces (Zhou et al. 2006).
Table 1. Igneous rock outcropped in SE China in Mesozoic and associated deposits.

<table>
<thead>
<tr>
<th>No.</th>
<th>Locality</th>
<th>Lithology</th>
<th>Igneous classification</th>
<th>Age (Ma)</th>
<th>Error (Ma)</th>
<th>Related Deposits</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tong'an, Guangxi</td>
<td>Syenite</td>
<td>Shoshonitic</td>
<td>163</td>
<td>1</td>
<td>Sn</td>
<td>Ar-Ar hornblende</td>
<td>Li et al. (2004a)</td>
</tr>
<tr>
<td>2</td>
<td>Niumiao, Guangxi</td>
<td>Syenite</td>
<td>Shoshonitic</td>
<td>161</td>
<td>1</td>
<td>Sn</td>
<td>Ar-Ar hornblende</td>
<td>Li et al. (2004a)</td>
</tr>
<tr>
<td>3</td>
<td>Yangmei, Guangxi</td>
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<td>Shoshonitic</td>
<td>162</td>
<td>1</td>
<td>Unknown</td>
<td>Ar-Ar hornblende</td>
<td>Li et al. (2004a)</td>
</tr>
<tr>
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<td>Qinghu, Guangxi-Guangdong border</td>
<td>Syenite</td>
<td>Shoshonitic</td>
<td>156</td>
<td>6</td>
<td>Unknown</td>
<td>LA-ICPMS U-Pb zircon</td>
<td>Li et al. (2001a)</td>
</tr>
<tr>
<td>5</td>
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<td>161</td>
<td>1</td>
<td>Sn</td>
<td>SHRIMP U-Pb zircon</td>
<td>Zhu et al. (2006)</td>
</tr>
<tr>
<td>6</td>
<td>Guposhan, Guangxi</td>
<td>Biotite-granite</td>
<td>I-type</td>
<td>163</td>
<td>4</td>
<td>Sn</td>
<td>SHRIMP U-Pb zircon</td>
<td>Zhu et al. (2006)</td>
</tr>
<tr>
<td>7</td>
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<td>Fractionated I-type</td>
<td>159</td>
<td>2</td>
<td>W, Sn</td>
<td>SHRIMP U-Pb zircon</td>
<td>Li et al. (2007)</td>
</tr>
<tr>
<td>8</td>
<td>Fogang, Guangdong (N23°33′18″, E113°17′30″)</td>
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<td>Fractionated I-type</td>
<td>163</td>
<td>3</td>
<td>W, Sn</td>
<td>SHRIMP U-Pb zircon</td>
<td>Li et al. (2007)</td>
</tr>
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<td>Fogang, Guangdong (N23°42′26″, E113°28′14″)</td>
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<td>Fractionated I-type</td>
<td>165</td>
<td>2</td>
<td>W, Sn</td>
<td>SHRIMP U-Pb zircon</td>
<td>Li et al. (2007)</td>
</tr>
<tr>
<td>10</td>
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<td>5</td>
<td>Unknown</td>
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<td>Li et al. (2001b)</td>
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</tr>
<tr>
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<td>Description</td>
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<td>Sample</td>
<td>Reference</td>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>Biotite-granite</td>
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<td>W, Sn, Cu, Mo, et al.</td>
<td>Li et al. (2004b)</td>
<td></td>
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<td>Xishan, Hunan</td>
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<td>A-type</td>
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<td>Mo</td>
<td>Fu et al. (2004)</td>
<td></td>
<td></td>
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<td>Granodiorite</td>
<td>I-type</td>
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<td>2</td>
<td>Pb, Zn, Ag, et al.</td>
<td>Wang et al. (2002)</td>
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<td>155.5</td>
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<td>Fu et al. (2004)</td>
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<td>Unknown</td>
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<td></td>
<td>156</td>
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<td>Unknown</td>
<td>Fu et al. (2004)</td>
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Table 1. (Continued)

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Note: Although more than 2000 radiometric age data have been accumulated for igneous rocks in SE China since the early 1960s, previously published age data needs to be re-examined largely due to limitations of the early dating techniques and complications caused by multiple magmatic and tectonothermal activities in this region. Ages listed in this table are regarded as good-quality data obtained in reputable laboratories using the new generation of mass spectrometers. Among them, most are U–Pb zircon ages by SHRIMP or single-grained zircon TIMS methods. High precision Ar/Ar and K–Ar ages were obtained from well-established laboratories.
Late Mesozoic granitic rocks are often associated with equivalent silicic volcanic rocks with some basalt (10%). It has been proposed that late Mesozoic igneous rocks are closely related to the subduction of the Pacific plate (Gilder et al. 1991; Zhou and Li 2000; Zhou et al. 2006; Li and Li 2007). According to previous studies, late Mesozoic igneous rocks fall into two main age groups: 180–125 Ma and 125–90 Ma (Zhou et al. 2006), whereas the 125–90 Ma magmatism exhibits an obvious ocean-ward migration towards the SE (Chen and Jahn 1998; Zhou et al. 2006; Wong et al. 2009).

To better understand the formation of late Mesozoic magmatism, we focus on magmatism between 180 and 125 Ma, before the Pacific plate changed its drifting direction (Sun et al. 2007a). The distribution of these magmatism is further classified using refined time intervals of 180–160 Ma, 160–150 Ma, 150–140 Ma, and 140–125 Ma. Four overlapping regions are identified, with the regions becoming progressively younger towards the NE (Figure 1B), similar to that described by Zhou et al. (2006):

1. Early Jurassic (180–160 Ma) igneous rocks are mainly distributed in the Nanling Range (Li et al. 2007b; Wang et al. 2005b and papers therein; Wang et al. 2002; Yao et al. 2005; Zhou et al. 2006; Zhu et al. 2006), with some adakitic porphyries (Wang et al. 2006) in Dexing, Jiangxi Province.

2. Slightly younger (160–150 Ma) igneous rocks outcrop mainly in SE Hunan, SW Jiangxi, and northern Guangdong provinces (Li et al. 2004b, 2007c; Wang et al. 2005b; Zhao et al. 2006), and were probably formed in an intracontinental rift region like those in the Nanling Range.

3. The Late Jurassic to Early Cretaceous (150–140 Ma) igneous rocks mainly outcrop in Jiangxi province with some part of Guangdong and Hunan provinces.

4. The Early Cretaceous (140–125 Ma) igneous rocks are widespread in Jiangxi, Anhui, Fujian, Zhejiang, and Jiangsu provinces, and are mainly volcanic rocks (Zhou and Li 2000; Wang et al. 2003; Jiang et al. 2005) with some intrusive rocks, such as Honggong pluton (128 Ma) and Sucun granite (133 Ma) in Zhejiang, Da’an A-type granite (139 Ma) in Fujian (Wang et al. 2005b). The compositions of the rocks are mainly I-type or S-type granites (Zhou and Li 2000; Wang et al. 2005b; and references therein) with some A-type granites (Zhu et al. 2006; Wong et al. 2009). Moreover, there are huge amounts of intrusive rocks between 140 and 125 Ma along the Lower Yangtze River Belt (Chang et al. 1991; Yang et al. 2007; Xie et al. 2008; Xie et al. 2009; Li et al. 2011), which are likely associated with a ridge subduction and the associated slab window (Ling et al. 2009).

Remarkably, A-type granites of different ages are much more abundant in SE China than previously thought (Wang et al. 2005a,b; Wong et al. 2009). A-type granitic magma is generally taken as an indication of lithospheric extension (Collins et al. 1982; Whalen et al. 1987). A-type granites or alkaline intrusive rocks, for example, Sucun geode-like Kf-granite in Zhejiang (133 Ma) (Wang et al. 2005b), Qianlishan Sn/W-bearing A-type granites in southwestern Hunan (Li et al. 2004b), Pitou granite in Jiangxi (171 Ma) (Chen et al. 2002), Fogang (159–165 Ma) and Nankunshan alkaline granites (158 Ma) in northern Guangdong (Li et al. 2007c) with the occurrence of the early Yanshanian bimodal volcanic rock associations (Ningyuan, 173 Ma) (Li et al. 2004a) in western Hunan, southern Jiangxi (Baimianshan, 172 Ma) (Wang et al. 2003), and eastern Guangxi (Huilongyu, 161–163 Ma) (Li et al. 2004a), suggest that SE China was periodically in an extensional environment from approximately 180 Ma to the Cenozoic.
Major metallogenic belts

SE China is famous for W–Sn deposits, with more than 50% of the world’s total W reserves. There are also a large number of large ore deposits of precious metals (Au and Ag), base metals (Cu, Pb, Zn), and rare metals (Nb, Ta, Y, etc.) in this region (Table 1). Most of the ore deposits are spatially and temporally associated with igneous rocks. Over the last century, many studies have focused on these ore fields, including petrological and mineralogical research on the geological settings of metallogenesis, geological features of the deposits, sources of ore-forming materials, and the signatures of ore-forming fluids. In particular, some large ore deposits, such as the Dexing porphyry Cu deposit in Jiangxi Province, the Shuikoushan Pb–Zn polymetallic deposits in Hunan Province, the Shizhuyuan–Xianghualing–Furong W–Sn polymetallic deposits in South Hunan Province, etc., have been studied by many researchers (Hua et al. 2003; Li et al. 2006, 2007d; Wang et al. 2006; Li and Sasaki 2007; Mao et al. 2007, 2009; Zhang et al. 2007b). Three metallogenic belts are recognized from NE to SW (Figure 2A): (1) Cu–(Au) belt in the NE; (2) Pb–Zn–Ag belt in the middle; and (3) W–Sn belt in the SW.

![Figure 2. (A) Three Mesozoic metallogenic belts are identified in SE China with different colours where the representative deposits are located. From the NE to the SW are the porphyry Cu–(Au) belt distributed mainly in Jiangxi, Anhui Provinces; the centre Pb–Zn–Ag belt located mainly in Hunan, Jiangxi, and north Guangxi Provinces; and the inner W–Sn belt covered mainly in Hunan, Guangxi, and Guangdong provinces. This is consistent with the Pacific plate drifting southwestward during 180–125 Ma. (B) Metallogenic belts distributed in South America, with Fe oxide, porphyry Cu–Au deposits close to the subduction zone, followed by Pb–Zn–Ag deposits and then Sn–W deposits, analogous to SE China. (C) A model explaining the connection between metallogenic belt formation and subduction depth and oxygen fugacity. Green upward lines represent fluids released during subduction. The thickness and length of the lines represent the amount of fluid. Blue bars represent the oxygen fugacity in subduction zone. Thicker and longer bars represent higher oxygen fugacity.](image-url)
(1) The Cu–(Au) metallogenic belt is mainly located in the NE corner of the South China Block. The Dexing porphyry Cu–(Au) deposit in Jiangxi province is one of the largest porphyry Cu deposits in China and contains 150 Mt of ores at 0.43% Cu, 0.02% Mo, 0.16g/t Au, and 1.9g/t Ag, approximately equivalent to 6.45 Mt Cu, 0.25 Mt Mo, 24 t Au, and 285 t Ag (Zhu et al. 1983). It is associated with granodiorite porphyries of Yanshanian age (171 Ma) (Wang et al. 2006) that intruded in slate and phyllite of the Mesoproterozoic Shuangqiaoshan Group. The granodiorite porphyries lie along the intersection of a NW-trending fault and a NE-trending anticlinal axis. It consists of three major porphyries: Tongchang (0.7 km²) in the central part of the region, Fujiawu (0.2 km²) to the SE, and Zhushahong (0.06 km²) in the NW (Zhu et al. 1983; He et al. 1999; Wang et al. 2006).

(2) Pb–Zn–Ag deposits are mainly distributed in Jiangxi, Hunan provinces, and northern Guangdong province, with the Lengshuikeng deposit in Jiangxi (Zuo et al. 2008), Shuiikoushan deposit in south Hunan province (Zhang et al. 2007b), and Fuwang Ag, Songxi Ag (Sb), and Chadong As–Ag–Au deposits in Guangdong province (Zhang et al. 2001; Liang et al. 2005, 2007). The Lengshuikeng Ag deposit, Jiangxi Province, is one of the most important Ag deposits in China. It is a polymetallic deposit with 6000 t Ag, 0.1 Mt Pb, and 0.2 Mt Zn (Bureau of Geology and Mineral Resources of Jiangxi Province 1984). There are two types of mineralization in Lengshuikeng district: the first type mainly occurred in porphyry granites, represented by Yinluling, Yinzhushan, and Baojia deposits; the other type is strata-bounded mineralization, which occurred in the volcanic rock of Upper Jurassic strata, represented by Baokeng, Linkeng, and Yinglin deposits (Yan et al. 2007). The SHRIMP zircon age of porphyry granite is 162 Ma and sericite 40Ar/39Ar age is 162.8 Ma (Zuo 2008). The Shuiikoushan deposit is a polymetallic deposit, with 0.5 Mt of Pb and Zn each, and 1400 t Ag and 28 t Au (Zeng et al. 2000; Zhang et al. 2007b). It contains two major deposits: the Kangjiawan Au–Ag–Pb–Zn and the Shuiikoushan Pb–Zn–Au–Ag deposits. Ore body-host rock contact relationships differ between the Kangjiawan and Shuiikoushan deposits. At Kangjiawan, ore bodies are mainly hosted in the brecciation zones developed in the silicified section of the Permian limestone. In the Shuiikoushan deposit, ore bodies are mainly hosted in the breccia contact zones between the granodiorite intrusive body, the Permian limestone, and shale–marl unit, or in faults situated in the core of an overturned anticline (Zhang et al. 2007b). The mineralization of both deposits is related to Yanshanian magmatic intrusions, and mineralizing fluids are at least partially derived from the associated intrusive bodies. The age of the Shuiikoushan granodioritic intrusions is approximately 163.2 Ma (Mao et al. 2006a).

(3) SE China hosts more than half of the world’s W–Sn reserves, mostly concentrated in southern Hunan and Jiangxi, northern Guangdong, and Guangxi provinces (Chen et al. 1992; Li et al. 1993; Shen et al. 1994; Mao and Li 1995; Yin et al. 2002; Lu et al. 2003; Li et al. 2004b, 2007d; Mao et al. 2004, 2007; Zhao et al. 2005; Peng et al. 2006; Gu et al. 2007; Hua et al. 2007; Yuan et al. 2007; Zaw et al. 2007). The W–Sn deposits are represented by Shizhuyuan W–Sn and Furong Sn polymetallic deposits in southern Hunan, both of which are among the largest and economically important skarn–greisen–vein tungsten–polymetallic deposits in China (Mao and Li 1995; Yin et al. 2002; Lu et al. 2003). The Shizhuyuan W–Sn deposit occurs along the contact between a Late Devonian dolomitic limestone and a Jurassic to Cretaceous granitoid pluton (Lu et al. 2003). This deposit contains
750,000 t WO₃, 490,000 t Sn, 300,000 t Bi, 130,000 t Mo, and 200,000 t Be with combined WO₃ grades ranging from 1 to 5% (Wang et al. 1987; Zhang et al. 1998; Lu et al. 2003). In addition, the deposit is rich in fluorine with a reserve of 76 Mt at 2% fluorite, making it one of the largest fluorite deposits in China (Liu et al. 1995; Lu et al. 2003). The Shizhuyuan deposit is thought to be related to the Qianlishan granite complex, which consists of medium- to coarse-grained biotite-granite (locally porphyritic), fine-grained biotite-granite, granite-porphyry, and quartz-porphyry. Geochemical and chronological investigations of the granitic rocks have been carried out by many geologists (Yin et al. 2002; Li et al. 2004b). Porphyry biotite-granite related to the deposit is approximately 152 Ma (Li et al. 2004b).

Remarkably, the distribution of mineralization belts in SE China is analogous to metallogenic belts in South America (Sillitoe 1972a, 1972b; Mlynarczyk and Williams-Jones 2005) (Figure 2B). South America hosts a succession of roughly parallel, N–S-trending metallogenic belts, which comprise four overlapping zones from W to E: the iron deposits of the Coastal Belt; the porphyry Cu–Mo–Au deposits of the Western Cordillera; the polymetallic vein- and replacement-type Cu–Pb–Zn–Ag deposits, and sedimentary Cu deposits of the Altiplano; and finally the vein and porphyry Sn–W–(Ag) deposits of the Eastern Cordillera (Sillitoe 1976; Mlynarczyk and Williams-Jones 2005). This distribution of deposit types was explained as the result of a sequential incorporation of different metal suites in magmas generated at progressively greater depths above a shallow-dipping subduction zone below the Andean orogen (Sillitoe 1972b). It may also be related to oxygen fugacity (Liang et al. 2006; Sun et al. 2007b) and element mobility (Bebout et al. 1999; Bebout 2007; Ding et al. 2009), both of which are sensitive to subduction.

**Oblique subduction model**

The special distributions of magmatism and metallogenic belts between 180 and 125 Ma in SE China can be best interpreted by southwestward oblique subduction of the Pacific plate. The southwestward subduction of the Pacific plate may have started sometime between 180 and 200 Ma during the ‘magmatic gap’ in SE China (Zhou and Li 2000; Zhou et al. 2006). Consequently, eastern China became an active continental margin (Maruyama 1997; Zhou and Li 2000; Scotese 2002). This marked the transformation of the tectonic regime from Indosinian to Pacific in SE China. Adakites and other magmatism, as well as associated ore deposits, for example, the Dexing porphyry Cu-(Au) deposit, were probably formed during the early stage of the subduction. As the subduction continued, slab rollback of the Pacific plate started, resulting in back-arc extension and associated magmatism and mineralization. The slab-rollback-induced magmatism started from the far end of the subducted slab and became younger towards the subduction zone (Figure 2). Meanwhile, mineralization belts change from W–Sn deposits in the far end, to Pb–Zn–Ag deposits in the middle, and to porphyry Cu deposits close to the subduction zone (Figure 2C).

According to our model, the southwestward subduction of the Pacific plate in the Early Jurassic can feasibly interpret major Mesozoic geologic observations in SE China, including (a) the age distribution of Mesozoic magmatic belts in SE China. It is also consistent with the drifting history of the Pacific plate before 125 Ma (Sun et al. 2007a). The distribution and ages of island chains on the Pacific plate indicate that the Pacific plate was drifting towards SW in the Early Cretaceous (Sun et al. 2007a). Consistent with
Figure 3. The magnetic anomalies in the Pacific Ocean floor, showing the drifting direction of the Pacific plate between 132 and 175 Ma (modified after Ludden et al. 2006). The dotted line is the apparent drifting direction, which was likely bent by the opening of the South China sea (Morley 2002) and/or seaward jumping of the subduction zone (Shimamura 1989), as well as slower subduction rate near SE China. The solid line is the estimated drifting direction before 125 Ma.

This theory, the magnetic anomalies in the ocean floor show that the Pacific plate was drifting roughly southward between 130 and 170 Ma (Figure 3) (Ludden et al. 2006), instead of northwestward as previously proposed (Zhou and Li 2000; Li and Li 2007). Interestingly, the drifting direction is not fully consistent with the distribution of deposits and magmatic rock in SE China. The apparent drifting direction was likely bent by the opening of the South China sea (Morley 2002) and, more importantly, the seaward jumping of the subduction zone (Shimamura 1989). Taking all of the above into consideration, the drifting direction of the Pacific plate was roughly consistent with the subduction direction defined by the distribution of the mineralization belts.

Iron deposits in the Lower Yangtze River Belt have been well studied (Zhai et al. 1996; Yu and Mao 2004, 2005; Jiang et al. 2006a; Ma et al. 2006b; Yu et al. 2007; Yu et al. 2008); however, the forming mechanism is still unclear. Apatite from the Washan and Dongshan iron deposits indicated a high f O 2 environment. The initial Sr isotopic compositions of the apatite from the iron deposits are similar to that of the volcanic rocks in the Ningwu basin and deposits in the basin, suggesting that the iron deposit has magmatic origination (Yu et al. 2007; Yu et al. 2008). The ages of iron deposits, however, are difficult to determine.
Limited $^{232}\text{Th}$-$^{208}\text{Pb}$ isotopic data of apatite yield an age of $124 \pm 41$ Ma, similar to the age of host volcanic rocks ($127$ Ma) (Jiang et al. 2006a). This age marginally predates the transformation of Pacific drifting (Sun et al. 2007a), and may well be due to ridge subduction (Ling et al. 2009). Nevertheless, if the metallogenic belts in SE China are indeed comparable to those in South America, there should be more Ningwu-type iron deposits, possibly of older ages, along the Lower Yangtze River Belt, closely related to the oblique subduction of Pacific plate in the late Mesozoic.

The oxygen fugacity ($fO_2$) of Jurassic magmatic rocks and related deposits in SE China decreases gradually from NE (Ningwu Fe deposits, Dexing porphyry Cu–Au deposit) to SW (Nanling W–Sn deposits), changing from magnetite-type to ilmenite-type. More precisely, apatite in the iron deposit in the Ningwu basin shows the highest $fO_2$ environment, with the Dexing porphyry Cu deposit as the second highest. It has long been recognized that most Cu–Au deposits are formed at convergent margins (Sillitoe 1997; Mungall 2002), and are closely associated with high $fO_2$ rocks (Sillitoe 1997; Sun et al. 2004; Liang et al. 2006). As the plate subducted to deeper depths, oxygen fugacity decreased, likely because of lower amounts of dehydration-released fluids. Correspondingly, Pb–Zn and then W–Sn ore deposits formed. Tin is dominantly in $4+$ valence in high $fO_2$ silica melts (Linnen et al. 1995). Sn$^{4+}$ ion radii similar to that of Ti$^{4+}$, as allomerism are formed minerals such as hornblende, biotite, ilmenite, etc. (Jiang et al. 2006b). Therefore, tin is not enriched in the late fluids or melts in high $fO_2$. By contrast, in reducing silica melts, Sn is mainly present as Sn$^{2+}$ with a larger ion radius, which is not concentrated in early formed minerals and enriched in later silica liquids to form tin deposits (Linnen et al. 1995; Webster et al. 1997; Thompson et al. 1999; Muller et al. 2001). This is consistent with our oblique subduction model (Figure 2). Oxygen fugacity in convergent margin magmas is usually considerably higher than in mid-ocean ridge and other geological settings (Brandon and Draper 1996; Parkinson and Arculus 1999; Sun et al. 2007b), likely due to subduction-released fluids (Brandon and Draper 1996; Sun et al. 2007b). Therefore, oxygen fugacity decreases gradually with increasing distance from the trench.

**Discussions**

SE China has undergone multiple tectonic and magmatic events and related metallogenic processes since the early Proterozoic, making it hard to study the ore formation processes. In addition, different kinds of deposits have usually been studied separately by different groups; little attention has been paid to the relationship among all deposits and associated igneous rocks.

As a result, polymetallic deposits in SE China have been attributed to a number of different tectonic environments. The Dexing Cu deposits have been related to the partial melting of the delaminated lower continental crust in an extensional tectonic regime in the intracontinent (Wang et al. 2003; Hou et al. 2007), whereas Pb–Zn metallogenic deposits in SE China have been attributed either to melting of sedimentary crust, for example, Huangshaping Pb–Zn–W–Sn deposits and Lengshuikeng Ag–Pb–Zn deposits (Yao et al. 2005, 2007; Zuo 2008; Zuo et al. 2008) or to I-type granite, for example, Shuikoushan Pb–Zn deposit (Wang et al. 2002; Yao et al. 2005) or taken as manganic skarn-type around or on some W–Sn deposit, for example, Nanfengao, Congshuban, and Shexing Pb–Zn deposits around Shizhuyuan W–Sn polymetallic deposit (Mao et al. 2009). By contrast, W–Sn deposits are usually associated with S-type granites (Jiang et al. 2008) with some mantle input (Zhu et al. 2006; Li et al. 2009), or highly evolved I/S-type granites (Cerny et al. 2005; Li et al. 2008). It has also been argued that W–Sn deposits formed in high
oxygen fugacity and post-magmatic hydrothermal alteration of the granite (Jiang et al. 2006b, 2008). Deposits in SE China in the Mesozoic were usually considered to be formed in an intracontinental rifting regime (Wang et al. 2002, 2006; Hua et al. 2003; Ma et al. 2004; Ma et al. 2006a; Hou et al. 2007). Other geologists proposed that these deposits were related to westward subduction of the Pacific plate (Niu 2005; Pei et al. 2007; Zaw et al. 2007).

Our model shares many common ideas with previously proposed Pacific subduction models (Zhou et al. 2006; Li and Li 2007). Previous models, however, proposed northwestward Pacific plate subduction, whereas the actual subduction direction was southwestward before approximately 125 Ma, as indicated by island chains (Sun et al. 2007a).

The flat subduction model (Li and Li 2007) can plausibly explain the present distribution of Mesozoic magmatism in SE China; however, this model does not consider the transformation in subduction direction of the Pacific plate and the rotation of the continent. SE China had experienced a clockwise rotation of about 70–90° from the Triassic to the Jurassic (Zhu et al. 1998) (Figure 4). From the model of Li and Li (2007), the subduction of the Pacific plate would be northwestward since the Triassic, which is not consistent with the magnetic abnormality in the present Pacific oceanic plate (Figure 3). Meanwhile, there are no Late Triassic adakitic rocks reported in the Cathaysia Block, and syenitic and A-type granitic intrusions (Wang et al. 2005b) also cannot support the conclusion that the granitic magmatic evolution during the Mesozoic followed such a pattern (Chen et al. 2008).

Others have proposed that the Pacific subduction system started at 101 Ma, and that the E–W-trending basalt array extending from the Cathaysia interior to the Cathaysia Folded Belt, which decreases in age from 175 to 98 Ma, is related to the post-orogenic (Indosinian) extension based on different sources (Chen et al. 2008). This model, however, cannot explain the decreasing of the magmatic ages and the ore deposit belts illustrated in this study (Figures 1 and 2). We propose that the southwestward subduction of the Pacific plate may have started sometime between 180 and 200 Ma, during the ‘magmatic gap’ in SE China (Zhou and Li 2000; Zhou et al. 2006). Consequently, eastern China became an active continental margin (Maruyama 1997; Zhou and Li 2000; Scotese 2002; Sun et al. 2007a). This marked the transformation of the tectonic regime in SE China from the Indosinian to the Pacific.

Conclusions

We propose an oblique subduction model to explain the distribution of late Mesozoic (180–125 Ma) magmatism and metallogenic events in SE China. We infer that the Pacific plate was subducting southwestward during this period. This model can plausibly explain the temporal–spatial distribution of mid-Mesozoic large-scale igneous events and associated mineralizations in SE China. Granitoid plutons are mainly Jurassic (180–160 Ma) in the Nanling region in the SW, and become progressively younger northeastward to approximately 140–125 Ma in the Lower Yangtze River Belt, which is consistent with southwestward subduction followed by a northeastward slab rollback. The spatial distribution of the three Jurassic metallogenic belts is analogous to that in South America.

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Figure 4. Docking and rotation between North China Block (NCB) and South China Block [composed by the Yangtze Block (YZB) and Cathaysia Block (CSB)] from Triassic to Jurassic (modified after Zhu et al. 1998). The dotted line between the two blocks is speculative. The black solid line represents the latitude. The YZB and NCB docked in P₂–T₁ at 10°N and drifted to the north till T₃–J₁. The YZB and NCB joined together completely in the Early Jurassic. After that, they rotated anticlockwise by approximately 30° in the Late Jurassic and then rotated clockwise by approximately 30° in the Quaternary. This has influenced the present distribution of magmatic rocks and tectonic features in the SE China.

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Different origins of adakites from the Dabie Mountains and the Lower Yangtze River Belt, eastern China: geochemical constraints

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Cretaceous adakites are widely distributed in the Lower Yangtze River Belt (LYRB) and the Dabie Mountains, east-central China. Adakites from the LYRB in general are closely associated with Cu–Au deposits, whereas Dabie adakites lack any mineralization. Based on geochemical characteristics, we show that these adakites have different origins; for example, adakites from the Dabie Mountains have more variable Sr/Y (6.47–1303) and systematically higher La/Yb (20.8–402), Th/U (2.28–50.6), and Nb/Ta (5.07–65.2) compared to adakites from the LYRB, Sr/Y (28.8–185), La/Yb (14.1–49), Th/U (0.33–8), and Nb/Ta (7.5–23). The systematically higher La/Yb of Dabie adakites supports their continental origin, because the La/Yb of the lower continental crust is more than 10 times higher than that of mid-ocean ridge basalt (MORB). Moreover, the lower continental crust is also highly enriched in Sr, with Sr/Y > 10 times that of MORB. Interestingly, with the exception of those from Fuziling, most Dabie adakites have Sr/Y comparable to normal adakites, suggesting the presence of residual plagioclase. Because Th and U do not fractionate significantly from each other during magmatism, the high but variable Th/U suggests that the protolith of Dabie adakites underwent subduction. The LYRB adakites can be plausibly interpreted as being a result of Early Cretaceous partial melting of a young, hot, descending oceanic slab during ridge subduction. By contrast, Dabie adakites were likely formed by partial melting of the lower continental crust attending ridge subduction.

Keywords: adakites; Dabie; ridge subduction; Cu deposits; slab melting

1. Introduction

Adakite, defined by its unique geochemical features such as SiO\textsubscript{2} \(\geq\) 56 wt.\%, Al\textsubscript{2}O\textsubscript{3} \(\geq\) 15 wt.\%, Y \(\leq\) 18 ppm, Yb \(\leq\) 1.9 ppm, and Sr \(\geq\) 400 ppm, was initially named for rocks with clear contributions from partial melting of subducted young oceanic crust (Defant and Drummond 1990) and has gained wide interest in recent years. The formation of some adakites, however, is still controversial. In addition to slab melting, adakite was also proposed to be formed by partial melting of the lower continental crust (Chung \textit{et al.} 2003; Gao \textit{et al.} 2004), underplated new crust (Petford \textit{et al.} 1996), or fractional crystallization of normal arc magmas (Castillo 2006; Macpherson \textit{et al.} 2006; Richards and Kerrich 2007; Rodriguez \textit{et al.} 2007).

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Adakite has been reported to be closely associated with many ore deposits in the Lower Yangtze River Belt (LYRB), central eastern China (Wang et al. 2004a, 2004b, 2006, 2007b; Yang et al. 2007; Xie et al. 2008, 2009; Zhou et al. 2008), which is one of the most important metallogenic belts in China, containing more than 200 polymetallic (Cu–Fe–Au, Mo, Zn, Pb, Ag) deposits (Chang et al. 1991; Pan and Dong 1999; Mao et al. 2006), formed mainly at a very narrow period of time, that is, 138 ± 3 Ma (Sun et al. 2003b). Adakite from the LYRB was originally attributed to partial melting of thickened or delaminated lower continental crust, based mainly on isotopic characteristics and an assumption that there was no plate subduction in the Early Cretaceous (Zhang et al. 2001; Xu et al. 2002; Wang et al. 2004a, 2004b, 2006, 2007b).

Plate reconstruction and other observations, however, suggest that there was plate subduction in the Early Cretaceous (Zhou and Li 2000; Zhou et al. 2006; Li and Li 2007; Sun et al. 2007a; Wang et al. 2011). Based on the distribution of adakite and rock assemblages, Ling et al. (2011) proposed a ridge subduction model. According to that model, LYRB adakite was formed by partial melting of subducting young, hot oceanic slabs close to the subducting ridge between the Pacific and Izanagi plates. The enriched isotope characteristics can be explained by the assimilation of enriched mantle materials and the continental crust (Ling et al. 2009).

In recent years, adakite has also been reported in the Dabie Mountains (Wang et al. 2007a; Xu et al. 2007; Huang et al. 2008), which was considered to be formed by partial melting of the basement of an overthickened crustal root during the early stage of extensional collapse of the Dabie Mountains (Xu et al. 2007), partial melting of thickened amphibole or rutile-bearing eclogitic lower continental crust (Wang et al. 2007a), or partial melting of the thickened lower continental crust (Huang et al. 2008).

Considering the dramatic difference between the Dabie Mountains and the LYRB in terms of tectonic settings, we compared geochemical characteristics of adakite from these places (Huang et al. 2008; Ling et al. 2009 and references therein; Wang et al. 2007a; Xu et al. 2007). Our results show significant differences in geochemical characteristics between these two suites of adakites.

2. Geological background

2.1. The Dabie Mountains

The Dabie ultra-high-pressure metamorphic (UHPM) belt is the middle part of the Qinling-Dabie-Sulu Mountains in China (Mattauer et al. 1985; Meng and Zhang 1999, 2000; Sun et al. 2002a; Li and Yang 2003; Zhang et al. 2004), which is the largest UHPM belt in the world and resulted from the Triassic collision between the North and South China blocks (Figure 1a and b) (Li et al. 1993; Hacker et al. 1998; Lioiu et al. 2000; Ye et al. 2000; Sun et al. 2002b; Zhang et al. 2003, 2008; Liu et al. 2006; Yang et al. 2008).

The Dabie Mountains were divided into two terranes, the northern Dabie terrane and the southern Dabie terrane. The southern Dabie terrane is famous for coesite-bearing (Okay et al. 1989; Wang et al. 1989) and diamond-bearing eclogite (Xu et al. 1992), as well as other ultra-high-pressure mineral assemblages indicating that the continental crust has been subducted down to depths of more than 100 km (Ernst and Lioiu 1999; Ye et al. 2000; Zhang et al. 2007). Generally, the Dabie Mountains can be subdivided into five metamorphic zones from north to south: (1) Beihuaiyang greenschist-amphibolite facies zone; (2) Huwan cold eclogite melange zone; (3) northern Dabie complex zone; (4) southern
Dabie UHPM zone; and (5) Hong’an-Susong high-pressure metamorphic zone (Li et al. 1993, 2001 and references therein; Zhang et al. 2007; Wang et al. 2008).

Adakite in the Dabie Mountains is distributed in Yunfengding, Egongbao, Fuziling (Wang et al. 2007a), Tiantangzhai (Wang et al. 2007a; Xu et al. 2007), Chituling (Huang et al. 2008), Shigujian, Duzunshan, Guanyinci, Daoshichong, etc. (Xu et al. 2007). Those adakitic rocks are all attributed to partial melting of the lower continental crust (Huang et al. 2008).

2.2. The Lower Yangtze River Belt

The LYRB is located in the east part of the Yangtze block in central eastern China (Chang et al. 1991; Chen et al. 1991; Xing and Xu 1995; Pan and Dong 1999; Zhou and Yue 2000; Chen et al. 2001; Zhou et al. 2008; Xie et al. 2009) (Figure 1a), which is separated from the Cathaysia block to the south by the Jiangshan-Shaoxing fault, the Proterozoic suture between the Cathaysia and Yangtze blocks (Li 1992; Li et al. 2005). The Xiangfan-Guangji and Tan-Lu faults are the northern and western margins of the LYRB, respectively (Chen et al. 2001), separating it from the Dabie Mountains.

The magmatic rocks have been classified into three belts: the inner, south, and north belts (Chang et al. 1991; Xing 1999; Xing and Xu 1995) (Figure 1c). The inner belt contains high-K calc-alkaline intermediate-acidic intrusive rocks, high-sodium calc-alkaline intermediate-basic intrusive rocks, shoshonite, and A-type granite (Xing 1999). The south belt consists of calc-alkaline rocks, generally large plutons with some small bodies of granodiorite porphyry. Some A-type granites with younger ages have also been reported in the south belt (Wong et al. 2009). The north belt is also composed of calc-alkaline rocks, but it is poorly developed and seemingly more complicated than the other two belts, with fewer intrusive bodies (Xing 1999). Adakitic rocks from the LYRB are all distributed in the inner belt. A-type granites are systematically younger than adakite, which is probably related to a slab window (Ling et al. 2009). LYRB adakite was attributed either to partial melting of the lower continental crust (Zhang et al. 2001; Xu et al. 2002; Wang et al. 2006, 2007b) or to slab melting induced by ridge subduction (Ling et al. 2009).

3. Comparison of adakites from the Dabie Mountains and the LYRB

Given that the major elements (e.g. K₂O, Na₂O, and MgO) and isotopes (e.g. Sr, Nd) have been intensively investigated by previous authors, this article mainly focuses on the trace element characteristic of the adakites. A comparison of geochemical characteristics of adakites from the Dabie Mountains and the LYRB is made in this study, using data from the literature (Huang et al. 2008; Ling et al. 2009 and references therein; Wang et al. 2007a; Xu et al. 2007). Referring to Sr/Y–Y and La/Yb–Yb diagrams (Figures 2 and 3), most of the data collected from published literature fall in the adakite area confined by the global database GEOROC (GEOROC 2009).

Figure 1. Distribution map of adakite from the Dabie Mountains and the Lower Yangtze River Belt in China. (a) Sketch map of eastern China with the locations of the Dabie Mountains and the Lower Yangtze River Belt (modified from Wang et al. 2007a). (b) Distribution map of adakite from the Dabie Mountains (modified from Wang et al. 2007a). (c) Distribution of magmatic rocks in the Lower Yangtze River Belt (modified from Ling et al. 2009). Granodiorite, quartz diorite, granite, syenite, etc. distributed in the inner belt are adakites.
Figure 2. Diagram of Sr/Y versus Y. The adakite and andesite areas are defined using data from the GEOROC database (GEOROC 2009). Nearly all of the data are distributed in the adakite area, in which adakite from the Dabie Mountains has a relatively larger range than that from the Lower Yangtze River Belt and also slightly lower Sr/Y ratios, except adakite from Fuziling, which has extremely high Sr/Y up to 1303.

Figure 3. Diagram of La/Yb versus Yb. Symbols are the same as in Figure 2. The adakite and andesite areas are defined using data from the GEOROC database (GEOROC 2009). As in Figure 2, data of adakite from the Dabie Mountains are in a wide range, in which adakite from Fuziling has the highest La/Yb ratios. Adakite from the Lower Yangtze River Belt has much lower La/Yb than that from the Dabie Mountains.
Adakites from the Dabie Mountains and the LYRB have obviously different geochemical characteristics, for example, adakite from the Dabie Mountains has Sr concentration ranging from 142 to 1300 ppm, Y concentration from 0.452 to 28.9 ppm, and highly varied Sr/Y (6.47–1300), whereas adakite from the LYRB has much higher Sr concentration (369–2300 ppm), nearly the same range of Y concentration (5.51–24 ppm), and less variable Sr/Y (28.8–185) (Figure 2). Also, adakite from the Dabie Mountains has a wide range of La/Yb, varying from 20.8 to 402, whereas that of LYRB adakite ranges from 14.1 to 49 (Figure 3). It is worth mentioning that adakite from Fuziling in the Dabie Mountains has the highest Sr/Y and La/Yb among all samples studied (Figures 2 and 3), probably because of the combination of their lower continental origin and large amount of residual garnet in the source (see detailed discussion below). Furthermore, Dabie adakite has highly variable Th/U, ranging from 2.28 to 50.6 (Figure 4), with Nb/Ta ranging from 5.07 to 65.2 (Figure 5) and Zr/Hf from 25.4 to 47.4 (Figure 6). In contrast, LYRB adakite has much lower Th/U (0.33–8) (Figure 4), relatively lower Nb/Ta (7.5–23) (Figure 5), and almost the same range of Zr/Hf (23.3–40.2) (Figure 6).

Aforementioned evidence clearly shows that adakites from the Dabie Mountains were very likely formed by partial melting of the lower continental crust, whereas those from the LYRB were formed by partial melting of subducting oceanic slab.

4. Discussion

4.1. Sr/Y

Adakite from the Dabie Mountains is generally attributed to partial melting of the lower continental crust (Wang et al. 2007a; Huang et al. 2008). The lower continental crust has Sr/Y of more than 30, which is about 10 times higher than that of mid-ocean ridge basalt (MORB) (Sun and McDonough 1989; Rudnick and Gao 2003; Sun et al. 2008). Most adakite so far published has Sr/Y ranging from 20 to 200. Adakite from the LYRB has relatively concentrated Sr/Y (28.8–185) (Figure 2), well within the range of global adakite. In contrast, adakite from the Dabie Mountains has highly varied Sr/Y (6.47–1300) (Figure 2). All the samples with high Sr/Y were from Fuziling. Strontium is generally taken as a moderately incompatible element during mantle magmatism (Sun and McDonough 1989). It
is, however, highly compatible in plagioclase (GERM 2009), with a partition coefficient of \( \sim 3.7 \) for plagioclase in basaltic rocks (GERM 2009). Yttrium is also a moderately incompatible element during mantle magmatism (Sun and McDonough 1989), with geochemical behaviour similar to that of heavy rare earth elements. It is highly compatible in garnet. Therefore, plagioclase and garnet are the two most important minerals that control Sr/Y ratios.

LYRB adakite has Sr/Y comparable to global adakites. Considering that the lower continental crust has Sr/Y about 10 times higher than that of MORB, a large amount of
residual plagioclase is required to form these adakites from partial melting of the lower continental crust. In this case, the partial melting occurred at fairly shallow depths. Alternatively, adakite formed by slab melting at eclogitic facies generally has no plagioclase in the source (Rapp and Watson 1995; Rapp et al. 2003; Xiao et al. 2006; Xiong 2006), such that the Sr/Y ratios can be dramatically elevated during slab melting. Therefore, LYRB adakite can be plausibly interpreted as being a result of ridge subduction induced partial melting, with limited contamination from enriched mantle sources and the continental crust (Ling et al. 2009).

The large variation of Sr/Y for the Dabie samples can be plausibly interpreted as being a result of partial melting of the lower continental crust with different proportions of garnet and plagioclase in the source. The high Sr/Y of Fuziling adakite indicates more residual garnet, with or without minor plagioclase. Other Dabie samples have Sr/Y comparable to those of the LYRB samples and adakites worldwide, indicating residual plagioclase. It is true that Sr/Y of Dabie samples can also be interpreted as being a result of slab melting. In other words, with the exception of very high Sr/Y, e.g. Fuziling samples, Sr/Y itself cannot discriminate slab melting from partial melting of the lower continental crust.

4.2. La/Yb

The lower continental crust has La/Yb ratio of ~10, which is ~15 times higher than that of MORB (Sun and McDonough 1989; Rudnick and Gao 2003; Sun et al. 2008). Lanthanum is an incompatible element, whereas Yb is moderately incompatible during mantle magmatism (Sun and McDonough 1989). Ytterbium, however, is highly compatible in garnet, whereas La is not. Therefore, La/Yb ratios of adakites are very sensitive to garnet. In contrast to Sr/Y ratios, La/Yb is not obviously affected by plagioclase. Moreover, garnet is a major mineral in both eclogite and granulite (for the lower continental crust). For these reasons, adakites formed by partial melting of the lower continental crust in the presence of garnet should have systematically higher La/Yb, which is much more sensitive than Sr/Y in discriminating slab melting from lower continental crust melts. This is exactly the case for Dabie adakite.

As shown in Figure 3, adakite from the Dabie Mountains has wide-ranging La/Yb ratios, ranging from 20.8 to 402, which is systematically higher than normal adakites. The high La/Yb ratios support models of the lower continental crust partial melting (Wang et al. 2007a, Huang et al. 2008), whereas the large range of La/Yb ratios is consistent with the large variation of Sr/Y, which indicates variable amount of residual garnet in the source. It is worth mentioning that adakite from Fuziling in the Dabie Mountains has the highest Sr/Y and La/Yb ratios (Figures 2 and 3), likely because of more residual garnet, less residual plagioclase in the source.

LYRB adakite has La/Yb ranging from 14.1 to 49 (Figure 3), comparable to normal adakites (Figure 3). A garnet-free source is required to form this kind of adakites by partial melting of the lower continental crust (with La/Yb of ~10). Given that garnet is a major mineral in both eclogitic and granulitic rocks, this assumption is unfavourable. Therefore, we propose that La/Yb of the LYRB adakite can be plausibly interpreted as being a result of slab melting.

4.3. Th/U

Adakite from the Dabie Mountains has highly varied Th/U, as well as U and Th concentrations (Figure 4). Large variations of U concentration and Th/U of adakite from the Dabie Mountains can be explained by U loss during subduction and collision in the Triassic, because U is more mobile than Th (Hawkesworth et al. 1997), especially at temperatures lower than 600°C. This is supported by the negative linear trend in a Th/U versus U diagram (Figure 4a).
The Th/U values of LYRB adakite is systematically lower and much less variable, falling around the field of slab melts (Figure 4). Considering the similarity between U and Th, the variable Th/U of LYRB adakite is still significant. It is likely because of Th/U fractionation during subduction. Nevertheless, the Th/U characteristics strongly support the slab melting model (Ling et al. 2009).

4.4. **Nb/Ta**

Adakite from the Dabie Mountains has Nb/Ta = 5.1–65.2, Nb = 1.01–27.3 ppm, Ta = 0.023–2.28 ppm, whereas that from the LYRB has relatively lower Nb/Ta (7.5–23, with an average of 15.1), Nb = 0.3–22.4 ppm with an average of 10.0 ppm, and Ta = 0.04–1.4 ppm with an average of 0.7 ppm (Figure 5). Adakite from Fuziling has much higher and more fractionated Nb/Ta than others. With the exception of Fuziling samples, adakites from the Dabie Mountains and the LYRB have nearly the same range of Nb/Ta, which are from 5.1 to 27.6 with an average of 14.1 and from 7.5 to 23 with an average of 15.1, respectively (Figure 5).

Niobium and Ta are usually not fractionated from each other. Highly fractionated Nb/Ta ratios have been reported in subduction zones, which are attributed to dehydration during the prograde blueschist to amphibole–eclogite transformation before rutile appeared (Xiao et al. 2006; Ding et al. 2009; Liang et al. 2009). The highly variable Nb/Ta suggests that both Dabie and LYRB adakites are related to plate subduction. Given that the LYRB is dramatically different from the Dabie Mountains in tectonic settings, that is, it has not been subducted during the Triassic collision, the fractionated Nb/Ta in LYRB adakites, in fact, also supports the ridge subduction induced slab melting model.

4.5. **Ridge subduction**

All the facts discussed above support the ridge subduction model for LYRB adakite. According to that model, there was a ridge subduction affecting the LYRB in the Cretaceous, and adakite from the LYRB was formed by partial melting of subducting young, hot oceanic slabs close to the subducting ridge between the Pacific and Izanagi plates (Ling et al. 2009). Subduction resulted in higher oxygen fugacity (Brandon and Draper 1996; Sun et al. 2007b), which is favourable for Cu–Au mineralization (Mungall 2002; Sun et al. 2004; Liang et al. 2006).

In contrast to the LYRB adakite, the geochemical features of Dabie adakite indicate obvious lower continental crust origin (Figures 5 and 6). It is well known that the Dabie Mountains was formed during the Triassic collision between the North and South China blocks (Li et al. 1993; Hacker et al. 1998; Ye et al. 2000; Sun et al. 2002b; Zheng et al. 2003; Liu et al. 2006), with dehydration and retrograde metamorphism during continental subduction. The Triassic collision and subduction had thickened the lower continental crust, resulting in a high-pressure metamorphic belt. Dabie adakite was most likely formed during the destruction of the thickened mountain belt. Nevertheless, most Dabie adakites were formed at shallow depths in the presence of plagioclase, therefore, they were not likely related to delamination. Remarkably, Dabie adakite formed at nearly the same period of time. In case LYRB adakite was formed during ridge subduction, Dabie adakite may also be genetically related to ridge subduction in the Early Cretaceous. In other words, Dabie adakite was triggered by ridge subduction: the flat subduction of the ridge may have physically destroyed the root of the Dabie Mountains, whereas the following slab window provided additional heat, which promoted the partial melting (Figure 7).
The different origin of Dabie and LYRB adakites is also consistent with the fact that LYRB adakite is closely associated with Cu–Au deposits, whereas Dabie adakite is not. MORB has Cu (and Au) several times higher than that of the lower continental crust (Sun and McDonough 1989; Rudnick and Gao 2003; Sun et al. 2003a; Sun et al. 2004), therefore slab melting is much more favourable for Cu (Au) mineralization (Sun et al. 2011).

5. Conclusions
Geochemical features indicate different sources for adakites from the Dabie Mountains and the LYRB. The source of the Dabie adakite magma was subduction-modified lower continental crust, characterized by the presence of residual plagioclase. We propose that the Dabie adakites formed by partial melting of the lower continental crust, initiated by Cretaceous ridge subduction. In contrast, the LYRB adakites were formed by partial melting of a subducting young, hot oceanic slab close to the spreading ridge, contaminated by enriched components or the continental crust.

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Review of the stable isotope geochemistry of Mesozoic igneous rocks and Cu-Au deposits along the middle-lower Yangtze Metallogenic Belt, China

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Ore deposition took place in the Yangtze Valley episodically during the Jurassic and Cretaceous periods, generating approximately 200 polymetallic Cu-Fe-Au, Mo, Zn, Pb, and Ag deposits. We analysed the stable isotopes of sulphur, oxygen, and hydrogen from the Cu-Au deposits and correlated our new data with published stable isotope for associated Yanshanian (Mesozoic) igneous rocks. The latter bears a close relationship to Cu-Au mineralization in the area. Cu-Au deposits in the middle-lower Yangtze Valley can be divided into three types: skarn, porphyry, and volcanic. The S–O–H isotopic values allow constraints to be placed on the conditions of origin of these famous Cu-Au ores and their related igneous rocks.

Sulphur from the sulphide ores mostly was derived from a magmatic source; however, a few deposits reflect a sedimentary source of sulphur. Oxygen isotope values in quartz from the Shaxi porphyry Cu-Au deposit and from the Tongling skarn Cu-Au deposits range from 2.6‰ to 12.5‰ and from −1.3‰ to 24.5‰, respectively; these values represent larger variations compared with those from other Cu-Au deposits in this metallogenic belt. Hydrogen versus oxygen isotope plots of the Cu-Au ore-forming fluids demonstrate that the fluids came from different sources: the most important involved the mixing of magmatic and meteoric water; the second most important was strictly magmatic water; and the third most important may have been a mixture of formation water or meteoric water that had reacted with carbonate wall rocks.

Keywords: porphyry Cu-Au deposits; stable isotope geochemistry; sulphur; hydrogen; oxygen isotopes; middle-lower Yangtze metallogenic province

Introduction

The Yangtze Valley is one of China’s most important metallogenic provinces. Fe-Cu ore deposition in the eastern Yangtze Craton of central to eastern China was controlled by faults and aulacogens during the early Yanshan Epoch of the Jurassic period (Chang et al. 1991; Zhai et al. 1996). The associated igneous rocks can be grouped into two series according to their relationship to the metallogenesis: the Fe-related group and the Cu-related group. In this article, we mainly study the relationship between the igneous rocks of the Cu-related
mineralization. Ore deposition was controlled by the dominant WNW and E–W deep faults that characterize the whole region.

The study area is located along the northern margin of the Yangtze platform and in the southeastern part of the Sino-Korean platform (Ren et al. 1980). The Yangtze River, which developed along deep fracture zones, is about 450 km long, extending from SE Hubei eastward to Zhenjiang. The area along the middle and lower reaches of the Yangtze River is commonly referred to as the lower Yangtze region. Mesozoic igneous rocks in this region are closely associated with important copper, iron, gold, and sulphur ore deposits (Chang et al. 1991), and this region is one of the richest copper production areas in China. The lower part of the Yangtze Valley, from Wuhan in Hubei Province in the W to Zhenjiang in Jiangsu Province in the E, contains more than 200 polymetallic (Cu, Fe, Au, Mo, Zn, Pb, and Ag) deposits.

In this study, we have focused on several intrusive bodies situated along the lower part of the Yangtze Valley related to Cu–Au mineralization: the Shaxi diorite porphyry, the Anqing diorite, the Tongling granite, and the Chuxian granite. We also studied the Luzong volcanic basin to compare such extrusive rocks with the intrusives because the source magmas seem to have a close relationship with the Cu–Au mineralization.

**Geological setting**

The dominant W–NW and E–W lithospheric faults control the distributions of Cu (±Au or Mo) mineralization. Igneous rocks of the region have been intensely studied throughout the past century. As early as the 1920s, Chinese geologists recognized that granitoids from the lower Yangtze region were different from those of the Nanling region in southeastern China.

Figure 1 is the regional sketch of a geological–tectonical map, showing the distributions of the granitoids related to Cu–Au mineralization. Altogether five localities of granitoid rocks associated with Cu–Au mineralization are recognized: the Shaxi porphyry intrusive and the Huangtun diorite intrusive related to porphyry Cu–Au deposits; the Anqing diorite intrusive related to massive hydrothermal and skarn Cu–Au deposits; and both the Tongling granitic intrusive and the Chuxian diorite intrusive heavily related to the skarn Cu–Au deposit. In addition, we also studied for comparison the igneous rocks in the Luzong volcanic basin located in between these Cu–Au deposits, because this volcanic basin belongs to the Jurassic to Cretaceous periods (Ren et al. 1991), in which many relatively small-scale hydrothermal Cu–Au deposits are distributed. The main igneous rocks are Cu-related intrusives that form several types of Cu deposits, but in most of them Au is associated with Cu mineralization.

Comparing with these Cu–Au deposits along the lower parts of the Yangtze Metallogenic Valley, we first summarize the detailed information on geology, tectonical background, some geochemical features, and the mineralization (Table 1).

The five Cu–Au deposits distributed in the lower part of the Yangtze Metallogenic region in East China have some common characteristics: the age of the intrusive or volcanic activities in the middle to late Mesozoic period, ranging from 80 Ma to 170 Ma. Except for the volcanic thermal-type Cu–Au deposits in the Luzong volcanic basin (Ren et al. 1991; Yang 1996), the Cu–Au deposits are related to the granitoid intrusives, some of which have high potassic contents (Chang et al. 1991; Yang 1996). The geological setting of the study areas includes the tectonical depression of the SE margin of the Dabie orogenic belt along the edge of the Tanlu fault zone.
Figure 1. Distributions of famous metallic deposits and their forming ages along the middle–lower Yangtze Metallogenic Belt (ML YMB), based on the collection maps from Chang et al. (1991), Zhai et al. (1992), and Pan and Dong (1999); isotopic ages are based on Mao et al. (2006).

Note: Dexing porphyry Cu–Au deposit is not shown in the main map. It belongs to the ML YMB, shown in the box map; Yulong and Duobaoshan porphyry Cu–Au deposits are not distributed along the ML YMB, but they are two other famous porphyry Cu–Au deposits in China; their localities are also shown in the box map.

**Petrography and petrochemistry**

**Petrography**

There are several kinds of intrusive rocks associated with the porphyry and skarn Cu–Au in the Yangtze Metallogenic Valley. These intrusives comprise quartz diorite porphyry, biotite-quartz diorite porphyry, and fine- to medium-grained diorite porphyry, which have a subhedral seriate texture. These rocks contain phenocrysts of plagioclase and alkali-feldspar. The size of the plagioclase and feldspar crystals ranges from matrix dimensions up to 8–3 mm and 5–1.5 mm, respectively. Some feldspars were severely altered to sericite, chlorite, and kaolinite in the alteration zones. The diorite is composed of amphibole, microcline, biotite, quartz, muscovite, pyrite, magnetite, apatite, sphene, and rare rutile. Some quartz has undulatory extinction and is of several generations; most of them contain inclusions of other minerals and needles of some metallic minerals, of which most are magnetite and pyrite. The microcline occurs as subhedral crystals with cross-hatch twinning, showing the characteristics of microperthitic intergrowth with some plagioclase. The subhedral plagioclase in the diorite porphyry usually occurs as polysynthetically twinned crystals, which have the composition of oligoclase to andesine (mostly An25–An45) and some plagioclase is oligoclase-albite (An5–An20) because of its thermal alteration (Chang et al. 1991; Yang 1996). The amphibole crystals usually occur as subhedral with sizes usually ranging from 1.3 mm to 0.1 mm, up to 10 mm. In some diorite porphyry, amphiboles can make up...
Table 1. Characteristics of copper (-gold) polymetallic deposits in the lower Yangtze region, China.

<table>
<thead>
<tr>
<th>Cu-Au province</th>
<th>Name of deposit</th>
<th>Commodity</th>
<th>Tectononical setting/orogeny</th>
<th>Host rock/period</th>
<th>Igneous rocks/size and age (Ma)</th>
<th>Resource of Cu (t)</th>
<th>Grade (%)</th>
<th>Major ore minerals</th>
<th>Alteration minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central Anhui Province, East China</td>
<td>Shaxi porphyry deposit</td>
<td>Cu-Au</td>
<td>At the edge of Tanlu fault; southeastern margin of Dabie Mountains</td>
<td>Silty stone, muddy stone, and sandstone/S_{1-2,D}, J_{1-2}</td>
<td>Porphyrite, diorite (1-2 km²)/130 ±</td>
<td>5 × 10⁵</td>
<td>0.2–0.5</td>
<td>Cp, Py, Mo, Bor, Ga, Sph, Hem, Mt</td>
<td>Ser, Anh, Gy, Kf, Mus, Bi, Chi, Ep, Kao</td>
</tr>
<tr>
<td>Southwest Anhui Province, East China</td>
<td>Anqing skarn deposit</td>
<td>Cu-Fe-Mo-Au</td>
<td>Between depression and uplifting, southern margin of Dabie Mountains</td>
<td>Carbonate, shale, dolomite, and sandstone/C-P-T</td>
<td>High-potassic diorite (10-90 km²)/105-145</td>
<td>2–3 × 10⁵</td>
<td>2–5</td>
<td>Cp, Py, Mo, Bor, Hem, Mt</td>
<td>Ser, Kf, Mus, Anh, Gy, Bi, Chi, Ep, Kao</td>
</tr>
<tr>
<td>South Anhui Province, East China</td>
<td>Tongling skarn deposit</td>
<td>Cu-Au</td>
<td>Uplifting, South China granitoids</td>
<td>Carbonate, shale, dolomite, and sandstone/C-P-T</td>
<td>Diorite and granite (&lt;10 km²)/110-168 Ma</td>
<td>&gt; 1 × 10⁶</td>
<td>2–5</td>
<td>Cp, Py, Bor, Hem, Mt</td>
<td>Ser, Kf, Mus, Anh, Gy, Bi, Chi, Ep</td>
</tr>
<tr>
<td>East Anhui Province, East China</td>
<td>Chuxian skarn deposit</td>
<td>Cu-Au</td>
<td>Uplifting, East China granitoids</td>
<td>Carbonate, shale, dolomite, and sandstone/C-P-T</td>
<td>Diorite(&lt;5 km²)/ Mesozoic</td>
<td>10 × 10⁵</td>
<td>2–5</td>
<td>Cp, Py, Bor, Hem, Mt</td>
<td>Ser, Kf, Mus, Anh, Gy, Bi, Chi, Ep</td>
</tr>
<tr>
<td>Central Anhui Province, East China</td>
<td>Luzong volcanic thermal deposit</td>
<td>Cu-Au-S-Ag</td>
<td>Cenozoic volcanic basin; depression, southeastern margin of Dabie Mountains</td>
<td>Mudstone, sandstone, carbonate, and dolomite/J-K</td>
<td>Potassic granitoids and andesite (1–100 km²)/80-160</td>
<td>Unknown</td>
<td>5–10</td>
<td>Cp, Py, Bor, Hem, Mt</td>
<td>Ser, Kf, Mus, Anh, Gy, Bi, Chi, Ep</td>
</tr>
<tr>
<td>Location</td>
<td>Deposit Name</td>
<td>Metal(s)</td>
<td>Deposit Type</td>
<td>Rock Type</td>
<td>Area (km²)</td>
<td>Age (Ma)</td>
<td>Other Minerals</td>
<td>Abbreviations</td>
<td></td>
</tr>
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<tr>
<td>Northern Jiangxi Province, East China</td>
<td>Dexing porphyry deposit</td>
<td>Cu-Mo-Pb-Zn</td>
<td>Uplifting, East China granitoids</td>
<td>Silica and aluminium sedimentary rocks/Pt</td>
<td>80 x 10⁶</td>
<td>0.3-0.5</td>
<td>Cp, Py, Mo, Bor, Ga, Sph</td>
<td>Anh, Bi, Bor, bornite, Ga, galena, Gy, epidote, Kao, Kaoinite, Kf, potassic feldspar, Mo, molybdenite, Mt, magnetite, Mus, muscovite, Py, pyrite, Ser, sericite, Si, silification, Sph, sphalerite.</td>
<td></td>
</tr>
<tr>
<td>Eastern Tibet, SW China</td>
<td>Yulong porphyry deposit</td>
<td>Cu-Mo-Fe</td>
<td>Tethyan-Himalaya tectonic belt, SW China granitoids</td>
<td>Shale and limestone/T</td>
<td>&gt; 12 x 10⁵</td>
<td>0.3-0.5</td>
<td>Cp, Py, Mo, Bor, Hem, Kf, Ser, Si, Bi, Chl, Ep, Kao</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heilongjiang, EW China</td>
<td>Duobaoshan porphyry deposit</td>
<td>Cu-Mo</td>
<td>Regional extensional fault zone</td>
<td>Tuff, andesite, and limestone/O</td>
<td>5 x 10⁵</td>
<td>0.3-0.5</td>
<td>Cp, Py, Mo, Bor, Ser, Kf, Cc, Bi, Chl, Ep, Kao</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
as much as 15% of the total mineral volume. Some amphibole is replaced by chlorite alteration at the edges where general muscovite and quartz formed. The muscovite and biotite are all subhedral; however, biotite is more abundant than muscovite in the diorite porphyry. Figure 2 shows the petrological characteristics of the intrusives from the Shaxi, Anqing, Tongling, Chuxian, and Luzong areas, from which some information can be obtained about
the different types of Cu–Au mineralization in the lower part of the Yangtze Metallogenic Belt.

Figure 3 shows the petrological characteristics observed in several Cu–Au ore deposits, where some relationships can be determined regarding the different mineralization periods of ore minerals in different types of Cu–Au mineralization in the area.

Petrochemistry
Late Mesozoic igneous rocks with Cu–Au mineralization form regional outcroppings in the lower Yangtze region. They intrude into Neoproterozoic low-grade metamorphic rocks or Palaeozoic to Triassic sedimentary strata. Several rock types are identified: in Figure 4, the K₂O versus SiO₂ identifies shoshonites, which are mostly distributed in the Luzong meso-volcanic rocks, some of which lie in the Tongling region with skarn Cu–Au mineralization. The K-enriched rock association in the other ore deposits contains both shoshonite series and ultra-potassic rocks identified by high values of Na₂O + K₂O (8.1–12.0%), high K₂O values (4.1–8.5%), and with K₂O/Na₂O ratios of 0.8–1.4. They also outcrop to the N of the Yangtze River and along the Yangtze River (Anhui 1987; Wang and Yang 1996; Xing and Xu 1999). They are plotted in basaltic trachyandesite, trachyandesite, and syenite fields in composition. However, the Shaxi porphyry Cu–Au deposit shows characteristics of calc-alkaline series magmatism. The rocks in the Anqing and Tongling areas belong to the high-potassic calc-alkaline series. The rock series with Na-enriched alkaline mafic association in the region show low values of SiO₂ (46–56%), high alkali values of K₂O (5.0–7.1%), and high values of Na₂O/K₂O ratio (1.4–4.3) (Yang 1996; Xing and Xu 1999; Chen et al. 2001). These rocks occur along the Yangtze River near the cities of Nanjing, Wuhu, and Tongling with one outcrop close to the Tancheng-Lujiang fault. The associations of high-potassic calc-alkaline series or calc-alkaline series occurring in the area N of the Yangtze River consist of monzonite and granite stocks. Diorite, quartz diorite, and granodiorite stocks are distributed along the Yangtze River. These rocks are closely associated with the important copper, iron, sulphur, and gold ore deposits (Chang et al. 1991). Intrusions distributed in the region S of the Yangtze River include granites and granodiorites, occurring as batholith and stocks. They are sulphur-type granites in terms of
chemical composition and mineralogy (Chen et al. 1993). Some molybdenum ore deposits are associated with this group of intrusions (Chang et al. 1991).
**Isotopic geochemistry**

**Sulphur isotope**

To determine the isotopic variations of the ores, we systematically collected samples from the different ore bodies. We separated the minerals by handpicking and by standard heavy liquid and magnetic separator techniques. We broke down the samples into less than 120 meshes to obtain purified pyrite and chalcopyrite. Sulphur isotope data measured in this deposit and those of typical Cu deposits in China are summarized in Table S1 (see online supplementary data available at http://www.informaworld.com/tigr). Some measurements were performed at the Institute of Coal Science, Xi’an, China, using standard techniques. The reappearance of the data is good and the accuracy is below 0.5‰. All the results are expressed relative to the CDT standard.

The sulphur isotopic ratios in the Shaxi–Changpushan porphyry Cu–Au deposit range from $-0.3‰$ to $3.0‰$ in $\delta^{34}S$ values; it can be calculated that the total $\delta^{34}S$ value is nearly $1.1‰$ with the paragenesis of sulphides (Pickney 1972). The very narrow variation in $\delta^{34}S$ values is similar to those of the larger or superlarge porphyry Cu deposits such as those porphyry Cu–Au deposits in Dexing, Yulong, and Duobaoshan in China (Rui et al. 1984). The result shows the very homogeneous resources of sulphur and ore solution during mineralization, demonstrating that the mineralization mechanism in the Shaxi–Changpushan porphyry Cu–Au deposit is similar to those large or superlarge porphyry Cu deposits in China. However, the sulphur isotope composition in the adjacent areas such as the Tongling skarn Cu–Au deposit, the Luzong volcanic basin, and the Anqing deposit shows a larger difference, ranging from $-29.6‰$ to $15.3‰$, $-11.2‰$ to $18.8‰$, and $-11.1‰$ to $15.2‰$, respectively.

The regional variations of sulphur isotope compositions from some Cu–Au deposits in China are shown in Figure 5. It can be seen that the sulphur isotope values from sulphides are very homogeneous in the Shaxi porphyry Cu–Au deposit, the Duobaoshan porphyry Cu deposit, the Yulong porphyry Cu deposit, and the Dexing porphyry Cu deposit; whereas in the Tongling skarn Cu–Au deposit, the Luzong volcanic area, and the Wushan skarn Cu–Au deposit, the sulphur isotope values are very heterogeneous. The narrow sulphur isotope values in these Cu–Au deposits may indicate that sulphides have a relatively homogeneous source in contrast to those deposits with an inhomogeneous source of sulphides.
Figure 4. SiO₂ versus Al₂O₃, K₂O, and Na₂O/K₂O diagrams (after Rickwood 1989; Rollinson 1993), which show variations of the different igneous rock associations concerning the Cu–Au mineralization in Anhui Province (data after Chang et al. 1991; Ren et al. 1991; Xing and Xu 1995; Xing and Xu 1996; Xing 1998; Xing and Xu 1999; Yang et al. 2006).

The sulphur isotopes in these deposits show a large range distribution according to their different sources of ore-forming processes during the formation of these different types of Cu–Au deposits. This can be explained by the different Cu–Au mineralizations caused by different geological processes and fluid interaction.
Figure 5. Histogram diagram showing the regional variations of sulphur isotope compositions of sulphides in Cu–Au deposits in China.

Oxygen and hydrogen isotopes

Oxygen and hydrogen isotopic data from some typical Cu deposit in China are summarized in Table S2 (see online supplementary data). Figure 6 plots the range of oxygen isotope values for some Cu–Au deposits. It can be seen that the largest variations in quartz are in the Shaxi porphyry Cu–Au deposit and the Tongling skarn Cu–Au deposits with ranges from −1.3‰ to 24.5‰. Variations in quartz in the Anqing massive hydrothermal Cu–Au deposit and the Yulong porphyry Cu deposit in Tibet have narrow values ranging from 6.7‰ to 13.8‰ and from 7.3‰ to 10.3‰, respectively. However, the oxygen isotope values vary in fluids in equilibrium with quartz and other monominerals: around −4.7‰ to 5.5‰ variations in the Shaxi porphyry Cu–Au deposit; 2.1–8.9‰ variations in the Anqing massive hydrothermal Cu–Au deposit; around −2.6‰ to 8.0‰ variations in the Dexing porphyry Cu deposit; −6.9‰ to 8.3‰ variations in the Yulong porphyry Cu deposit; and 1.3–10.7‰ variations in the Tongling skarn Cu–Au deposits. These characteristics may reflect the different fluid histories during the formation of each deposit.

According to the hydrogen isotopic data from fluid inclusion and oxygen isotopic data from quartz and other monominerals in this study and other studied results (e.g. Riu
X.-Y. Yang and I. Lee

Figure 6. Histogram diagram showing the regional variation of oxygen isotope compositions in the Cu-Au deposits in the lower Yangtze region in China.

et al. 1984; Chang et al. 1991; Ren et al. 1991), δD and δ¹⁸O values of ore-forming fluids range from −59.9‰ to −82.4‰ and from 3.5‰ to 5.5‰ in the Shaxi-Changpushan porphyry Cu-Au deposits, respectively; from −46.1‰ to −127.3‰ and from −3.4‰ to 10.0‰ in the Dexing porphyry Cu deposit, respectively; and from −94.0‰ to −102.1‰ and from −6.9‰ to 5.5‰ in the Yulong and Malasongduo porphyry Cu deposits in Tibet, respectively. This indicates that the ore-forming fluids in these different porphyry Cu-Au deposits have different evolutionary histories with large variations in oxygen and hydrogen isotopic compositions. In other kinds of Cu-Au deposits along the middle and lower parts of the Yangtze region, such as the Tongling, Anqing, Luzong, and Wushan regions, the δD and δ¹⁸O values of ore-forming fluids range from −53‰ to −191‰ and from 0.2‰ to 11.8‰, respectively; from −62‰ to −78‰ and from 2.1‰ to 8.9‰, respectively; from −66‰ to −111‰ and from −5.6‰ to 11.2‰, respectively; and from −51.6‰ to −84.4‰ and from −3.5‰ to 9.6‰, respectively. The ore-forming fluids for these different types of Cu-Au deposits have even larger variations of oxygen and hydrogen isotopic compositions compared with those of the porphyry Cu-Au deposits along the middle–lower parts of the Yangtze region.
Figure 7 shows $\delta D$ versus $\delta^{18}O$ of the ore fluids from different Cu–Au deposits, from which it can be seen that most of the data from the Wushan Cu–Au deposit show the mixtures of magmatic water and meteoric water: one sample near the box of origin of magmatic water and one sample within the box of origin of magmatic water. In the Shaxi Cu–Au deposit, four data sets show the mixture of magmatic water and meteoric water. Two samples are plotted in the box of origin of magmatic water, and three samples are near the edge of the box of magmatic water; however, there are several samples plotted far outside the box of magmatic water, which cannot be interpreted as simply a mixture of magmatic water and meteoric water. In the Luzong volcanic thermal Cu–Au deposit, two samples belong to a mixture of magmatic water and meteoric water and one sample is outside the box of magmatic water. In the Tongling skarn Cu–Au deposit, most of the plots are located within the box of magmatic water but some samples are outside the box, which could be interpreted as a participation of formation water or meteoric water that reacted with carbonate wall rock during the Cu–Au mineralization.

**Summary**

(1) Cu–Au mineralization in the middle-lower Yangtze Valley consists mainly of three types: skarn, porphyry, and volcanic/thermal mineralization. The sulphur isotope study shows that the major source of sulphur in the sulphides was magmatic in origin, whereas some was derived from a sedimentary source.

(2) Oxygen isotope values for quartz in the Shaxi porphyry Cu–Au deposit and the Tongling skarn Cu–Au deposit – ranging from 2.6‰ to 12.5‰ and from $-1.3‰$ to 24.5‰, respectively – exhibit wide variations compared with other Chinese Cu–Au deposits.

(3) Sulphur isotope data indicate a very homogeneous source of sulphur and ore solutions during most porphyry Cu–Au mineralization, although relatively large, heterogeneous variations of sulphur and ore solutions were present during skarn Cu–Au mineralization.

Figure 7. Hydrogen versus oxygen isotope diagram of the ore fluids in Cu–Au deposits in China.
(4) Based on the hydrogen and oxygen isotopic data, we infer that the ore-forming fluids had different origins. The most important involved mixtures of magmatic water and meteoric water (such as in the Wushan, Shaxi, and Luzong regions); the second most important was a strictly magmatic water source (also as in the Wushan, Shaxi, and Luzong regions); and the third most important probably was from a mixture of formation water and meteoric water that reacted with carbonate wall rocks (such as in the Tongling, Shaxi, and Luzong regions).

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