Geochronology and geochemistry of submarine volcanic rocks in the Yamansu iron deposit, Eastern Tianshan Mountains, NW China: Constraints on the metallogenesis

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1. Introduction

Dill (2010) classified iron ores into four types: magmatic, structure-related, sedimentary and metamorphic. The magmatic iron deposits are further divided into five subgroups: 1) Fe–Ti–(V) deposits related to mafic intrusions; 2) apatite-bearing Fe oxide deposits (Kiruna-type); 3) apatite-bearing Fe oxide deposits related to alkaline igneous rocks; 4) volcanic-hosted Fe (unmetamorphosed) deposits; and 5) contact metamorphic Fe deposits (Fe skarn). Most of the major high-grade iron ores of the world are predominantly sourced from sedimentary and metamorphic iron deposits (Clout and Simonson, 2005). In contrast, skarn type deposits constitute the most important source for high-grade iron ores in China (Zhou et al., 2004), together with some Kiruna-type and submarine volcanic-hosted iron ore deposits.

The metallogenesis of submarine volcanic-hosted iron ore deposits is poorly understood (Dill et al., 2008). Most of these deposits in China are commonly characterized by extensive skarn alteration, such as the Mengku in Altai (Xu et al., 2010); Beizhan and Chagangnuoer in western Tianshan (Hong et al., 2012; Zhang et al., 2012); and Dahongshan in southern Yangtze craton (Zhao and Zhou, 2011). However, these skarns lack any clear spatial link with intrusive rocks and are therefore distinct from the conventional types (e.g., Einaudi et al., 1981), leading to debates on the genesis of these deposits over decades (e.g., Jiang and Wang, 2005). Some authors suggest that the skarns could be genetically related to a buried intrusion (Mao et al., 2005), whereas others consider them to be related to coeval submarine volcanism (Jiang, 1983). Accordingly, these deposits have been classified into two contrasting types: intrusion-related skarn deposit (e.g., Mao et al., 2005; Pirajno, 2010; Yang et al., 2010) and submarine volcanic exhalation sedimentation type (e.g., Jiang, 1983).

The Yamansu iron deposit in Eastern Tianshan Mountains (Pirajno, 2010) is a typical example for the latter type of deposit. The iron
mineralization in the Yamansu deposit is stratabound, with thickness varying from 100 to 130 m, and spatially related to the garnet-dominant skarns (Mao et al., 2005). In this paper, we report zircon LA-ICP-MS ages for both volcanic rocks and garnet skarn, with a view evaluating their genetic linkage. From bulk-rock geochemistry and Sr–Nd isotopic compositions of the ore-hosting volcanic rocks, we discuss the petrogenesis and geodynamic setting of the iron deposit.

2. Geological setting

2.1. Regional geology

The Tianshan orogenic collage extends for about 2400 km—from the Aral Sea eastwards through Uzbekistan, Tajikistan, and Kyrgyzstan, to Xinjiang in China and is an important component of the Central Asian Orogenic Belt (CAOB; De Grave et al., 2012; Dong et al., 2011; Kröner et al., 2011, 2013; Lei et al., 2011; Long et al., 2012; Rojas-Agramonte et al., 2011; Windley et al., 2007; Wong et al., 2010; Xiao et al., 2004a,b, 2010, 2013; Xiao et al., 2012). The Paleozoic tectonic evolution history of the Eastern Tianshan remains controversial. Some researchers have suggested that the Eastern Tianshan resulted from the southward subduction of the Junggar Ocean along the Dananhu–Tousuquan belt (Ma et al., 1993; Qin, 2000; Zhang et al., 2004), whereas others consider a northward subduction of the south Tianshan Ocean (Wang et al., 2006b). The main structures of the Eastern Tianshan consist of a series of approximately east–west-trending faults, including the regional-scale Kalamaili, Kanggur, Aqishan–Yamansu, Weiya, Aqqikkudug and Kumishi faults (Fig. 1).

The Eastern Tianshan is bound to the north by the Turpan–Hami (commonly abbreviated as Tuha) basin, which is a part of the Junggar block, and to the south by the Aqqikkudug fault, which separates this northern belt of the Tianshan from the Middle Tianshan (or Central Tianshan). The Eastern Tianshan mainly consists of three tectonic units: Bogeda–Haerlike Belt in the north, Jueluotage Belt in the center and Middle Tianshan Microblock in the south (Fig. 1; Xu et al., 2009).

The Bogeda–Haerlike Belt is made up of well developed Ordovician–Carboniferous volcanic rocks, granites and mafic–ultramafic complexes (BGMRXUAR, 1993; Gu et al., 2001; Li et al., 2006). The Middle Tianshan microblock is composed of Precambrian crystalline basement (BGMRXUAR, 1993; Qin et al., 2002), and is bound by the Aqikudud–Shaquanzi Fault in the north and the Hongliuhe Fault in the south (Fig. 1). Abundant granites and granite gneisses are exposed in the Precambrian crystalline basement of this block (BGMRXUAR, 1993; Qin et al., 2002; Xu et al., 2009).

The Jueluotage Belt is characterized by Middle Paleozoic volcanic and sedimentary rocks, including subaerial volcanics, sandstones and pelitic slates with inter-layered limestones, mudstones, siltstones and conglomerates (BGMRXUAR, 1993). This belt can be further subdivided, from north to south, into the Wutongwozi–Xiaorequanzi belt, Dananhu–Tousuquan belt, Kanggur–Huangshan ductile shear zone and Yamansu belt (Fig. 1; Qin et al., 2002). The Dananhu–Tousuquan belt is made up of Devonian to Carboniferous volcanic and intrusive rocks, and several porphyry copper deposits (e.g. Tuwu and Yandong) occur in this belt (Fig. 1. Gu et al., 2001; Li et al., 2006). The high-Mg andesites, adakite and Nb-rich basalts recognized in this belt have led to the interpretation of an arc setting (Wang et al., 2006b). The Wutongwozi–Xiaorequanzi belt and Kanggur–Huangshan ductile shear zone are characterized by Carboniferous sedimentary rocks, and the latter hosts Cu–Ni deposits associated with mafic complexes (e.g. Huangshan and Xiangshan) as well as porphyry deposits (e.g. Sanchakou Cu–Mo and Baishan Mo–Re), located between the Kanggur and Aqishan–Yamansu faults (Fig. 1). The Yamansu belt lies between the Aqishan–Yamansu fault, which marks the southern boundary of the Kanggur–Huangshan ductile shear zone, and the Aqqikkudug fault (Fig. 1). The exposed rocks comprises a ~5 km thick succession of Mississippian bimodal volcanic rocks of the Yamansu Formation, Pennsylvanian flaky of the Shaquanzi Formation, and clastic rocks, andesitic tuff, and intercalated carbonate rocks of the Tugutublak Formation and overlying Permian marine and terrestrial clastic rocks, which are intercalated with bimodal volcanic rocks and carbonate rocks. Extensive Carboniferous–Permian magmatism resulted in the emplacement of high-Na, relatively
oxidized, sub-alkaline magmas (Qin et al., 2002, 2003). Although many workers proposed that the volcanic rocks in the Yamansu formation were generated in a back-arc basin setting (Li et al., 2002; Xiao et al., 2004a,b) the tectonic regime of the belt is still debated. Several high-grade iron ore deposits such as the Yamansu, Kumutag, Bailingshan and Hongyuntan, have been recognized in these volcanic rocks (Fig. 1).

2.2. Deposit geology

2.2.1. Stratigraphy and igneous rocks

The Yamansu iron deposit occurs about 80 km south of Hami City (Fig. 1). Regionally, the exposed strata consist of Lower Carboniferous Yamansu Formation, Upper Carboniferous Shaquanzi Formation, and Lower Permian Aqikebulake Formation. Around the Yamansu open pit, the Yamansu Formation comprises intermediate-mafic lava and pyroclastic rocks, limestone and minor felsic rocks. The Shaquanzi Formation mainly comprises flysch, and is overlain by the Lower Permian marine and terrestrial clastic rocks, which are intercalated with bimodal volcanic rocks and carbonate rocks. A number of faults have been recognized surrounding the deposit, and they include five NNE to ENE-trending faults (Fig. 2).

The lava flows are predominantly basaltic with minor andesite in the Yamansu deposit. The basaltic and andesitic lavas display a gradational contact, and the two rock types cannot be easily distinguished in hand specimen. These flows are generally several meters thick, rarely up to 100 m. The lava flows are interbedded within pyroclastic rocks. The basalts are dark gray to dark green, and are locally amygdaloidal with calcite, chalcedony and chlorite. These rocks show typical porphyritic texture (Fig. 3a), and contain phenocrysts of partially to completely altered plagioclase (~40%), amphibole, pyroxene altered to chlorite (~30%), and minor biotite. The groundmass is fine grained, with interstitial or intergranular texture, and consists predominantly of plagioclase and augite with minor accessory anhedral iron oxides,apatite, biotite and hornblende. The andesites possess a mineral assemblage and textural features similar to those of the basalts, but with considerably lower contents of clinopyroxene.

No intrusions have been identified at the Yamansu deposit, except for the subvolcanic pyroxene–diorite porphyry exposed about 500 m southwest of the orebodies (Fig. 2a). However, a gravity survey suggests that some buried intrusive rocks might be present at depth (Mao et al., 2005). Several ancient volcanic edifices were recognized adjacent to the deposit on the basis of remote sensing and facies analysis of the

Fig. 2. Geological (a) and cross-section (b) map of the Yamansu deposit. Modified form Mao et al., 2005.
volcano-sedimentary rocks. The Yamansu volcanic lavas are considered to be located within or adjacent to a volcanic centre (BGMRXUAR, 2010).

### 2.2.2. Orebodies

The Yamansu iron deposit contains a reserve of 32 Mt with an average grade of 51% Fe (Mao et al., 2005). Eighteen orebodies have been recognized in the deposit and occur as EW-trending stratiform, banded podiform to lenticular bodies (Fig. 2). Nos. 1, 2, 4, 7 and 8 orebodies are the largest, and Nos. 1 and 2 orebodies are the most economic. No. 1 orebody is >940 m long, and dips southwards with the dip angle of 43° at surface (980 m above sea level) to 72° at 420 m above sea level. The average width of the No. 1 orebody is 8.6 m. The No. 2 orebody strikes ~1300 m discontinuously, dip southwards at 59° and is 7–17 m wide. Country rocks to orebodies are mainly mafic lavas and pyroclastic rocks intercalated with limestone of Yamansu Formation (Fig. 3c). The orebodies are mostly conformable with their country rocks (Fig. 2b).

Based on mineral assemblages, three types of ores have been identified: garnet–magnetite, garnet–magnetite–pyrite, and magnetite–pyrite (BGMRXUAR, 2010). Field evidence and petrographic observation indicate four stages of mineralization: (1) prograde stage: garnet + albite + apatite, (2) retrograde stage: magnetite + epidote + chlorite + quartz + amphibole + apatite, (3) sulfide stage: pyrite + chalcopyrite + pyrrhotite + chlorite + quartz + calcite + galena + sphalerite, and (4) supergene stage: hematite + malachite + siderite + quartz + calcite (BGMRXUAR, 2010). Magnetite is the predominant ore mineral which occurs together with minor hematite, pyrite and chalcopyrite. The gangue minerals consist of garnet, hornblende, biotite, chlorite, epidote, quartz, calcite and other calc-silicate minerals (Mao et al., 2005). Ore textures include massive, banded, disseminated and irregular.

The sulfide stage is dominated by pyrite, chalcopyrite and pyrrhotite. Pyrite occurs as cubes in massive veins (<5 mm) or as isolated grains with amphibole and plagioclase, which often display cavities and embayed margins. Calcite and minor quartz are the main gangue minerals in this stage. They usually cut the earlier formed minerals like garnet and amphibole as veins or stockworks. Hematite, siderite and malachite are restricted to the supergene stage.

### 2.2.3. Skarns

Skarn is ubiquitous and intensively developed in the Yamansu deposit, with a strike length of ~1000 m, a depth in excess of 600 m and an average width of 120 m as demarcated from surface mapping and diamond drilling (Fig. 2). The skarn shows a distinct boundary with the country rocks (Fig. 3d). The dominant skarn minerals are garnet with subordinate amphibole, epidote, chlorite, pyroxene, albite, as
well as magnetite, pyrite, chalcopyrite and pyrrhotite. Relics of garnet and epidote can be observed in massive ores (Fig. 3e). The prograde stage is characterized by formation of a large amount of garnet (grossularite–andradite; Fig. 3f). In contrast, pyroxene is very limited (<5%) and typically occurs as random pods (Ding, 1990). The retrograde stage is characterized by hydrous alteration, and dominated by epidote, and minor amphibole and chlorite (Fig. 3b), which replace the prograde minerals to variable degrees. The epidote is closely associated with the magnetite (BGMRXUAR, 2010). The amphibole veins commonly cut across garnets, indicating that amphibole formed later than garnet (Fig. 3f). During the late retrograde stage, a large quantity of magnetite, and epidote, amphibole, chlorite and garnet formed. Epidote is the most common mineral in the strongly retrograde altered rocks. Field relations and petrographic studies on the mineral paragenesis reveal that the skarn at Yamansu is similar to other conventional iron-bearing skarn deposits (Einaudi et al., 1981; Meinert, 1992).

3. Analytical methods

3.1. Zircon U–Pb dating and Lu–Hf isotopes

Zircons were separated from one ~20 kg basalt sample (YMS–44) and ~30 kg mineralized garnet skarn sample (YMS–45) by conventional heavy liquid and magnetic techniques, and then handpicked under a binocular microscope. Zircon grains were mounted on adhesive tape then enclosed in epoxy resin and polished to about half of their diameter. In order to observe textures of the polished zircons, CL imaging was carried out using a Hitachi S3000-N scanning electron microscope (SEM) with Mono CL3 Cathodoluminescence System for high resolution imaging and spectroscopy at the Institute of Geology, Chinese Academy of Geological Sciences (CAGS). Zircon U–Pb dating was performed by Finnigan Neptune multi-collector ICP-MS with a Newwave UP213 laser-ablation system at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. Helium was used as the carrier gas to enhance the transport efficiency of the ablated material. The analyses were conducted with a beam diameter of 25 μm with a 10 Hz repetition rate and a laser power of 2.5 J/cm² (Hou et al., 2009). The masses 206Pb, 207Pb, 204Pb + Hg and 202Hg were measured by multi-ion-counters, while the masses 208Pb, 232Th, 235U and 238U were collected by Faraday cup. Zircon G1 was used as the standard and zircon Plesovice was used to optimize the machine. U, Th and Pb concentrations were calibrated using 206Pb as the internal standard and zircon M127 (U: 923 ppm; Th: 439 ppm; Th/U: 0.475, Nasdala et al., 2008) as the external standard. 207Pb/206Pb and 206Pb/238U ratios were calculated using the ICPMSDataCal 4.3 program (Liu et al., 2008). The common-Pb was not corrected because of the high 206Pb/204Pb ratios (> 1000). Data with abnormally high 204Pb counts were deleted. The zircon Plesovice is dated as unknown samples and yielded weighted mean 206Pb/238U age of 337 ± 2 Ma (2SD, n = 12), which is in good agreement with the recommended 206Pb/238U age of 337.13 ± 0.37 Ma (2SD) (Sláma et al., 2008). The age calculation and plotting of concordia diagrams were performed using Isoplot/Ex 3.0 (Ludwig, 2003).

The zircon Hf analytical procedures followed those described in K.J. Hou et al. (2007). All analyses were performed using a Neptune MC–ICP-MS located at CAGS. This mass spectrometer is equipped with double-focusing multi-collectors. A Geolas 200M laser ablation system (MicroLas, Göttingen, Germany) was used equipped with an ArF excimer 193 nm laser. In this study, a 40 μm laser spot size was selected during the ablation with a repetition rate of 8 Hz. Measured 176Hf/177Hf ratios were not corrected for isotopic interferences of 176Lu on 177Hf due to the extremely low 176Lu/177Hf in zircon (normally ~0.002). 177Lu/176Hf = 0.02655 was used for elemental fractionation correction. Isotopic interference of 176Yb on 177Hf was corrected using the mean fractionation index proposed by liuzuka et al. (2005). The applied value of 176Yb/172Yb is 0.5886 (Vervoort et al., 2004). A 176Hf/177Hf ratio of 0.282007 ± 7 (2σ, n = 36) was obtained for zircon G1, which is identical to values obtained by the solution method (K.J. Hou et al., 2007). Analytical data of this study were corrected using a 176Hf/177Hf ratio of 0.281994 ± 15 of zircon G1 (mean square weighted deviation = 2.2, n = 12).

3.2. Mineral chemistry

Microprobe analyses of garnets in skarn were performed by wavelength dispersive analysis (WDS) using standard procedures on the JXA-8200 electron microprobe at Washington University in St. Louis (MO, USA), using “Probe for Windows” for data reduction (see http://www.probesoftware.com/). Electron microprobe analyses were performed on clinopyroxene, plagioclase and magnetite, and the measured data were corrected using CITZAF after Armstrong (1995). Oxide and silicate standards were used for calibration (e.g., Amelia albite for Na, Si; microcline for K; Gastes wollastonite for Ca; Alaska Anorthite for Al; synthetic fayalite for Fe; synthetic forsterite for Mg; synthetic TiO2 for Ti; synthetic Mn-olivine for Mn; synthetic Cr2O3 for Cr).

3.3. Major and trace elements

After screening under the microscope, relatively fresh samples of the basalts were selected and sawed into slabs and the central parts were used for whole-rock analyses. Specimens were crushed in a steel mortar and ground in a steel mill to powders of ~200 mesh. Major elements were acquired through the analysis of fused glass disks using a scanning wavelength dispersion X-ray fluorescence (XRF) spectrometer at the Key Laboratory of Orogenic Belts and Crustal Evolution, Ministry of Education, School of Earth and Space Sciences, Peking University. The analytical uncertainties are less than 1%, estimated from repeated analyses of two standards (andesite GSR-2 and basalt GSR-3). Loss on ignition was determined gravimetrically after heating the samples at 980 °C for 30 min.

Trace elements were determined by solution ICP-MS performed at the ICP-MS Laboratory at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. After complete dissolution, powders (~40 mg) were dissolved in distilled HF + HClO4 in 15 ml Savillex Teflon screw-cap breakers. Precision for most elements was typically better than 5% RSD (relative standard deviation), and the measured values for Zr, Hf, Nb and Ta were within 10% of the certified values. Two standards (granite GSR-1, basalt GSR-3) were used to monitor the analytical quality.

3.4. Sr–Nd isotopes

Relatively fresh samples of basaltic lava were chosen for Sr–Nd isotope analyses. Rb–Sr and Sm–Nd isotopic compositions were obtained using a Finnigan Triton TI mass spectrometer at the Department of Earth Sciences, Nanjing University. Sr and Nd isotopic ratios were normalized against 86Sr/88Sr = 0.1194 and 146Nd/144Nd = 0.7219, respectively. 87Sr/86Sr for the NIST987 Sr standard was 0.710268 ± 0.000007 (2σ standard deviation, n = 8), and 143Nd/144Nd for the La Jolla Nd standard was 0.511842 ± 0.000006 (2σ standard deviation, n = 6). Total blanks were 100 pg for Sr and 80 pg for Nd, and negligible for the determination of isotopic compositions.

4. Results

4.1. Zircon U–Pb dating and Hf isotope

Zircon grains separated from the basalt (sample YMS–44) are generally transparent, euhedral, and prismatic, with clear oscillatory zoning (Fig. 4a) and high Th/U values (1.03–2.48, Table 1), typical of igneous zircons (Corfu et al., 2003). The measured U–Pb isotopic ratios are...
presented in Table 1. A group of seven zircon grains defines a concordia age of 324.4 ± 0.94 Ma (95% confidence level, MSWD of 1.7; Fig. 4a), interpreted as the crystallization age for the basalts of Yamansu Formation.

Compared with the zircon grains in the basalt, those from the skarn (sample YMS-45) are much darker, lack any obvious oscillatory zoning (Fig. 4b), and show lower Th/U values (0.85 – 1.27; Table 1). These features indicate zircon precipitation from hydrothermal fluids similar to those reported by Hu et al. (2004) from a quartz vein in the Rushan lode gold deposit in the Jiaodong Peninsula, Eastern China. Five zircon grains yield ages between 322.6 to 324.7 Ma, with a mean weighted age of 323.47 ± 0.95 Ma and MSWD of 0.68 (Fig. 4b), coeval with the basalts. Since most of the zircons from the basalts were damaged during age determinations, Lu–Hf analyses are given only for two grains, which show $\varepsilon_{Hf}(t)$ range of +10.13 to +13.51. Five zircons from the mineralized skarn define a relatively wide $\varepsilon_{Hf}(t)$ range of −1.26 to +8.40, significantly lower than those for basalts (see Table 2).

4.2. Garnet compositions

Electron microprobe analyses show that all garnets in the Yamansu deposit are calcium-rich in composition (Table 3). End-member calculations show that the garnet is mainly andradite and grossular (>90%; Fig. 5) with a compositional range of $\text{And}_{52.65-97.16}\text{Gro}_{0.00-42.13}(\text{Spe} + \text{Alm})_{1.09-5.08}\text{Py}_0.05-0.76$. Zoned garnets are characterized by a relatively Fe-rich core and Al-rich rim. On ternary plots of garnet compositions from major skarn types (Fig. 5), our data plot within the fields defined by conventional iron skarn (Meinert, 1992) and iron skarn related to submarine volcanic rocks in China (Hong et al., 2012; Xu et al., 2010), but are markedly different from those associated with VMS deposits, which are typically dominated by Mn- and Fe-rich spessartine and almandine, such as the Sawusi Pb–Zn–Fe oxide deposit in Chinese Altai (Liu et al., 2012) and the Aguilar Pb–Zn–Ag deposit in Argentina (Gemmell et al., 1992) which are typically dominated by Mn- and Fe-rich spessartine and almandine (Fig. 5).

4.3. Geochemical variations of volcanic rocks

The major elements of the samples are recalculated on a volatile free basis, because some of the samples show loss on ignition up to 4.88 wt.%, possibly due to post-magmatic alteration (Fyfe, 1976; Melson et al., 1968). According to their degree of alteration, the basalts can be classified into two types: basalts and epidote-alteration basalts. The basalts are characterized by a slight variation in $\text{SiO}_2$. 

Fig. 4. CL image and U–Pb concordia diagrams for zircons from basalt (YMS-44) and skarn (YMS-45).
initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.706 to 0.709), and of a primary mantle source (e.g., Frey et al., 1978). Parent magmas presumed to have been derived from partial melting of the Yamansu basalts are given in Table 5. The data show variable $^{207}\text{Pb}/^{206}\text{Pb}$ (17.32–19.93) and $^{176}\text{Yb}/^{171}\text{Hf}$ (46.61 wt.%), $^{207}\text{Pb}/^{206}\text{Pb}$ (0.08–0.12 wt.%), $^{176}\text{Hf}/^{177}\text{Hf}$ (44.54 ppm), $^{71}\text{Mg} (71.91 \text{ ppm}), \text{Co} (4.79 \text{ ppm}), \text{MnO} (0.35 \text{ wt} \%.), \text{MnO} (0.35 \text{ wt} \%), \text{and TiO}_2 (0.74–8.14 \text{ wt} \%).$...  }
5.2. Volcanic series and magma evolution

Confirming which volcanic rock series the Yamansu volcanic rocks belong to is very important to discriminate the tectonic setting of the volcanic rocks. The Nb/Y ratios (< 0.06), and the Zr/TiO2 versus Nb/Y relations (Fig. 7a) show that they are sub-alkaline (Winchester and Floyd, 1976). Plots of the Yamansu basalts in Zr versus Y diagram (e.g. Green, 1976; Hanson and Langmuir, 1978). Hence, the Mg# range between 45 and 62 for the Yamansu basalts, together with low Cr (44.54–71.91 ppm), Co (4.79–24.92 ppm) and Ni (17.32–34.83 ppm) indicate that the basalts of the Yamansu Formation are evolved.

In the Yamansu deposit, the basalts contain clinopyroxene and plagioclase phenocrysts with Fe–Ti oxide minerals in the groundmass as interstitial phases (Fig. 3a). Furthermore, SiO2, Al2O3 and total Fe2O3 show a weak negative correlation with MgO, whereas TiO2 remains constant with decreasing MgO (Fig. 8a–d). These features, combined with the low Ni and Cr contents as stated above, suggest the fractionation of olivine-, clinopyroxene- and plagioclase during magma chamber processes. Previous mineral chemistry studies on clinopyroxene phenocrysts in Yamansu basalts suggest crystallization temperatures around ~1150 °C (G.S. Hou et al., 2007). Thus, the depth of crystallization of the clinopyroxene phenocryst is about 4–10 km, indicating the existence of a shallow magma chamber under the sea floor. Considering that the Yamansu lavas are located near the ancient volcanic centre, we infer that the magma chamber was not far away from the ore deposit. This inference is also supported by a gravity survey which indicates an additional buried pluton may be present beneath the deposit. This inference is also supported by a gravity survey which indicates an additional buried pluton may be present beneath the deposit. This inference is also supported by a gravity survey which indicates an additional buried pluton may be present beneath the deposit. This inference is also supported by a gravity survey which indicates an additional buried pluton may be present beneath the deposit. This inference is also supported by a gravity survey which indicates an additional buried pluton may be present beneath the deposit.

The εNd(t) values (Table 5), the depleted LREE patterns and MORB-like signatures for most of the samples indicate that these rocks originated by partial melting of an asthenospheric mantle source with a depleted Nd isotopic composition similar to present day MORB. Therefore, the enrichment of the LILEs (e.g. Th), relative depletion of suggested Mg# ≥ 67 and FeOt/MgO ratios < 1.1, whereas Tsubumi and Eggs (1995) have documented Mg# > 70 and FeOt/MgO ratios < 1 for primary basaltic magmas. Moreover, primary magmas are characterized by 250–300 ppm Ni, 500–600 ppm Cr and 27–80 ppm Co contents (Frey et al., 1978; Perfit et al., 1980; Wilkinson and Le Maitre, 1987). Hence, the Mg# range between 45 and 62 for the Yamansu basalts, together with low Cr (44.54–71.91 ppm), Co (4.79–24.92 ppm) and Ni (17.32–34.83 ppm) indicate that the basalts of the Yamansu Formation are evolved.

5.2. Nature of the mantle source

Generally, magmas originating from the asthenospheric mantle are characterized by depletion in incompatible elements and high εNd(t) values (Saunders et al., 1992). This is the case for the most of Yamansu basalts. The positive εNd(t) values (Table 5), the depleted LREE patterns and MORB-like signatures for most of the samples indicate that these rocks originated by partial melting of an asthenospheric mantle source with a depleted Nd isotopic composition similar to present day MORB. However, the enrichment of the LILEs (e.g. Th), relative depletion of
The high-field strength elements (HFSEs) (Nb and Ti), and the HREE (Yb) are characteristic features of magmas generated in supra-subduction zone settings (e.g., Wilson, 1989). The basalt sample YMS-29 shows a variable enrichment in LREE (Fig. 6) with (La/Yb)N ratio of 2.62, and LILE (e.g. Th = 0.15 ppm) (Table 4). Therefore, the Yamansu volcanic rocks were derived from slightly enriched mantle in source areas because fluids derived from a subducted slab is known to result in high Th and low Nb in the upper mantle wedge (Pearce et al., 1995).

The whole-rock REE contents of primary magmas are mainly controlled by mantle composition and degree of partial melting and they have been widely used to determine the origin of magmas (e.g., Green, 2006; Gurenko and Chaussson, 1995; Johnson, 1998; Münker, 2000). The REE are moderately incompatible during melting of mantle peridotite (Pearce et al., 1995). Clearly indicating a subduction component in their source areas because fluid/melt released from a subducted slab is known to result in high Th and low Nb in the upper mantle wedge (Pearce et al., 1995).

The high-field strength elements (HFSEs) (Nb and Ti), and the HREE (Yb) are characteristic features of magmas generated in supra-subduction zone settings (e.g., Wilson, 1989). The basalt sample YMS-29 shows a variable enrichment in LREE (Fig. 6) with (La/Yb)N ratio of 2.62, and LILE (e.g. Th = 0.15 ppm) (Table 4). Therefore, the Yamansu volcanic rocks were derived from slightly enriched mantle influenced by a crustal/subduction component. The HFSE depletions (e.g. Nb) are generally believed to be caused by the immobility of HFSE in fluids dehydrated from the subducting oceanic crust and/or sediments in a convergent margin (e.g., McCulloch and Gamble, 1991; Pearce and Peate, 1995 and references therein). For example, the typical Nb contents of arc basalts (tholeiites) are about 1.7 ppm (Pearce, 1982). It has been reported that the altered oceanic crust and fluids derived from altered oceanic crust are also characterized by low to extremely low Nb contents (1.22 and 0.364, respectively; Chiaradia, 2009). In the Nb/Ta vs. Zr/Sr diagram, our sample data overlap the arc magma field (Fig. 9b), suggesting the contribution of an arc-like source (Foley et al., 2000; Saunders and Tarney, 1984). This is further supported by the Nb/Yb vs. Th/Yb relationship (Fig. 9a), where our samples plot above the MORB-OIB array (Pearce and Peate, 1995), clearly indicating a subduction component in their source areas because fluid/melt released from a subducted slab is known to result in high Th and low Nb in the upper mantle wedge (Pearce et al., 1995).

The whole-rock REE contents of primary magmas are mainly controlled by mantle composition and degree of partial melting and they have been widely used to determine the origin of magmas (e.g., Green, 2006; Gurenko and Chaussson, 1995; Johnson, 1998; Münker, 2000). The REE are moderately incompatible during melting of mantle peridotite (Johnson, 1998), and thus, their concentrations and ratios are not greatly affected by mantle depletion and fluid influx (Münker, 2000; Pearce and Peate, 1995). In general, the heavy REE (e.g. Yb and Y) are preferentially retained by garnet during melting (cf. Zhang et al., 2008), and thus, low La/Yb ratios reflect a melting regime dominated by relatively large melt fraction and/or spinel as the predominant residual phase, whereas high La/Yb ratios are indicative of smaller melt fractions and/or garnet control (Yang et al., 2007). Hence, nearly-flat to slightly fractionated chondrite-normalized HREE patterns, and the relatively high HREE and Y contents (Yb: 1.28±1.57 ppm, Lu: 0.19±0.25 ppm, 2–12 times the chondritic values; Y: 7.84–13.99 ppm) for Yamansu basalts suggest absence of garnet in the residue (cf. Maheo et al., 2009; Wilson, 1989). This inference is further supported by the results obtained from the mantle melting modeling for the Yamansu basalts using La/Sm versus Tb/Yb ratios. All the basalt samples plot within the field of spinel peridotite (Fig. 9c), suggesting that the Yamansu basalts were produced by partial melting of the spinel-facies, asthenospheric mantle peridotite which was affected by slab-derived materials at depths of <60–70 km (McKenzie and Bickle, 1988).

Table 4

<table>
<thead>
<tr>
<th></th>
<th>YMS25</th>
<th>YMS26</th>
<th>YMS27</th>
<th>YMS28</th>
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<tr>
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<td>12.66</td>
<td>9.36</td>
<td>8.14</td>
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<tr>
<td>CaO</td>
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<tr>
<td>MgO</td>
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<td>6.53</td>
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<tr>
<td>MnO</td>
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<td>0.60</td>
<td>0.65</td>
<td>0.35</td>
<td>0.88</td>
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<tr>
<td>K₂O</td>
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<td>3.33</td>
<td>2.06</td>
<td>2.15</td>
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<tr>
<td>P₂O₅</td>
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<td>0.12</td>
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<tr>
<td>LOI</td>
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<td>99.82</td>
<td>99.88</td>
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Fig. 6. Chondrite-normalized rare earth element patterns and primitive-mantle-normalized multi-element diagrams for the Yamansu basalts. N-MORB and E-MORB values, REE abundances for chondrites and trace element abundances for primitive mantle are after Sun and McDonough (1989).
Note: Chondrite uniform reservoir (CHUR) values ((143Sm/144Nd)0 = 0.1967) are used for the calculation. λms = 1.42 × 10−11/year (Steiger and Jäger, 1977), λmn = 6.5 × 10−12/year (Lugmair and Hart, 1978), (143Nd/144Nd)m and εNd(t) were calculated at 320 Ma.

Table 5
Sr and Nd isotopic compositions of Yamansu basalts.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>YMS-26</th>
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<th>YMS28</th>
<th>YMS29</th>
<th>YMS-30</th>
</tr>
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<tr>
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<td>2.18</td>
<td>1.66</td>
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<tr>
<td>Nd</td>
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<td>4.72</td>
<td>3.41</td>
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</tr>
<tr>
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<td>0.709520</td>
<td>0.706653</td>
<td>0.706292</td>
<td>0.720526</td>
</tr>
<tr>
<td>143Nd/144Nd</td>
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<td>0.5124816</td>
<td>0.5124052</td>
<td>0.5122952</td>
<td>0.5123852</td>
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</table>

5.4. Tectonic setting of Yamansu basalts

Although the tectonic regime of the Yamansu belt has been widely discussed in previous works, debate surrounds the tectonic setting for the Lower Carboniferous Yamansu Formation (Li et al., 2002; Xiao et al., 2004a,b). Specifically, the bimodal signature of the volcanic rocks of the Yamansu Formation and their exceptional thickness (~5 km), led to the suggestion by Li et al. (2002) that they represent volcanism in a rift zone. An island arc model has also been proposed (Xiao et al., 2004a,b).

Back-arc basin basalts (BABB) are generated by decompression melting with eruption along spreading ridges in a manner indistinguishable from that of true MORB and in most compositional aspects are similar to MORB (Klein and Langmuir, 1987). At the same time, a subduction component is also clearly involved (Gribble et al., 1996, 1998; Hawkins et al., 1999; Holm et al., 1997). Thus, they generally show compositional aspects of both MORB and arc volcanic rocks. For example, Mariana and Manus BABBs, and Kuerti mafic rocks in the Chinese Altai, both show arc volcanic-like and MORB-like compositional characteristics (Gribble et al., 1996, 1998; Sinton et al., 2003). Such a compositional feature is generally acknowledged to be unique to BABB (Hollings and Kerrich, 2000).

The Yamansu lavas show positive εNd(t) values (+1.4 to +5.1), zircon εNd(t) values (+10.13 to +13.51) and variable depletion of LREE, reflecting that the mantle source is moderately depleted, and this inference is consistent with other geochemical features, most of the samples plotting subparallel to the MORB trend in trace element diagrams, and possessing flat HREE patterns (Fig. 6). However, the εNd(t) values (+1.4 to +5.1) of the Yamansu basalts are obviously lower than the typical MORB values (εNd(t) = +10; Dosso et al., 1993; Mahoney et al., 1992, and references therein). Together with the significantly negative Nb anomalies displayed by our samples, we infer the possible involvement of slab-derived materials. Consequently, the Yamansu basalts have both arc-like and MORB-like geochemical affinities, which are typical features of BABB. Such an inference is supported by the results obtained from the tectono-magmatic discrimination diagrams (Fig. 10a–d) that clearly exhibit transitional features between island arc and mid-ocean ridge basalts.

Mafic rocks with a high Nd isotopic signature occur in some forearc regions where they are commonly associated with boninitic and intermediate to felsic volcanic rocks such as in the Izu–Bonin forearc (Taylor et al., 1992), Acgeo block in the Zambales ophiolites (Evans et al., 1991; Hawkins and Evans, 1983) and in the Trinity ophiolites (Wallin and McHattie, 1998). Although most of the Yamansu basalts are highly depleted in light REE and have an elevated Nd isotopic ratio, no boninitic and high-Mg andesite rocks have been found within the suite. However, Mississippian high-Mg andesites, adakite and Nb-rich basalts have been recognized in the Dananhu–Tousuquan arc (Fig. 1; Wang et al., 2006a,b), suggesting that the Dananhu–Tousuquan volcanic rocks were most likely generated near a forearc environment. Thus, it appears that the Yamansu and the Dananhu–Tousuquan arc volcanic rocks comprise a backarc–arc/forearc pair along the Junggar Ocean margin (Qin, 2000). Consequently, we concur that an island arc–backarc basin system existed along the
Junggar Ocean margin in the Eastern Tianshan. The Junggar Ocean is believed to have existed to the north of Eastern Tianshan during the Paleozoic (c.f. Xiao et al., 2004a, b). Because it is located to the north of the Yamansu back-arc basin, we infer that an island arc (Dananhu–Tousuquan)–backarc basin (Yamansu) system was formed in response to the southward subduction of the Junggar Ocean rather than the northward subduction of the south Tianshan ocean.

5.5. Genesis of skarn

The skarn mineralization in the Yamansu iron deposit does not exhibit a clear spatial link with any intrusions, but occurs stratabound within the host volcanic rocks.

Fig. 8. MgO variation diagrams for Yamansu basalts showing trends consistent with fractional crystallization. For reference, typical BABB from the Manus are also shown. MgO vs. Al₂O₃ (a), MgO vs. Fe₂O₃* (total iron) (b), MgO vs. TiO₂ (c), MgO vs. SiO₂ (d). Symbols are same as in Fig. 6.

Fig. 9. a) Th/Yb vs. Nb/Yb diagram (after Pearce and Peate, 1995) for Yamansu volcanic rocks. In this diagram, most Yamansu volcanic rocks plot between MORB and typical oceanic-arc basalt compositional fields; b) Nb/Ta vs. Zr/Sm diagram (Foley et al., 2000). c) (La/Sm)ₙ vs. (Tb/Yb)ₙ diagram for the Yamansu volcanic rocks. The horizontal dashed line separates fields expected for melting garnet- and spinel-bearing peridotite as determined for the Cenozoic basalts in the Basin and Range province (Wang et al., 2002). Symbols and data source are same as in Fig. 6.
the intermediate-basic volcanic lava and clastic rocks. These features are comparable with both volcanic exhalation–sedimentation deposits and skarn deposits. Therefore, a volcanic exhalation–sedimentation model has been proposed to explain the origin of the Yamansu skarn and related iron oxide deposit (e.g., Jiang, 1983). According to the volcanic exhalation–sedimentation model, the skarn formation occurs by reaction between hydrothermal fluids and submarine seafloor rocks (volcanic rocks and limestone). Stratiform skarns have been proposed and described by many researchers (e.g., Ashley and Plimer, 1989; Stanton, 1987), and represent essentially isochemically metamorphosed calc-silicate-rich submarine exhalative beds. This model provides an explanation for the observation that all Fe-rich skarn orebodies in the Eastern Tianshan Mountains are stratabound and hosted by volcanic rocks. Similar models have also been proposed for the formation of skarns at shallow depth in Broken Hill in eastern Australia, Nuuk in West Greenland and the Lower Yangtze River Valley in China (Appel, 1994; Gu et al., 2007; Plimer, 1986; Stanton, 1987). It is widely accepted that the volcanic exhalation–sedimentation–skarn and related deposits are syn-volcanic (Franklin et al., 2005). Our zircon U–Pb age data of skarn and volcanic host rocks shows synchronous formation (Fig. 4), supporting the model of syngentic volcanic exhalation–sedimentation process (e.g., Macelland et al., 2006).

However, a common characteristic of many stratiform submarine exhalites, including many of the “stratiform skarns”, is the preservation of compositional layering, often on a fine scale (Ashley and Plimer, 1989; Stanton, 1987). Although the skarn lenses are stratabound at Yamansu, there is no internal layering which could be interpreted as bedding. If this model is applicable, considering the submarine mafic volcanic environment, it may be expected that the skarn is accompanied by other facies of chemical exhalite (Pirajno, 2009), such as pyritic chert, jasper, Fe–Mn oxide deposits. However, these have not been recognized in the Yamansu deposit. In addition, the garnet compositions at the Yamansu ore are different from those of typical volcanic exhalative sedimentation deposits both in the Chinese Altai (Liu et al., 2012) and elsewhere (Gemmell et al., 1992). The garnets at Yamansu are Ca-rich (90% andite + grossular) whereas garnets associated with other volcanic exhalative sedimentation deposits are predominantly Mn- and Fe-rich spessartine and almandine (Fig. 5), consistent with enrichment of Fe and Mn, such as the Fe–Mn crust on the seafloor (Burton et al., 1999).

Deep intrusion-related fluids can travel some distance from their source to interact with appropriate country rocks to generate skarns (Meinert et al., 2005). The similar ages of basalts and skarn (Fig. 4) suggest that the skarn is closely related to the subaqueous volcanism including the eruption of volcanic rocks of the Yamansu Formation. The presence of clinopyroxene and plagioclase phenocrysts suggests the existence of a shallow magma chamber beneath the deposit. In this case, when the fluids driven by heat from the shallow magma chamber ascended and encountered the Ca-rich volcanic rocks and carbonates of Yamansu Formation, release of calcium from the carbonate (CaCO3 + 2NaClaq = CaCl2,aq + Na2CO3,aq; Newton and Manning, 2002) probably resulted in the formation of Ca-rich skarn minerals, such as garnet. The involvement of carbonate in the interaction process is evidenced by the lower εHf(t) values of zircon separated from the skarn than those of the volcanic rocks (Table 2). In contrast, at Mengku iron skarn deposit in Chinese Altay, the U–Pb zircon age of skarn is much younger than that determined from volcanic rocks (Wan et al., 2012), and thus was interpreted to be related to the synchronous movement of the nearby regional shear zone and fault rather than the syn-volcanic rocks.

### 5.6. Iron mineralization

Previous fluid inclusion studies had yielded formation temperatures of around 340–330 °C for magnetite and 220–150 °C for pyrite, with salinities between 12.9 and 2.7 wt.% NaCl equiv., indicating
hydrothermal fluids (Mao et al., 2005). Experimental studies suggest that the solubility of Fe in solutions is dependent on the activity of NaCl (Bell and Simon, 2011); when the content of cations in solutions reaches about 30 wt.%, the solubility of Fe could be up to 8 wt.% (Kwak et al., 1986). The moderate to high salinity of Fe-bearing fluids favors transportation of Fe as a chloride complex (Bell and Simon, 2011). Since the skarn at Yamansu was probably formed by interaction between hydrothermal fluids and Ca-rich volcanic rocks and/or carbonates as stated above, the iron ores possibly have a similar origin. The common occurrence of Cl-rich hornblende and other hydrous minerals such as apatite, epidote and chlorite in the skarn and iron ores indicates aqueous chloride solutions as carriers of dissolved Fe (Bell and Simon, 2011).

The geochemical data presented in this study favor a mantle source for the submarine volcanic rocks of Yamansu Formation, metasomatized by subduction-related fluids. Thus, a relatively higher content of volatiles would be expected in the mantle-derived magma (e.g. Johnson et al., 2009). In addition, the fractional crystallization of anhydrous minerals such as olivine, clinopyroxene and plagioclase is also capable of enhancing the volatile content of the residual magma. This is consistent with the presence of some igneous hydrous minerals (hornblende and biotite) which occur as interstitial phases in the basalts. The volatile- and chlorine-rich mafic magma favors the formation of hydrothermal fluids by exsolution or degassing during the late magmatic stage (e.g. Halter and Webster, 2004; Webster et al., 1999) especially when the magma is emplaced at shallow depth under the seafloor (e.g. Woods and Pyle, 1997). The s\(^{18}O\) values of magnetites in this deposit range from 5.3‰ to 12.8‰ (Mao et al., 2005 and references therein), suggesting that the magma-derived fluids mixed with meteoric water, probably seawater. Given the submarine environment, it can be inferred that the hydrothermal fluids could have been derived from a mixture of evolved magmas and seawater heated by the shallow magma chamber beneath the Yamansu deposit.

With respect to the iron source, it is difficult to explain the carbonate rocks as the potential source, because they have very low iron contents. The mafic volcanic rocks of the Yamansu formation are relatively enriched in iron (Table 4). This is substantiated by the tholeiitic evolution trend (Fig. 7b) which elevates the iron concentration in the residual magma (Osborn, 1959). Therefore, the volcanic rocks are the potential candidate for the source of most of the iron in the Yamansu deposit. However, the negative correlation between total Fe\(_2\)O\(_3\) and loss-on-ignition (LOI) of our samples (Fig. 11) indicates post-magmatic hydrothermal removal of iron in the basalts rather than enrichment of iron. Since the major iron mineralization is closely related to the formation of epidote in wall rocks, it is very likely that leaching of erupted basalts could account for the enrichment iron in the ores. Considering that most of the ore bodies show stratabound affinity and the volcanic exhalation–sedimentation had been excluded, a fluid source at depth is considered to be most reasonable. Moreover, such a distal expression model is also consistent with the compositional zoning of garnet from skarn environments, where garnet growth, i.e. Fe-rich core and Al-rich margin (Table 3), reflects the interplay of heating and fluid infiltration (e.g., Jamtveit, 1997). The garnet composition changes during the passage of the ascending fluids and alteration front, and the zonation patterns therefore differ with proximity to the fluid source (Meinert et al., 2005), and the Fe decrease on the garnet rim probably corresponds to the onset of the iron oxide mineralization (e.g., Chiaradia, 2003).

Based on the above discussion, and considering the extensive occurrence of faults in these deposits, a convection cell driven by temperature gradients established by the active magma chamber can be envisaged. Circulation of ore-forming fluids is accommodated by the faulting of the submarine rocks of Yamansu Formation and the resulting enhanced...
permeability (Doyle and Allen, 2003), with involvement of sea water. Our proposed genetic model envisages convecting, aqueous chloride solutions, as illustrated by Fig. 12. The solutions circulate to the cold end of the cell, where they came in contact with CaCO₃ in the wall rocks and formed skarns between volcanic rocks and limestone. The erupted basalts were leached by these formed skarns between volcanic rocks and limestone. The erupted basaltic lavas were derived from a deep seated active magma chamber with the involvement of seawater and submarine rocks of Yamansu Formation, represented by submarine rocks of Yamansu Formation, i.e. volcanic rocks and limestone. This hypothesis requires the presence of a “magma chamber” that gave rise to both the submarine volcanism and the ore-forming fluids, as separate events.

6. Conclusions

The LA–ICP-MS zircon U–Pb age data obtained in this study show that the Yamansu volcanic rocks and skarns in the Eastern Tianshan of NW China are broadly coeval, yielding ages of 324.4 ± 0.94 and 323.47 ± 0.95 Ma, respectively. The Yamansu basalts possess a geochemically transitional character between MORB and IAB, suggesting that they were possibly generated in an oceanic back-arc basin tectonic setting related to the southwestern subduction of the Junggar oceanic crust beneath the Eastern Tianshan region. Furthermore, they were probably derived from a spinel-facies assemblage manto source which had been metamorphosed by subduction-related materials. The skarns and iron ores were formed in the interaction of fluids which were derived from a deep seated active magma chamber with the involvement of seawater and submarine rocks of Yamansu Formation, represented by volcanic rocks and limestone.

Acknowledgment

Financial support for this work was supported by 973 program (2012CB416806) the Special Fund for Scientific Research in the Public Interest (200911007-25), the “Fundamental Research Funds for the Central Universities”, the 111 Project (B07011), and PCSIRT. This study also contributes to the 100 Talent Award to M. Santosh from the Chinese Government. We are sincerely thankful to the Editor-in-Chief, Franco Pirajno for his support over the years. Official reviews by Dr. Walter Witt and an anonymous reviewer are gratefully acknowledged.

References


