Chemical compositions of garnet and clinopyroxene and their genetic significances in Yemaquan skarn iron–copper–zinc deposit, Qimantagh, eastern Kunlun

Pengfei Zuo a, Xuefei Liu a,b, Jinhua Hao b, Yashuai Wang a, Rui Zhao a, Songsheng Ge c

a State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China
b Academy of Science, China University of Geosciences, Beijing 100083, China
c State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

A R T I C L E   I N F O

Article history:
Received 28 December 2014
Revised 25 June 2015
Accepted 14 July 2015
Available online 26 July 2015

Keywords:
Skarn iron–copper–zinc deposit
Prograde skarns
Skarn zonation
Mineralization zonation
Yemaquan

A B S T R A C T

The Yemaquan skarn deposit in the northwestern part of the Qimantagh is located in the eastern Kunlun orogenic belt. The deposit is hosted in carbonate rocks, siltstones, and sandstones of the Cambrian–Ordovician Tanjianshan Group and Late Carboniferous Di'aus Formation. These rocks are intruded by Triassic calc-alkaline granitoid that extended NW–SE. Three stages of mineralization have been identified, i.e., pre-ore stage, syn-ore stage, and post-ore stage. The prograde skarn stage, which corresponds to the pre-ore stage, is dominated by clinopyroxene and garnet. Clinopyroxene is much more abundant than garnet in the deposit and consists of three types of clinopyroxene in the deposit. In terms of the end-members diopside (CaMgSi$_2$O$_6$), hedenbergite (CaFeSi$_2$O$_6$), and johannsenite (CaMnSi$_2$O$_6$), namely, type I (with an average composition of Di$_{92}$Hd$_{7}$Joh$_{1}$), type II (with an average composition of Di$_{62}$Hd$_{36}$Joh$_{2}$), and type III (with an average composition of Di$_{24}$Hd$_{54}$Joh$_{22}$) occurred from the proximal intrusions to the distal wall rocks. Type I, II, and III clinopyroxenes are associated with copper–iron, iron, and zinc–lead mineralization, respectively. Garnet mostly occurred in the middle of exoskarn zonations and is associated with type II clinopyroxene. The distribution of the garnet in the skarn zonation could be explained by the stability fields of clinopyroxene, which is strongly dependent on composition. Based on mineral assemblages, the formation of type II and type III, comparative to type I clinopyroxene, is in more reduced condition in the distal skarn. Moreover sulfur isotope carried out on sulfide minerals from both the prograde and retrograde stages show a variable and wide range of δ$^{34}$S values (−6.9 to 4.2%), δ$^{34}$S, suggesting that the skarn-forming fluid may have been affected by the reduced wall rocks. The low garnet clinopyroxene ratios observed at the deposit might be caused by the clinopyroxene composition variations and reduced wall rocks.

1. Introduction

Skarn deposit zonation models based on the mineral assemblages have been widely used in mineral exploration. The development of a specific type of skarn depends on the local geological environment, such as the compositions of the sedimentary protolith and associated igneous rocks, depth of formation, and sulfur and oxygen fugacity (Cepedal et al., 2000; Ciobanu and Cook, 2004; Einaudi and Burt, 1982; Grammatikopoulos and Clark, 2006; Kamvong and Zaw, 2009; Lehrmann et al., 2009; Meinert, 1995; Meinert et al., 2005; Shimazaki, 1980). Although skarns cannot be solely characterized by their garnet or clinopyroxene compositions, consideration of both yields a relatively unique fingerprint, which serves as an additional aid in defining environments of formation (Gao et al., 2014a; Gaspar et al., 2008; Jamtveit and Hervig, 1994; Jamtveit et al., 1993, 1995; Liu et al., 2013; Smith et al., 2004; Somarain, 2004; Zhai et al., 2013; Zhao, 1997; Zhao et al., 1997, 2002). Meinert (1992) and Meinert et al. (1997a, 2005) have discussed the relationship between the ratios of garnet clinopyroxene and oxidation state within different skarn zonations.

The diopside, hedenbergite, and johannsenite are typical clinopyroxene in iron, copper, and lead–zinc skarn deposits, respectively and are widely utilized to study the ore-forming processes and ore exploration, especially johannsenite, which commonly develops far from intrusions (e.g., Bonev et al., 2005; Bussell et al., 1990; Canet et al., 2009; Einaudi et al., 1981; Einaudi and Burt, 1982; Mao et al., 1996; Meinert, 1982, 1987; Palinkaš et al., 2013; Zhao et al., 1983, 2002) and has been studied by many researchers (Abrecht, 1980; Angel, 1984; Burt, 1977; Capitani et al., 2003; Dimanov and Sautter, 2000; Vassileva and Bonev, 2001, 2002, 2003).

The Qimantagh in the eastern Kunlun orogenic belt is one of the most important Fe–Cu resource bases in China. Most of the ore deposits are concealed skarn deposits that have been geologically researched very little. Mn-, Fe-, and Mg-rich skarn deposits, including Yemaquan, Galinge,
Sijiaoyang, and Kendekelde deposits, are developed widely in the district. The Yemaquan Fe–Cu–Zn deposit in the Qimantagh is one typical representative of the skarn deposits in this area (Liu et al., 2013; Zhang, 2012; Zhao et al., 2013). The geological features of both intrusions and skarns, ages of intrusions and metallogenic epoch, origin of the deposits, and the metallogenic setting have been comprehensively investigated (Feng et al., 2010, 2011a; Gao et al., 2014b; Liu et al., 2013; Song et al., 2010; Wang et al., 2009; Zhang, 2012; Zhao et al., 2013). However, the low ratios of garnet/clinopyroxene and their links to the mineralization are still obscure. In this paper, a comprehensive petrographic, mineralogical, and sulfur isotope study of the skarns developed at different spatial positions relative to the intrusions were conducted with the aim of gaining a better understanding of the skarn and mineralization zonations in the Qimantagh.

2. Regional geology

The eastern Kunlun orogenic belt lies on the northern Tibetan Plateau with the Songpan–Garzê accretionary complex to the south and Qaidam Basin to the north. It can be subdivided into three tectonic zones according to the major faults: North, Middle, and South Kunlun Fault (Fig. 1a) (Jiang et al., 1992; Li et al., 2013a; Meng et al., 2013, 2015; Xia et al., 2014; Xu et al., 2014; Yang et al., 1996). The Qimantagh district is located in the northwestern part of the North Zone.

The Precambrian basement in the Qimantagh is mainly composed of Paleoproterozoic to Neoproterozoic medium- to high-grade metamorphic rocks, carbonate formations, and meta-elastic rocks (Jiang et al., 1992; Wang et al., 2010, 2012). It was overlain by the Tanjianshan Group, Cambrian to Ordovician in age, which includes shallow and
deep-water clastics, carbonate rocks, volcanic rocks, and volcanic clastic rocks (Jiang et al., 1992; Pan et al., 1996; Wang et al., 2010, 2012; Yin and Harrison, 2000; Yin and Zhang, 1997). A molasse formation deposited from Late Silurian to Early Devonian indicated the closure of the Qimantagh Ocean (Proto-Tethys Ocean) (Pan et al., 1996; Jiang et al., 2000; Hao et al., 2014; Wang et al., 2014; Li et al., 2015b; Xiong et al., 2015; Hao et al., 2015). Carboniferous marine sedimentary rocks (Di'aosu Formation) of the active continental margin developed in the district (Chen et al., 2006; Feng et al., 2011a; Jiang et al., 1992; Li et al., 2008; Zhang et al., 2015).

Magmatism was very active in the Early Paleozoic (518–420 Ma) and related with the northward subduction of the Qimantagh Ocean (Cui et al., 2011; Li et al., 2013a; Meng et al., 2013, 2015). Accretion/collision magmatism developed from the start of the Late Silurian (~406 Ma–~350 Ma) and indicated that this district formed part of the collisional orogeny stage (Chen et al., 2006; Li et al., 2013a; Liu et al., 2012). From the Permian to Middle Triassic, abundant granitoids (280 Ma–250 Ma) intruded during this period and were associated with the Paleo-Tethys oceanic basin subducting northward (Deng et al., 2014b; Huang et al., 2014; Li et al., 2001, 2013a, 2013b; Mo et al., 2007; QRGST, 1981; Xiong et al., 2013; Yang et al., 1996). The granitoids of Middle Triassic to Early Jurassic (230–190 Ma) indicated the closure of the Paleo-Tethys Ocean and the Eastern Kunlun area entered the intracontinental orogenic stage (Deng et al., 2015b; Guo et al., 1998; Kui et al., 2010; Li et al., 2015c; Mo et al., 2007; Li et al., 2015d; Ding et al., 2015; Hu et al., 2015; Wang et al., 2016). A great number of skarn-type and porphyry-related poly-metallic deposits are temporally and spatially related to Middle to Late Triassic granitic intrusions (235–219 Ma) (Fig. 1b) (Chang et al., 2009; Feng et al., 2011a, 2011b, 2012; Gao et al., 2012; Li et al., 2008; Liu et al., 2006; She et al., 2007; Xi et al., 2010; Xiao et al., 2013; Zhao et al., 2013).

3. Geology of the Yemaquan deposit

Based on outcrops and drill cores (Figs. 1c and 2), the strata at Yemaquan mainly consists of the Tanjianshan Group of Cambrian and Ordovician, the Maoniushan Formation of Late Devonian, the Di’aosu Formation of Late Carboniferous, and the Dachaigou Formation of Early and Middle Permian. Ore-bearing strata are dominated by the limestone in the Tanjianshan Group and the Di’aosu Formation (Chen et al., 2006; Feng et al., 2011a; Jiang et al., 1992; Li et al., 2008; Zhang et al., 2004).

Magmatism was very active in the Early Paleozoic (518–420 Ma) and related with the northward subduction of the Qimantagh Ocean (Cui et al., 2011; Li et al., 2013a; Meng et al., 2013, 2015). Accretion/collision magmatism developed from the start of the Late Silurian (~406 Ma–350 Ma) and indicated that this district formed part of the collisional orogeny stage (Chen et al., 2006; Li et al., 2013a; Liu et al., 2012). From the Permian to Middle Triassic, abundant granitoids (280 Ma–250 Ma) intruded during this period and were associated with the Paleo-Tethys oceanic basin subducting northward (Deng et al., 2014b; Huang et al., 2014; Li et al., 2001, 2013a, 2013b; Mo et al., 2007; QRGST, 1981; Xiong et al., 2013; Yang et al., 1996). The granitoids of Middle Triassic to Early Jurassic (230–190 Ma) indicated the closure of the Paleo-Tethys Ocean and the Eastern Kunlun area entered the intracontinental orogenic stage (Deng et al., 2015b; Guo et al., 1998; Kui et al., 2010; Li et al., 2015c; Mo et al., 2007; Li et al., 2015d; Ding et al., 2015; Hu et al., 2015; Wang et al., 2016). A great number of skarn-type and porphyry-related poly-metallic deposits are temporally and spatially related to Middle to Late Triassic granitic intrusions (235–219 Ma) (Fig. 1b) (Chang et al., 2009; Feng et al., 2011a, 2011b, 2012; Gao et al., 2012; Li et al., 2008; Liu et al., 2006; She et al., 2007; Xi et al., 2010; Xiao et al., 2013; Zhao et al., 2013).

3. Geology of the Yemaquan deposit

Based on outcrops and drill cores (Figs. 1c and 2), the strata at Yemaquan mainly consists of the Tanjianshan Group of Cambrian and Ordovician, the Maoniushan Formation of Late Devonian, the Di’aosu Formation of Late Carboniferous, and the Dachaigou Formation of Early and Middle Permian. Ore-bearing strata are dominated by the limestone in the Tanjianshan Group and the Di’aosu Formation (Xiao et al., 2013; Zhang, 2012). The Tanjianshan Group consists of granoblastic-to-hypautomorphic-marble, chert, and lepidogranoblastic hornfels interbedded with basalt. The Di’aosu Formation can be divided into three parts from the bottom to the top, based on the Tectonic Geology Map of Qinghai (Qinghai, 2010), i.e., (1) skarn and silicated limestone; (2) hornfels, quartz sandstone, silty mudstone, siltstone, greywacke, and brecchia; (3) marble and carbonaceous limestone. Small granodiorite and syenogranite intrusions (Fig. 3a, b) and other neutral or felsic rocks were emplaced during the...
intense magmatism period from the Late Triassic to Early Jurassic (Feng et al., 2010, 2011a; Gao et al., 2014b). LA-ICP-MS U–Pb zircon dating reveals that the biotite diorite, quartz adamellite, and syenogranite at Yemaquan were emplaced at 220.0 ± 0.45 Ma, 223.3 ± 0.54 Ma, and 213 ± 1.0 Ma, respectively (Gao et al., 2014b; Zhang, 2012).

Prominent faults strike NWW, N–E, and N–W, representing favorable sites for mineralization (TEIGMRQ, 2010). The locations of the orebodies generally run parallel to the bedding of the host rocks (Fig. 2). It is hard to find fresh granitoid rocks within the deposit, most of them having been chloritized, silicified, albitized, and/or kaolinized (Fig. 3). The skarns developed along the contact zones between the main intrusion and the marble, siliceous limestone, silty limestone, and carbonaceous limestone. The major ore types are Fe-, Zn-, and Cu-bearing skarns. Unambiguously, the mineralization zonations of Fe, Cu within the deposit are proximal to the intrusions, whereas those for Zn, Pb occur far from the intrusions (Fig. 2). In the Yemaquan skarn deposit, clinopyroxene is widely developed in both the proximal and the distal parts of the skarn, but garnet is less abundant and mostly occurs in the middle part of the skarn zone (Figs. 2 and 4) (TEIGMRQ, 2010). The skarn zonation is different from most skarn deposits, which have a general spatial zonation pattern ranging from endoskarn alteration within the causative intrusion, proximal garnet, distal clinopyroxene at the contact between skarn and marble (Einaudi and Burt, 1982; Meinert et al., 1997a, 2005).

4. Sampling and analytical methods

Sixty-six skarn samples of the drill cores of ZK6813 (42 samples), ZK13209 (13 samples) and ZK10864 (6 samples), were collected consecutively from the intrusive body to wall rocks. These samples were cut into thin, polished sections in the laboratory of China University of Geosciences (Beijing) and used for textural and mineral paragenetic sequence studies. Nineteen of them were analyzed for mineral composition and six samples in the ZK6813 drill core for sulfur isotope analyses (for locations, see Fig. 4a) in the State Key Laboratory of GPMR, China University of Geosciences (Beijing).

Fig. 4. (a) Schematic column showing the zonation of skarns and mineralization in no. ZK6813 diamond drill core. (b) Average mole percentage of clinopyroxene end members in the drilling core (ZK6813).
In order to investigate the formation of the prograde skarn, several points were analyzed on a single grain of clinopyroxene and garnet using an electron microprobe (EPMA-1600). Wavelength dispersive spectrometry (WDS) analyses were carried out at the following conditions: for silicates: 15 kV, 10 nA, beam diameter of 1 μm, and a counting time of 30 s. Detected limits in terms of weight percent oxides for the elements in these analyses are estimated as follows: SiO₂, Al₂O₃, MgO, K₂O, Na₂O—0.05 wt.%; CaO—0.04 wt.%; and, TiO₂, Cr₂O₃, FeO, MnO, and ZnO—0.03 wt.%.

The chemical formulae of garnet and clinopyroxene were obtained using the method of oxygen atom calculation (Zheng, 1983), and the ratios of Fe²⁺ and Fe³⁺ of clinopyroxene and garnet were obtained on the basis of the balance of electrovalence. Corrections for matrix effects were applied according to procedures described by Bence and Albee (1968) and Albee and Ray (1970).

The sulfur isotope analysis procedure has been described by Robinson and Kusakabe (1975) and was performed with an EA-ISOPRIME100. Sulfur isotope ratios are reported as δ³⁴S relative to the Vienna-Canyon Diablo Troilite (V-CDT). The analytical precision for δ³⁴S is ±0.15‰.

5. Mineral paragenetic sequence

The prograde minerals are predominantly clinopyroxene and garnet. Small amounts of wollastonite, chalcopyrite, magnetite, and pyrrhotite

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Pre-ore stage</th>
<th>Syn-ore stage</th>
<th>Post-ore stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinopyroxene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garnet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wollastonite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphibole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sphalerite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galenda</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheelite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sericite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Serpentine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemaitite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limonite</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Mineral paragenesis for the Yemaquan iron-copper-zinc deposit.

Fig. 6. Photomicrographs of sample at the Yemaquan Fe–Zn deposit. (a) and (b) Coarse, bladed diopsidic (Type I) clinopyroxene with interstitial magnetite. Sample B6. (c) Coarse, bladed clinopyroxene with interstitial pyrrhotite and metasomatic magnetite. Sample B9. (d) Clinopyroxene associated with metasomatic magnetite and pyrite. Sample B10. (e) Needle amphibole associated with chalcopyrite, sphalerite and pyrite. Sample B12. (f) and (g) Garnet replaced clinopyroxene (Type II). Coarse-grained and zoned garnet with pyrite and pyrrhotite (g, Type II garnet). Sample B17. (h) Saccharoidal garnet replaced clinopyroxene (Type II) and various degrees of selective replacement of garnet by chlorite (i). The replacement mostly occurs along certain bands of garnet, whereas some occurs as veins cutting across the bands (BSE). Sample B23. (j) Type III clinopyroxene associated with sphalerite. Sample B37. (k) Calcite and chlorite replaced clinopyroxene (Type III). Galena occurs as vein within sphalerite (l). Sample B42. Abbreviations: Mt—magnetite; Po—pyrrhotite; Cpx—clinopyroxene; Ccp—chalcopyrite; Sp—sphalerite; Py—pyrite; Grt—garnet; And—andalusite; Gro—grossular; Alm—almandine; Chl—chlorite; Cal—calcite; Gn—galena.
developed. The early retrograde skarn consists of amphibole, quartz, and the metallic minerals, with minor fluorite, serpentine, chlorite, apatite, and calcite. A final stage of retrograde alteration is characterized by calcite, quartz, sericite, hematite, and chlorite. The main metallic minerals are magnetite, sphalerite, galena, pyrite, chalcopyrite, and pyrrhotite. Based on previous studies (e.g., Li et al., 2013a; Song et al., 2010; Zhang, 2012) and our petrographic investigations, three stages of ore deposition during skarnization have been identified. The later stage commonly partially replaced earlier stages. The paragenetic sequence is illustrated in Fig. 5. These three stages are (1) pre-ore stage; (2) syn-ore stage; and (3) post-ore stage.

5.1. Pre-ore stage

Similar to many skarn systems, prograde minerals like clinopyroxene and garnet in this stage represent the earliest skarn-forming phase. Based on characteristics of mineral assemblages and structures, three types of clinopyroxene have been identified. Type I clinopyroxene is about 0.5 mm across, platy or flaky, much bigger than type II and III, and is associated with magnetite, chlorite, and pyrrhotite (Fig. 6a, b, and c). Type II clinopyroxene fills interstices of clinopyroxene with straight fringes and occurs as isolated banding (Fig. 6b), while pyrrhotite is also interstitial within the clinopyroxene (Fig. 6c). By contrast, Type II and Type III clinopyroxenes are subhedral to anhedral (Fig. 6f, h, and j). Type II clinopyroxene is typically associated with garnet, magnetite, pyrite, pyrrhotite, and minor chalcopyrite (Fig. 6d, f, g, and h). Type III clinopyroxene is commonly associated with sphalerite and galena (Fig. 6j, k, and l).

Two types of garnet also developed. Type I garnet is very small (ca. 0.25 mm) (Fig. 6f and h), euhedral to subhedral, and replaced clinopyroxene (Fig. 6f and h). The garnets are colorless to light tan in thin section and typically display anomalous birefringence with sector zoning. They are commonly rimmed and replaced by later chlorite (Fig. 6i).

5.2. Syn-ore stage

Syn-ore stage is characterized by the frequent occurrence of metasomatic sulfides, magnetite, and minor scheelite (Fig. 5). Retrograde minerals in this stage coexisting with these sulfides mainly include quartz, calcic amphiboles, calcite, and chlorite with lesser garnet. Amphibole is often difficult to distinguish in hand specimen, but it appears as radiating clusters under the microscope and is associated with sphalerite and chalcopyrite mineralization (Fig. 6e). The Cu–Fe–Zn–Pb mineralization zone is shown in Fig. 4a. The ore minerals commonly cut the skarn minerals and/or interstices between them. It is clear, therefore, that ore deposition in this stage occurred later than the precipitation of the clinopyroxene.

5.3. Post-ore stage

During the post-ore stage, only some low-temperature alteration minerals were formed. Among them, calcite is dominant, with minor limonite, hematite, quartz, sericite, serpentine, chlorite, apatite, and...
fluorite. These minerals occur as veinlets crosscutting skarns and sulfides.

### 6. Analytical results

#### 6.1. Chemical compositions of garnet and clinopyroxene

EPMA results of the clinopyroxene and garnet from the deposit are listed in Tables 1 and 2. The compositions of the clinopyroxene are expressed in terms of mole fractions of the three end members, i.e., hedenbergite (Hd), johannsenite (Joh), and diopside (Di) as there is no miscibility gap between hedenbergite–diopside on one side and johannsenite on the other (Abrecht, 1985). The chemical data of all analyzed clinopyroxenes are plotted together and cluster into three different areas within the diopside–hedenbergite–johannsenite ternary plot (Fig. 7a). Type I clinopyroxene falls in the Fe–range, type II in the Fe range and type III in the Zn range.

The more manganese-rich clinopyroxene formed from fluids, which are distal in the overall zonation sequence (Di et al., 2006; Gemmell et al., 1992; Meinert, 1987; Zhao et al., 2003). In contrast, clinopyroxene formed in proximal locations is rich in magnesium and iron (Fig. 4b). The chemical compositions of the three types of clinopyroxene show the correlation, which is consistent with our observation under the microscope. Based on BSE images and EPMA data, type I and II clinopyroxenes are plotted together and cluster into three different areas within the diopside–hedenbergite–johannsenite ternary plot.

<table>
<thead>
<tr>
<th>Type</th>
<th>Ti</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Na/Al</th>
<th>K/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>II</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>III</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Compared with clinopyroxene, garnet shows less regular iron enrichment. Fig. 7b shows the ternary proportion of its grossular–andradite–pyroxalite, and the relationships with the Cu, Fe and Zn skarn deposits worldwide. Type I garnet (And$_{0.4}$Gro$_{0.6}$Alm$_{0.7}$) not associated with mineralization is poikilitic. Overall, type II garnet forms an essentially andradite–grossular solid solution from And$_{0.4}$Gro$_{0.6}$Alm$_{0.7}$ to And$_{0.8}$Gro$_{0.2}$Alm$_{0.7}$, with spessartine and pyrope less than 7 and 2 mol%, and fills the area of Zn, Fe and Cu skarn deposits. Generally, type II garnet replaced type I clinopyroxene and is associated with iron mineralization (Fig. 6f, g and h).

#### 6.2. Sulfur isotopes

Sulfur isotope compositions of pyrite, chalcopyrite, pyrrhotite, sphalerite, and galena from the ores are listed in Table 3 and are associated with both prograde and retrograde skarn. The $\delta^{34}$S values for sulfides vary from $-6.9$ to $+2.4$‰. The chalcopyrite sample of the prograde skarn stage has $\delta^{34}$S value of $+4.2$‰. While the other samples, i.e., pyrite, pyrrhotite, and sphalerite, are from the retrograde skarn stage. One pyrite sample has a $\delta^{34}$S value of $-6.5$‰ and two other pyrite samples have $\delta^{34}$S values of 1.8 and 2.6‰. The sphalerite and pyrrhotite have $\delta^{34}$S values of 3.2 and 2.8‰. Based on these results, there is evidence that these samples become more depleted in $34$S content as the distance from the intrusive body increases.

### 7. Discussion

The skarn zonation is controlled by temperature, depth of formation, fluid/rock ratios, compositions and oxidation state of associated intrusions and wall rocks (Chowdhury and Lentz, 2011; Deng et al., 2011, 2014c; Fuertes-Fuente et al., 2000; Kuçu et al., 2002; Levresse and Gonzalez-Partida, 2003; Meinert et al., 2005; Oyman, 2010; Pons et al., 2010; Scheepers, 2000; Somarín and Moayyed, 2002; Williams-Jones, 2010).
et al., 2010). The garnet/clinopyroxene ratios can give important clues about these fundamental geological variables, serve as a crude indicator of the general oxidation state of the system, and be applied to both the classification and exploration of the skarn deposits (Einaudi, 1981; Gaspar et al., 2008; Logan, 2000; Lu et al., 2003; Meinert et al., 1997b; Öztürk and Helvaci, 2008; Somarin, 2004).

7.1. Physicochemical conditions of prograde skarn formation

Based on the uplift and exhumation studies in the district, the depth of formation of the Yemaquan deposit was at 7 km and the pressure was roughly 2 kb (Wang et al., 2003; Yuan et al., 2006). The relatively deep environment is consistent with field observations such as the absence of brecciation and brittle fracture associated with mineralization, widely developed calc-silicate hornfels, and the intrusive contacts subparallel to bedding (Meinert et al., 2005). Conditions for the Mt-Po-Py invariant point fixed at 550 °C with a log fS2 value of −3.25 and log fO2 value of −18.7 (Fig. 8; Ciobanu and Cook, 2004). The upper fO2 limit is considered to lie below the Hu/Mt buffer, based on the absence of hematite. Type I clinopyroxene in association with the magnetite has a magmatic afﬁliation (Fig. 6b) (Zharikov, 1970), including MgO contents of up to 3 wt.%. In addition, the upper limit temperature of the magmatic magnetite in equilibrium with type I clinopyroxene is estimated to be 650 °C (Ciobanu and Cook, 2004). The absence of wollastonite that associated with type I clinopyroxene indicates X(CO2) ≤ 0.1 (Greenwood, 1967) (Fig. 8). Andradite stability in fO2–fS2 space is temperature dependent: below 600 °C, andradite is stable with Py; whereas from 500 to 300 °C, andradite is stable with Py plus magnetite (Gamble, 1982). Due to the lack of more complete experimental data on clinopyroxene solid solutions, it is not possible to offer the stability ﬁelds of type II (Di62Hd36Joh2) and type III (Di24Hd54Joh22) clinopyroxenes. However, as pointed out by Gamble (1982) and Burton (1982), manganese is far more effective than magnesium at expanding the clinopyroxene stability ﬁeld. Gamble (1982) showed that at 2 kb, Di75Hd25 coexisting with

Table 2

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Type</td>
<td>II</td>
<td>II</td>
<td>I</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>II</td>
</tr>
<tr>
<td>Weight percentage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>37.59</td>
<td>38.03</td>
<td>40.15</td>
<td>38.37</td>
<td>39.10</td>
<td>37.34</td>
<td>38.22</td>
<td>38.54</td>
<td>37.14</td>
<td>37.70</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.07</td>
<td>0.00</td>
<td>0.58</td>
<td>0.42</td>
<td>0.16</td>
<td>1.04</td>
<td>0.30</td>
<td>0.07</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>Al2O3</td>
<td>4.29</td>
<td>12.52</td>
<td>20.85</td>
<td>10.12</td>
<td>11.92</td>
<td>7.51</td>
<td>10.18</td>
<td>12.23</td>
<td>2.34</td>
<td>3.87</td>
</tr>
<tr>
<td>FeO*</td>
<td>25.11</td>
<td>14.94</td>
<td>2.69</td>
<td>17.70</td>
<td>15.80</td>
<td>20.46</td>
<td>17.99</td>
<td>15.60</td>
<td>27.64</td>
<td>25.63</td>
</tr>
<tr>
<td>MnO</td>
<td>0.46</td>
<td>0.98</td>
<td>0.08</td>
<td>1.05</td>
<td>0.94</td>
<td>2.08</td>
<td>1.08</td>
<td>1.16</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td>MgO</td>
<td>0.28</td>
<td>0.05</td>
<td>0.23</td>
<td>n.d.</td>
<td>0.05</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
<td>31.40</td>
<td>31.74</td>
<td>34.22</td>
<td>32.11</td>
<td>32.33</td>
<td>31.48</td>
<td>31.98</td>
<td>32.39</td>
<td>32.90</td>
<td>32.24</td>
</tr>
<tr>
<td>Total</td>
<td>99.18</td>
<td>98.26</td>
<td>98.80</td>
<td>99.76</td>
<td>100.29</td>
<td>99.92</td>
<td>99.74</td>
<td>100.00</td>
<td>99.72</td>
<td>100.03</td>
</tr>
</tbody>
</table>

Citations based on 12 oxygens

Si 3.05 3.03 3.05 3.03 3.05 2.99 3.03 3.02 3.03 3.04
Ti 0.00 0.00 0.03 0.02 0.01 0.06 0.02 0.00 0.00 0.00
Al 0.41 1.18 1.87 0.94 1.10 0.71 0.95 1.13 0.22 0.37
Fe3+ 1.55 0.81 0.72 0.94 0.86 0.81 0.86 0.85 0.85 1.75
Fe2+ 0.15 0.19 0.15 0.15 0.17 0.11 0.16 0.17 0.13 0.13
Mn 0.03 0.07 0.07 0.07 0.06 0.14 0.08 0.08 0.03 0.04
Mg 0.03 0.01 0.03 0.00 0.01 0.00 0.00 0.00 0.01 0.01
Ca 2.73 2.71 2.79 2.72 2.70 2.70 2.71 2.72 2.80 2.79
Total 7.96 7.98 7.94 7.96 7.96 7.97 7.97 7.98 7.98 7.97

Mole percentage

And 79.11 40.66 3.85 51.93 44.04 64.00 51.81 42.94 88.64 81.33
Pyr 1.15 0.20 0.88 0.00 0.02 0.00 0.00 0.00 0.00 0.00
Spe 1.06 2.23 0.18 2.38 2.10 4.79 2.46 2.59 1.11 1.11
Gro 13.58 50.52 91.79 40.52 47.93 27.47 39.98 48.66 5.51 12.92
Alm 5.10 6.39 3.29 5.17 5.73 3.75 5.76 5.81 4.38 4.26

Note: And—andalbite, Gro—grossular, Alm—almandine, Pyr—pyrope, Spe—spessartine.

Fig. 7. Ternary diagrams summarizing clinopyroxene (a) and garnet compositions at the Yemaquan iron–copper–zinc deposit (b). Colored areas indicate the clinopyroxene and garnet composition ranges for zinc, iron and copper skarn deposits summarized by Meinert (1992). Pyralspite = (pyrope + almandine + spessartine).
Py is stable only below 550 °C and Hs0D0 coexisting with Py below 395 °C. Therefore, the upper temperature limit for type II and type III clinopyroxenes is estimated to be 550 °C.

The garnet occurred in the middle of exoskarn zonation and was mainly associated with iron mineralization. This could be explained by the replacement of diopside–hedenbergite by pyrite, pyrrhotite, magnetite, and andradite, which show the change in the system leading to garnet, magnetite and iron sulfides deposition (Fig. 6g, h, and i) according to reactions (1) and (2) (Burton et al., 1982):

9CaFeSi2O6(Hd) + 2O2 = 3Ca3Fe2Si3O12(And) + 9SiO2(Qtz)
+ Fe3O4(Mt)

(1)

3CaFeSi2O6(Hd) + S2 = CaFe2Si3O12(And) + 3SiO2(Qtz)
+ FeS2(Py)

(2)

7.2. The formation of prograde skarn and ore

As pointed out by Dimanove and Wiedenbeck (2006), the (Fe, Mn)–Mg interdiffusion coefficient is strongly fo3 sensitive. More oxidizing conditions would favor the formation of andradite and diopside clinopyroxene relative to hedenbergite (Gamble, 1982; Gustafson, 1974). Furthermore, Gro-rich garnet (type II garnet, with an average composition of And3+3Gro32Spe2Alm5), is a garnet that requires lower fo3 than an And-rich equivalent (Einaudi and Burt, 1982). The clinopyroxene enrichment sequence Mg–Fe–Mn is interpreted as resulting largely from fluid depletion and temperature decrease (Capitan and Mellini, 2000; Meinert, 1987). For this reason, the probable path of prograde skarn formation has been shown in Fig. 8. The formation of type II and type III, comparative to type I clinopyroxene, therefore occurs attained in more reducing conditions in the distal skarn.

The wide range of δ34S values for all sulfides and the decrease in δ34S values in distal skarns suggest that the ore minerals might have been deposited as a result of the decrease in the oxidation state and temperature further from intrusions (Fu et al., 1991). Furthermore, the widespread occurrence of the carbonaceous limestone has also led to abnormal disturbance in electrical prospecting (TEIGMRQ, 2010). In spite of the fact that the sulfides postdate the skarn, a systematic correlation exists between specific prograde skarn mineral compositions and the presence of ore. This means that the ore-forming process was controlled in some way by the clinopyroxene skarn itself (Shimizu and Iiyama, 1982). Therefore, the tendency of the estimated physico-chemical environment during prograde skarn formation might also suggest the principal causes of ore formation are a reduction of the ore-forming fluid and a decrease in temperature. Furthermore, in reactions (1) and (2), the formation of magnetite and pyrite could also have been caused by the replacement of type II clinopyroxene. This is consistent with the fact type II clinopyroxene is mainly associated with iron mineralization.

8. Conclusion

(1) Compared to type I clinopyroxene, the formation of type II and III clinopyroxenes took place in more reducing conditions in the distal skarn. The low ratios of garnet/clinopyroxene in the deposit are caused by the compositions of clinopyroxene and the reduced wall rocks. The garnet, which is less abundant than the clinopyroxene, could have been produced by a progressive reduction of the mineralizing fluids as a result of their interaction with the organic matter of the carbonaceous limestone.

(2) Type I, II, and III clinopyroxenes are associated with copper–iron, iron, and zinc–lead mineralization, respectively. The tendency of the estimated physicochemical environment during prograde skarn formation might also suggest the principal causes of ore formation are a reduction of the ore-forming fluid and a decrease in temperature.

(3) An increase in hedenbergite and johannsenite and a decrease in the diopside content of clinopyroxene are observed through the deposit sequence Cu–Fe → Fe → Zn–Pb. Such associations could be used to identify skarn zonations and be useful in future exploration in this district.

Acknowledgements

We are grateful to Senior Engineers Dongsheng Li, Aikui Zhang, and other technical staff in the Third Exploration Institute of Geology and Mineral Resources of Qinghai, for their support during the fieldwork. Many thanks are extended to Prof. Jianping Chen, Dehui Zhang, and Dr. XiaoBo Zhao and Yaoyao Zhang. All of them have greatly assisted me with their constructive suggestions. We gratefully acknowledge the constructive reviews from Dr. Yi Cao, Martin-Izard, and two anonymous journal reviewers. This research was jointly supported by the


Meinert, L.D., Hefton, K.K., Mayes, D., Tasiran, I., 1997a. Application of skarn deposit terminology and Hf isotopes from the Phu Qiong skarn deposit, northern Loei Fold Belt, Thailand: evidence from fluid inclusions, rare earth elements, and stable isotope data. Econ. Geol. 98, 259–270.


Mezcala deposit, Guerrero, Mexico. J. Geochem. Explor. 78 (1–2), 65–82.


Ozoyan, T., 2010. Geochemistry, mineralogy and genesis of the Ayazmann Fe–Cu skarn deposit in Ayavik (Balkisir), Turkey. Ore Geol. Rev. 37 (3), 175–201.


