U-Pb Geochronology and Geochemistry of Stratiform Garnet from the Aqishan Pb-Zn Deposit, Eastern Tianshan, Xinjiang, NW China: Constraints on Genesis of the Deposit

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Abstract: The Aqishan lead-zinc deposit, located in the Jueluotag metallogenic belt of eastern Tianshan, Xinjiang, Northwest China, has a stratiform occurrence in the marine volcanic tuff of the Yamansu Formation. The ore body has a typical double-layer structure, having a stratified, stratoid, lenticular upper part and a veined, stockwork-like lower part. The occurrence of the upper orebody is consistent with that of the volcanic tuff wall rock. The ore minerals are mainly chalcopyrite, pyrite, sphalerite, galena and magnetite, the altered minerals mainly being silicified, such as sericite, chlorite, epidote, garnet. The garnetized skarn, being stratiform and stratoid, is closely related to the upper part of the orebody. Geological observations show that the limestone in the ore-bearing Yamansu Formation is not marbleized and skarnized. Spatially, it is associated with the ferromanganese deposits in the marine volcanic rocks of the Yamansu Formation. These geological features reflect the likelihood that the Aqishan lead-zinc deposit is a hydrothermal exhalation sedimentary deposit. The results from the EPMA show that the garnet is mainly composed of grossular–andradite series, contents being in a range of 34.791–37.8% SiO2, 32.493–34.274% CaO, 8.454–27.275% FeO, 0.012–15.293% Al2O3, 0.351–1.413% MnO, and lower values of 0.013–1.057% TiO2. The content of SiO2 vs. CaO and FeO vs. Al2O3 has a significant positive correlation. The results of ICP-MS analysis for the garnet show that the REE pattern is oblique to right in general. The total amount of rare earth elements is relatively low, 2REE = 71.045–826.52 ppm, which is relatively enriched for LREE and depleted for HREE. LREE/HREE = 8.66–4157.75, La/YbN = 23.51–984.34, with obvious positive Eu and Ce anomalies (ΔEu = 2.27–76.15, ΔCe = 0.94–1.85). This result is similar to the REE characteristics of ore-bearing rhyolite volcanic rocks, showing that the garnet was formed in an oxidizing environment and affected by clear hydrothermal activity. The U-Pb isotopic dating of garnet by fs-LA-HR-ICP-MS gives an age of 316.3 ± 4.4 Ma (MSWD = 1.4), which is consistent with the formation time of the Yamansu Formation. According to the study of deposit characteristics and geochemical characteristics, this study concludes that the Aqishan lead-zinc deposit is a hydrothermal exhalation sedimentary deposit, the garnet being caused by hydrothermal exhalative sedimentation.

Key words: garnet, LA-ICP-MS, U-Pb dating, hydrothermal exhalation sedimentary deposits, garnet trace element geochemistry, Aqishan Pb-Zn deposit

1 Introduction

The East Tianshan Jueluotag metallogenic belt, located to the south of the cities of Turpan and Hami in Xinjiang, northwestern China, is one of the most important metallogenic belts. The geotectonic structure is located in an orogenic collage between the Siberian plate and the Tarim plate, adjacent to the Danahu island arc zone by the Kangguer shear zone in the north, bordered by the Kumtuckduk fault to the south with the Tarim block. It is significantly including the Tuwu porphyry copper deposits (Rui et al., 2002), the Kanguer shear zone type gold and nickel deposit (Han et al., 2002), the Kangguer shear zone type gold and nickel deposit (Han et al., 2002; Mao et al., 2002, 2008; Wang et al., 2006; Wang and Xu, 2006; Chen et al., 2007; Pirajno et al., 2011), the Lubei copper-nickel sulfide deposit (Yang et al., 2017), the Weiqian silver and polymetallic skarn deposits (Han et al., 2002), Shilipo natural copper deposits (Dong et al., 2003), Hongyuntan, Yamansu and other Carboniferous marine volcanic iron formation of the ancient Asian Ocean, and tectonic closure prior to the Mesozoic (XBGMR, 1993; Li et al., 2002; Qin et al., 2002; Shu et al., 2002; Liu et al., 2003; Pirajno et al., 2011; Pirajno, 2013; Xiao et al., 2013) (Fig. 1). At present, more than 100 deposits have been discovered in this metallogenic belt (Chen et al., 2009), most significantly including the Tuwu porphyry copper deposits (Rui et al., 2002), the Kanguer shear zone type gold and polymetallic deposit (Han et al., 2002; Mao et al., 2002, 2008; Wang et al., 2006; Wang and Xu, 2006; Chen et al., 2007; Pirajno et al., 2011), the Lubei copper-nickel sulfide deposit (Yang et al., 2017), the Weiqian silver and polymetallic skarn deposits (Han et al., 2002), Shilipo natural copper deposits (Dong et al., 2003), Hongyuntan, Yamansu and other Carboniferous marine volcanic iron
deposits (Zheng et al., 2014; Li et al., 2015) and the VMS type deposits in Kalatage and Xiaorequanzi (Li, 2002; Liu et al., 2012). The famous copper–nickel sulfide metallogenic belt that extends from Huashan east to Tulaergen is located to the east, outside of the study area. The metallogenic age of these deposits is mainly late Paleozoic.

The Aqishan lead–zinc deposit is located about 400 km to the southeast of Urumqi, south of the Xiaorequanzi VMS deposit and the Kangguer gold and polymetallic deposit. It is a large deposit, discovered by the Xinjiang Geological and Mineral Investigation Institute in 2013, bounded by the Yamansu fault zone to the north, lying close to the Achikkuduk fault zone to the south (Fig. 1). The genesis of the deposit has been controversial since its discovery, as a result of stratiform garnet alteration close to the ore bodies (Chou et al., 2015; Xia et al., 2018; Deng et al., 2019). Some researchers have suggested that it is a skarn type deposit. According to others, the Aqishan lead-zinc deposit is a volcanic hydrothermal deposit, or a volcanically deposited–hydrothermally superimposed lead-zinc deposit, as a result of 306 ± 2.8 Ma granitic porphyry, sulfur isotopes and the ore bodies in marine volcanic rocks. Additionally, Chou et al. (2015) considered the Aqishan lead-zinc deposit to be VMS in nature, following their study.

In view of the above, this study aims to examine the geological characteristics, REE and trace elements of the stratiform garnets, as well as the geochronology for the Aqishan lead–zinc deposit, through the EPMA, fs-LA-ICP-MS garnet and U-Pb isotope analytical methods, in order to determine the origin and age of the Aqishan lead–zinc deposit.

2 Geological Setting

Eastern Tianshan is bounded by the Kangguer shear zone (Kangguer–Huashan flysch rock belt), which can be divided into the Ordovician–Devonian Dananhu island arc and the Carboniferous Jueluotag volcanic arc (XBGMR, 1993) (Fig. 1) in the study area, in which the Jueluotag volcanic arc is also referred to as the Yamansu rift trough (Li et al., 2002). During the Paleozoic, the East Tianshan Orogenic Belt experienced cracking and merging throughout the Early Ordovician, Late Devonian–Early Carboniferous cracking, the Late Carboniferous collision...
collaged with the Permo–Triassic intracontinental extension stages (XBGMR, 1993; Liu et al., 2003; Xiao et al., 2004).

A large number of volcanic rock geochemical studies have shown that the Jueluotag area of East Tianshan is likely to be a volcanic arc related to the subduction of oceanic crust in the late Paleozoic, but there are still disagreements regarding the location of the subduction zone and the polarity of that subduction. Many researchers believe that the Jueluotag volcanic arc and the Devonian Dananhu island arc on the north side of the Kangguer ductile shear zone are products of the same bidirectional subduction of the Kangguer ocean (Lin et al., 2009, 2013; Pirajno, 2010; Charvet et al., 2011; Wang et al., 2011; Ge et al., 2012; Xiao et al., 2013, 2014; Ma et al., 2014). Conversely, some suggest that the Kangguer ductile shear zone is the suture of the collision between the Juncgar–Turpan–Hami block and the Tarim block (Li et al., 2000; Han et al., 2002; Pirajno, 2010), the Jueluotag volcanic arc being a rift arc developed along the continental margin of the Tarim block (Li et al., 2002; Hou et al., 2006).

The mining area and its surrounding strata are mainly of the Lower Carboniferous Aqishan Formation, Yamansu Formation marine volcanics, the Upper Carboniferous Tugutubulak Formation continental volcanics and the Permian laeustrine volcaniclastic rock formation in the eastern part of the study area (XBGMR, 1993).

The Aqishan Formation in the northwestern part of the study area is generally constructed of medium–acid to fine marine volcaniclastic rocks of age 351 Ma–320 Ma (zircon U–Pb age) (Su et al., 2009; Luo et al., 2012; Wang et al., 2016; Zheng et al., 2017). Locally, a small amount of limestone occurs as lenses that can be seen in the dacite tuff, which is distributed around the submarine volcanic intrusions. The Yamansu Formation is not only a ferromanganese ore but also an important ore-bearing area of the Aqishan lead-zinc deposit. The lower rock assemblage is mainly composed of yellow–green tuff sandstone, siltstone and dacite tuff, garnet andesite tuff, with a small amount of thin limestone, conglomerate and tuff sandstone. The middle part is composed of grayish black pebbly tuffaceous siltstone, dacite tuff with limestone lenses, whilst the upper part is grayish green epidotic andesite. The andesite contains breccia tuff, tuff, volcanic breccia and andesite vitreous tuff, gray-green and fuchsia andesite tuff, lithic crystalline tuff with andesite and a small amount of thin-layer basalt assemblage. The upper part of the Yamansu Formation consists of tuffaceous siltstone, pozzolanic tuff, pebbly detritus tuff, dacite tuff, andesite with basalt and limestone. Zircon U–Pb indicates an age range from 330 Ma to 320 Ma (Li et al., 2011; Xu et al., 2014; Wang et al., 2016; Cui et al., 2018).

The Tugutubulak Formation is distributed south of the mining area and the north part of the Aqikkuduk fault. The overall lithological assemblage is intermediate-acid continental volcanic rock mixed with sedimentary rock, with a zircon U–Pb age of 314 Ma (Song et al., 2006). It is characterized by discontinuous limestone conglomerate at the bottom, to andesitic tuff and grayish green tuffaceous sandstone in the lower part, to mainly grayish green and purplish red dacite crystalline tuff, tuffaceous sandstone and siltstone, mixed with grayish white to yellowish white rhyolite crystalline tuff in the middle part, to grayish green–purplish red crystalline tuff, tuffaceous fine sandstone, siltstone in the upper, with a topmost layer of purplish red dacite volcanic breccia, breccia lava and tuff, mixed with grey-green andesite. The results of microscopic observation and electron probe microanalysis show that assemblages of graptolites and occurrences of chrysotile are commonly developed in this formation. The occurrence has a stable southeast tendency, the dip angle being about 60°.

Along with the geological events of the opening and closing of the Paleo–Asian Ocean in East Tianshan, Devonian granitic rocks (386.5 Ma–369.5 Ma, zircon U–Pb age) were mainly developed in the Dananhu island arc zone. The Early Carboniferous (349 Ma–330 Ma), Late Carboniferous to Late Permian (320 Ma–252 Ma) granodiorite, potassium feldspar granite (Zhou et al., 2010) and other batholiths, dykes and stocks are developed around the Bailingshan area to the south of the Aqishan mining area and the Caixiashan lead-zinc mine area. During the Permian, the basic-ultrabasic intrusions such as ultramafic rocks (peridotite, pyroxenite, etc.), mafic rocks (gabbro, norite, etc.) as well as a small amount of felsic rocks (diorite, etc.) related to the copper nickel sulfide deposits developed along the Kangguer shear zone, the formation time of the basic-ultrabasic intrusions mainly being concentrated around 290 Ma–260 Ma (Zhou et al., 2004; Mao et al., 2006; Tang et al., 2009; Sun et al., 2010; Wang et al., 2015). From the late Permian to the Triassic, the area was part of an extensional environment. A Triassic potassium feldspar granite intrusion is developed in Shyingtan (XBGMR, 1993). Additionally, a 306 Ma Permian monzogranite porphyry (Dai, 2019) and 275 Ma diabase dykes (Deng et al., 2019) are developed to the south of the Aqishan mining area.

The Aqishan lead-zinc deposit is located to the west of the Aqishan–Yamansu island arc belt. The northern part of the Aqishan–Yamansu island arc belt is connected to the Kangguer ductile shear belt by the Yamansu fault, the southern part being adjacent to the Central Tianshan block next to the Aqikkuduk–Shaquanzhi fault. The Yamansu fault is a north–south thrust nappe structure, which underwent ductile shear deformation in the Permian (Shu et al., 2002). The fault extends from east to west and inclines to the south with an angle of about 70°. The Aqieduk–Shaquanzhi fault has the same nature as the Yamansu fault, being a north–south thrust nappe structure, the fault trend being north–west (Fig. 1). The structural style of the mining area is simple, being an overall monoclinal structure. There is 1 NE-trending fault structure and 4 NW-trending secondary strike-slip faults in the area. The NE-trending fault structure is generally consistent with the trend of the strata. The NW-trending secondary fault is a left lateral translation fault, which cuts through the granite porphyry intrusive body. According to its occurrence characteristics, the fault has no obvious control over the ore body (Fig. 2), so it is speculated to be a post-mineralization fault (Chou et al., 2016).
3 Geological Characteristics of the Deposit

3.1 Ore body characteristics

The lead-zinc mineralization in Aqishan is concentrated in an area of 3600 m long and 180–800 m wide in the slope zone in front of the mountain. There are 42 ore bodies circled on the surface. The lead-zinc ore body is 80–3000 m long and 2–106 m thick with an average grade of 0.5%–1.21% Zn, 0.3%–0.9% Pb. The grade of Pb, Zn and Cu in the carbonaceous mudstone of the local drilling core is high, reaching the medium-to-large scale of the deposit. The ore body is stratiform, stratoid and lenticular, with a tendency to the SE and a dip angle of 35° to 45°, which is consistent with the strata (Figs. 2, 3). The upper lead-zinc ore body mainly occurs in the medium–coarse garnet skarn. The roof is fine-grained garnet skarn, the floor being albite lithic tuff. The lower lead-zinc ore body mainly occurs in the volcanic tuff and tuffaceous siltstone.

The principal ore minerals are sphalerite, galena, pyrite, chalcopyrite, arsenopyrite, magnetite, scheelite and specularite. The gangue minerals include calcite, quartz, epidote, barite, gypsum, tremolite and garnet. The ore structure type is relatively simple, mainly including automorphic-hypidiomorphic granular structure, allomorphic structure, cataclastic structure, metasomatic structure and emulsion texture. The ore structures in the mining area are mainly disseminated, banded, stratified, reticulated and brecciated (Fig. 4). The Aqishan lead-zinc deposit has the distribution characteristics of the upper layer and the lower vein structure, that is, the upper part is skarn-type layered zinc ore, the lower part is fissure vein and breccia-type zinc ore, with silicification, chloritization and epidotization.

3.2 Alteration

The main alteration types are garnet–diopside, albite–silicification, epidote–chlorite with localized barite and gypsum (Fig. 4). The garnet mineralization is closely related to the Aqishan Pb-Zn deposit, the orebody mainly being hosted in garnet skarn minerals (Fig. 3).

The characteristics of the garnet are that it is mostly granular and massive in the form of automorphic grains with the particle size of 0.01–0.1 mm. Its ring fabric is visible. Two kinds of morphology are recognized, one being in the form of an automorphic granular close inlay with obvious ring belt and internal alteration, the other is...
in the form of amorphous microcrystals. Quartz, carbonate and metal sulfides fill in the garnet crystal spaces and cracks.

The garnets are generally small at about 0.01 mm in size with epidote alteration, that content being about 10%. Generally, epidote is less than 0.02 mm in size, coarsely concentrated locally with a content of about 30%.

Diopside–tremolite alteration is mainly composed of tremolite at about 50% content, with about 8% diopside and a small amount of about 2% epidote. Tremolite occurs in the form of a radial aggregate that is columnar and fibrous. Diopside occurs as a semi-automorphic granular aggregate, with two groups of cleavage. Epidote occurs as an allomorphic granular aggregate.

The above-mentioned alteration is mainly developed in the roof of the upper orebody, while albitization is mainly developed on the floor of the upper orebody. Silicification, baritization and carbonation are mainly developed along the fractures within the rocks.

4 Samples and Methods

The garnet skarn samples AQ4801 and AQ4803 were collected from ZK4801 and ZK4803 (Fig. 2, 3) in the Aqishan Pb-Zn (Cu) deposit, respectively. Brown and grayish green garnet minerals can be seen in the garnet hand specimens from the Aqishan area. Under the microscope, the garnet is mainly hypidiomorphic to xenomorphic, with a grain size of 0.3–1 mm and a small quantity at 1–1.5 mm.

The garnet samples can be divided into two types: brown garnet sample AQ4803 and grayish green garnet sample AQ4801 (Fig. 5). The garnet sample AQ4803 was collected from the layered orebody, which was consistent with the occurrence of the ore body. The garnet developed a fragmented structure. A large amount of pyrite, chalcopyrite and sphalerite fill in the intergranular spaces and fissures of the garnet, chloritization being observed. AQ4801 is collected from the upper part of the stratiform orebody. The garnet is parallel to the bedding and the garnet surface has no obvious alteration characteristics. The samples were made into electron probe slices. After the garnet was observed, studied and photographed under the microscope, BSE was collected (Fig. 5) and the main elements of the garnet were analyzed by SEM and EPMA.

EMPA was completed at the Key Laboratory of Northeast Asian Mineral Resources Evaluation, School of Earth Sciences, Jilin University, using the electronic probe.
X-ray microanalyzer (Electron Microprobe), model JXA-8230. The analytical parameters were as follows: accelerating voltage 15 kV, current 20 nA, spot size 1 μm, standard sample SPI53 silicate or oxide.

U-Pb isotopic and trace element tests were carried out in the Key Laboratory of Mineralization and Resource Evaluation, Ministry of Land and Resources, Institute of Mineral Resources, Chinese Academy of Geosciences. The J200 Femtosecond Laser Ablation instrument (Applied Spectra, Inc.) was utilized for high-resolution inductively coupled plasma mass spectrometry (fs-LA-ICP-MS), the laser output wavelength being 343 nm, with laser pulse width <480 fs, the laser energy set at 50%, the beam spot at 60 μm and the frequency to 8 Hz. The inductively coupled plasma mass spectrometer system employed was the Thermo Scientific Element XR high resolution ICP-MS system. In the process of femtosecond laser ablation, helium was used as a carrier gas and argon as a compensation gas to adjust the sensitivity. The two were mixed through a T-shaped joint before entering the ICP. The total time for each test point was 3 min (15–20 s blank signal). The offline processing of the analytical data (including sample and blank signal selection, instrument sensitivity drift correction, element content and U-Th-Pb isotope ratio and age calculation) was completed by the software ICPMSDataCal (Liu et al., 2010). In this study, zircon standard 91500 was used as an external standard for fractionation correction of the garnet isotypes. Trace element content processing used the glass standard material NIST610 as an external standard for isotopic and trace element fractionation correction. 91500 and NIST610 standard samples were analyzed twice for every 5 sample points. The recommended U-Th-Pb isotopic ratios of zircon 91500 were based on Wiedenbeck et al. (1995). For a more detailed description of the analytical methods employed, see Zhang et al. (2020).

5 Results

5.1 Major element geochemistry

The major element analysis of garnet samples AQ4801 and AQ4803 by EPMA is shown in Supp. Table 1. The early garnet samples (AQ4803) were mainly grossular–andradite solid solution and range from And96Gro2Gro70 to And28Gro2Gro70 (illustrated in Fig. 6). Grayish green garnet (AQ4801) cores contained almost pure andradite, the edges being grossular–andradite. This result indicates that the garnet had concentrations of 34.791–37.738% SiO2, 32.493–34.815% CaO, 8.454–27.275% FeO, 0.012–14.905% Al2O3, 0.011–1.057% TiO2 and 0.351–0.849% MnO. The content of SiO2 and CaO is relatively stable and overall positively correlated. FeO and Al2O3 show significant positive correlation between brown and grayish green garnets.

5.2 REE geochemistry

The rare earth elements data is presented in Supp. Table 2. Overall, the REE (71.405–826.52 ppm) showed large variations and generally displayed LREE enrichment with HREE depletion and positive Eu and Ce anomalies (Fig.
of the two garnets are listed in Supp. Table 3. With 16 spots on sample AQ4803, the U isotopic compositions were conducted on sample AQ4801 using until recent years (Dewolf et al., 1996). Due to the discovery of the high content of U in the lattice of the grossular–andradite garnet, this technique has been widely used in metallocenic dating and has achieved good results (Deng et al., 2017; Seman et al., 2017; Gevedon et al., 2018; Wafforn et al., 2018; Zhang et al., 2018).

A total of 49 spot analyses for LA-ICP-MS U-Pb isotopic compositions were conducted on sample AQ4801 with 16 spots on sample AQ4803. The U-Pb isotopic data of the two garnets are listed in Supp. Table 3.

The U content of garnet in the AQ4801 garnet skarn is 1.33 ppm–32.2 ppm. The uncorrected data for AQ4801 in the Tera–Wasserburg diagram (Fig. 8a) yields a lower-intercept age of 316.3 ± 4.4 Ma (MSWD = 1.4), the individual 206Pb–238U ages for AQ4801 yielding a weighted average age of 314.6 ± 3.9 Ma (MSWD = 1.15). The U content of garnet in sample AQ4803 is 3.5 ppm–61.2 ppm. Similarly, the uncorrected data of AQ4803 in the Tera–Wasserburg diagram (Fig. 8b) yields a lower-intercept age of 321 ± 24 Ma (MSWD = 1.9), the individual 206Pb–corrected 207Pb/206Pb ages for AQ4803 yielding a weighted average age of 314.6 ± 3.9 Ma (MSWD = 0.81) (Fig. 8).

6 Discussion

6.1 Garnet geochemistry

The chemical formula of garnet is X3Y2[SiO4], in which X is usually a divalent cation and Y is a trivalent cation. Therefore, a large amount of Fe3+ is needed to occupy Y3+ in the andradite form. Research shows that Fe3+ exists more easily under oxidation conditions (Zhao, 1974; Liang, 1994; Gaspar et al., 2008). The results from EMPA in this study show that Al3+ is replaced by Fe3+ to form andradite, that is, in an oxidation environment, the change of this component not only making the brown garnet have the characteristics of a ring, but also reflects that the oxidation environment is conducive to the formation of lead-zinc mineralization (Fig. 5). Through this process, the MgO content in the garnet (AQ4803) increased, mainly due to Mg2+ being similar to Ca2+ in ionic radius, but only a small amount of Ca2+ was replaced. This result also indicates that the garnet was formed in an oxidative environment. Layered garnet as a whole has a lower content of terrigenous components such as TiO2 and Al2O3, while it is rich in hydrothermal components such as FeO, which is different from contact metasomatic skarn (Jamtev et al., 1994).

Rare earth elements have the characteristic of stable chemical properties and are widely used in the study of mineralization sources and evolution (Zhang et al., 2010). The garnet in the Aqishan area has lower total rare earth elements, which is characteristic of hydrothermal activity (Fleet, 1983). The distribution of rare earth elements has the same right deviation, LREE is relatively enriched, HREE is relatively deficient, Eu has a positive anomaly, which is similar to REE in submarine hydrothermal sediments. It shows that the formation process was affected by strong hydrothermal activity (Klinkhammer et al., 1994; Douville et al., 1999) and has the basic characteristics of thermal sedimentary formation (Zheng et al., 2006).

Generally, Ce has Ce3+ and Ce4+, the difference in Ce valency being caused by the redox character of the environment, in which Ce3+ is a soluble element and Ce4+ is an insoluble element. In an oxidation environment, Ce3+ is oxidized to Ce4+, which makes Ce4+ relatively enriched in the product. In contrast, Ce3+ occurs mainly in the form of a soluble element in a reducing environment, so Ce in the product is relatively deficient (De Baar et al., 1985; Feng et al., 1997). The garnet skarn Ce in the Aqishan lead–zinc mine area has the characteristics of positive Ce

Fig. 6. diagram of garnet division of the Aqishan lead-zinc deposit (base map according to Meinert et al., 2005). Gro–gроссуляр; And–андрадит; Alm–алмандин; Pyr–пироп; Spe–спессартине.

Fig. 7. Chondrite-normalized REE patterns of the Aqishan garnets.

Normalization values are from Sun & McDonough (1989).
anomalies except for some points with negative Ce anomalies, which indicates that the garnet was formed in a relatively oxidative environment.

Garnet in the Aqishan area has a distinct positive Eu anomaly, which is mainly due to the reaction of hydrothermal fluid and feldspar, which is consistent with the alteration of feldspar into sericite in rhyolitic breccia tuff (Fig. 4i).

Without considering the oxygen fugacity, Eu's valency is mainly affected by ion morphology and temperature (Sverjensky, 1984): generally, when the temperature is lower than 250°C, Eu ions are predominantly Eu$^{3+}$, the radius of eight coordinated Eu$^{3+}$ being close to that of eight coordinated Ca$^{2+}$, which is thus easy to replace, resulting in a positive Eu anomaly. When the temperature is higher than 250°C, Eu ions are mainly Eu$^{2+}$, the radius of eight coordinated Eu$^{2+}$ being significantly larger than Ca$^{2+}$, so it is difficult to replace them (Zhao, 1999). The pH value also has an effect on Eu, Cl$^{-}$ easily forming a stable complex with Eu$^{2+}$ under acidic conditions (Bau, 1991), which makes Eu exist in the fluid phase and the minerals show a negative Eu anomaly (Mayanovic et al., 2002; Allen et al., 2005; Mayanovic et al., 2007; Gaspar et al., 2008). The distinct positive Eu anomaly in the Aqishan deposit indicates that garnet may be formed under relatively low temperature and neutral or weakly acidic conditions. The positive abnormal increase in Eu of AQ4801 relative to AQ4803 indicates that the formation temperature is gradually decreasing.

6.2 U-Pb isotopic characteristics of garnet

The U-Pb ages of garnet of Aqishan deposit measured in this experiment were 314.6 ± 3.5 Ma (MSWD = 1.15, n = 49) and 321 ± 15 Ma (MSWD = 0.81, n = 16), which is consistent with the Early Carboniferous age of the Yamansu Formation. The U-Pb age of rhyolitic dacite in the western part of the Aqishan–Yamansu island arc belt was 341.7 ± 2.7 Ma (Su et al., 2009) and the zircon ages of dacite in the eastern, middle and western parts were 348 ± 1.7 Ma, 335.9 ± 2.4 Ma and 334 ± 2.5 Ma, respectively (Luo et al., 2012). The zircon ages of dacite in the Yamansu iron mine area were 345 ± 1.7 Ma, 335.9 ± 2.4 Ma and 334 ± 2.5 Ma, respectively, consistent with the figure of 334.7 ± 1.7 Ma from Wang et al. (2016), indicating formation in the Early Carboniferous. The LA-ICP-MS zircon U-Pb ages obtained from the rhyolites of the eastern and middle sections of the Aqishan–Yamansu island arc zone were 320.5 ± 1.2 Ma (Li et al., 2011) and 321.7 ± 1.7 Ma (Xu et al., 2014), the LA-ICP-MS zircon U-Pb age of the rhyolite in the Yamansu Formation in southern Aqishan is 318.6 ± 1.4 Ma (MSWD = 0.13, n = 21), the andesite zirconium zircon U-Pb age being 324.4 ± 1.5 Ma (MSWD = 0.096, n = 21) (Cui et al., 2018), forming in the Early Carboniferous–late Early Carboniferous. Combined with the spatial distribution characteristics of the Aqishan lead-zinc deposit, the orebody's metallogenic age can be regarded as 320 Ma.

6.3 Origin of the garnet and the deposit

More and more data show that the existence of skarn minerals does not mean that the deposit must be skarn-type in nature. Generally, skarn minerals are not only generated through contact metasomatism, but also by magmatism, metamorphism and hydrothermal exhalative sedimentation (Einaudi et al., 1982; Doyle et al., 2003; Meinert et al., 2005). So deposits related to the formation of garnet can also be formed through hydrothermal exhalation sedimentation (Wu, 1992; Lu et al., 1999; Yao et al., 2002; Yang et al., 2004).

There are a large number of garnet skarns in the roof and orebody of the Aqishan lead-zinc deposit. As there is no obvious regional metamorphism in the mining area, the garnet skarn was not formed by metamorphism; generally, magmatic skarn contains melt inclusions and the wall rock contact zone around the rock mass will have a fade zone. The rock mass shows the product of quenching and crystallization of high-temperature dense magma or melt (flow) body, which is clearly distinct from other genetic types. No melt inclusions are found in the garnet of the study area and no obvious fading zone is found in the limestone and other wall rock contact zones nearby, indicating that the garnet is not magmatic skarn. A large

Fig. 8. Concordia plots and weighted average $^{206}$Pb/$^{238}$U plots of the garnets.
number of stratiform and stratoïd garnet minerals are found amongst the strata of the Aqishan lead-zinc mine area, which are mainly produced in volcanic tuff, not near the granite porphyry, with there being no skarn in the limestone intercalation. Obviously, this geological feature is different from typical contact metasomatic garnet, but it is similar to the garnet in the Linong layered copper deposit in southwestern China (Lu et al., 1998). The contact metasomatic skarn formed by intermediate acid magmatic intrusion into carbonate rocks or calcareous sedimentary rocks is controlled by the contact zone, which is cistic, lenticular and irregular. The scale and zoning of contact metasomatic skarn indicate that the scale of metasomatism can reach from several meters up to hundreds of meters. In addition, the results from the electron microprobe show that garnets in this area are mainly composed of grossular–andradite and a small amount of spessartine, as well as obvious enrichment of light rare earth elements, relative depletion of heavy rare earth elements, the presence of a positive Ce anomaly and a distinct positive Eu anomaly, indicating that the garnet was affected by strong hydrothermal sedimentation and formed in a low temperature sea bottom or oxidation environment.

From the perspective of the spatial distribution of the Aqishan lead-zinc deposit, the volcanic rocks of the Yamansu Formation are located on the east and southwest sides of the Aqishan volcanic apparatus. The ore-bearing wall rocks are mainly marine rhyolite and rhyolitic tuff, which are relatively remote from the volcanic apparatus. The drill core results indicate that the upper part of the formation is made of marine andesite volcanic rock (Fig. 3). Not only are the ore minerals chalcopyrite, pyrite, sphalerite, iron-bearing sphalerite, galena, magnetite, hematite to Mn-Fe-Ti oxides from the center outwards, but also there are more or less marine volcanic Mn-Fe-Ti deposits occurring around the Aqishan deposit spatially (Fig. 1). Meanwhile, the mineralization pattern in the upper part is characterized by laminarity, as distinct from a small amount of stockwork and disseminated mineralization in the lower part. It is clearly different from a contact metasomatic sedimentary skarn deposit and similar to submarine hydrothermal exhalation sedimentary deposits (Barrie et al., 1999; Franklin et al., 2005). The age of the garnet is 321 Ma–314 Ma and the U-Pb age of the rhyolite zircon is 318.6 ± 1.4 Ma, which is consistent with the formation time of the volcanic tuff formation. The ore body in the Aqishan lead-zinc deposit is the same as that of the volcanic tuff formation. The ore body has an obvious double-layer structure, the upper part of which is stratiform or stratoïd, the lower part being stockwork mineralization, with the structural characteristics of a hydrothermal exhalative sedimentary deposit. A large area of stratiform garnet is developed around the orebody. EPMA results show that garnets in this area are mainly composed of grossular–andradite and a small amount of spessartine, as well as pronounced enrichment of light rare earth elements, relative depletion of heavy rare earth elements, the presence of a positive Ce anomaly and a clear positive Eu anomaly, indicating that the garnet was affected by strong hydrothermal activity.

The U-Pb isotope dating of garnet in the stratiform orebody is from 321 ± 15 Ma to 314.6 ± 3.9 Ma, which is consistent with the formation time of the volcanic tuff around the deposit and has the characteristics of a syngenetic deposit.

The formation of the Yamansu Formation around the ore body in the Aqishan lead-zinc mine area is as a set of coastal-shallow sea elastic deposits formed in an island arc environment. Combining the characteristics of the ore body and the main elements of the garnet, rare earth elements, as well as the U-Pb isotope dating results, the Aqishan lead-zinc deposit can be identified as a hydrothermal exhalation sedimentary deposit.

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