Textural and chemical evolution of magnetite from the Paleozoic Shuanglong Fe-Cu deposit: Implications for tracing ore-forming fluids

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ABSTRACT

The Aqishan-Yamansu belt in Eastern Tianshan (NW China) hosts several important Fe and Fe-Cu deposits, the origin of which is the subject of considerable debate. The coexistence of various types of ore-forming fluids makes it difficult to distinguish the genesis of the Fe-Cu deposits. We present detailed textural and compositional data on magnetite from the Paleozoic Shuanglong Fe-Cu deposit to constrain the formation of iron oxides and the evolution of the ore-forming fluids and thus define the genesis of the Fe-Cu ores.

Based on the mineral assemblages and crosscutting relationships of veins, two mineralization stages were established, including the early Fe mineralization and late Cu mineralization stage. Three types of magnetite, i.e., platy (MA), massive (MB), and granular (MC) magnetite occur in the Fe mineralization. Backscattered electron (BSE) images identified display oscillatory zoning in an early hematite and transformational mushketovite phase (MA-I), characterized by abundant porosity and inclusions, as well as two later generations, including an early dark (MA-II, MB-I, and MC-I) and later light magnetite (MA-III, MB-II, and MC-II). The MA-I has extremely high W contents and mostly displays as micro- and invisible scheelite inclusions, which were probably caused by the W expulsion during mushketovitization. The texture and composition of magnetite suggest that the later light magnetite formed via dissolution and reprecipitation of the precursor dark magnetite, and the temperature and oxygen fugacity of fluids decreased over time. Our study also shows the MB-II magnetite and coexisting chlorite display synchronous oscillatory zoning, with the calculated temperature from 444 to 212 °C. Such variations could indicate the incursion of external low-temperature fluids with high salinity, which can dissolve the primary dark magnetite. This study provides a good example of using magnetite to trace the complex evolution and multiple sources of ore-forming fluids.

Keywords: Magnetite, texture and chemistry, ore-forming fluid, Fe-Cu deposit, Eastern Tianshan

INTRODUCTION

Magnetite is a common mineral in many types of ore deposits, including Kiruna-type, BIF (banded iron formation), magmatic Fe-Ti oxide, Fe-skarn, IOCG, and porphyry deposits, and also in many igneous, metamorphic, and sedimentary rocks (Dare et al. 2014; Dupuis and Beaudoin 2011; Hu et al. 2015, 2017; Huang and Beaudoin 2019; Nadoll et al. 2012, 2014; Wu et al. 2019; Zhao et al. 2018a). It can accommodate a variety of trace elements into its inverse spinel structure by substitution with Fe³⁺ and Fe²⁺ in tetrahedral or octahedral sites (Nadoll et al. 2014), and its textures and chemical compositions vary in response to different mineralizing systems and physicochemical conditions

(Dare et al. 2014; Dupuis and Beaudoin 2011; Huang et al. 2019a; Nadoll et al. 2012). Previous studies have developed a series of discriminant diagrams to fingerprint various deposit types or ore-forming processes based on the compositional variety in magnetite (Dupuis and Beaudoin 2011; Nadoll et al. 2012). However, recent studies have also shown that the textural and chemical composition of magnetite can be significantly modified or reequilibrated by hydrothermal fluid and supergene processes (Broughm et al. 2017; Bain et al. 2021; Hu et al. 2014, 2015; Huang and Beaudoin 2019; Huang et al. 2018; Wen et al. 2017; Zhang et al. 2020b), for instance, mixing with high-salinity, chlorine-rich fluids have been suggested as an important mechanism for inducing coupled dissolution-reprecipitation (DR) reactions in magnetite from hydrothermal deposits such as skarn deposits and iron oxide-copper-gold deposits (Hu et al. 2014, 2015; Huang and Beaudoin 2019; Liang et al. 2020; Yin et al. 2017).

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The Aqishan-Yamansu belt in the Chinese eastern Tianshan hosts many important Fe-Cu deposits, including Heijianshan, Duotoushan, Shuanglong, and Shaquanzi (Fig. 1c; Zhao et al. 2017). These Fe-Cu deposits have been described as skarns (Mao et al. 2005), but the absence of some typical features of typical skarn deposit, such as the close relationships of orebodies with carbonate host rocks, and garnet-pyroxene skarn alteration, indicates that they are not typical skarn deposits. Recent studies reveal that these are possibly IOCG-like deposits according to the presence of hematite and calcite-rich Cu mineralization as well as the less amounts of pyrite, and the fluid inclusions and sulfur isotopes studies show involvement of seawater or basinal brine (Jiang et al. 2018; Zhao et al. 2017; Zhang et al. 2018b). Thus, investigation of fluid evolution is very important for its ore genesis. As magnetite is a common mineral in these Fe-Cu deposits, the study of its texture and composition can provide important information about the ore-forming fluid and can be used to investigate the source of the mineralization. The Shuanglong system is a typical Fe-Cu deposit in the Aqishan-Yamansu belt, located in the east of the Bailingshan complex (Fig. 1c). The existence of abundant magnetite in the Shuanglong deposit provides a good opportunity to investigate the sources and evolution of ore-forming fluids during Fe and Cu mineralization based on the textural and chemical characteristics of magnetite.

We present detailed textural and compositional data using backscattered electron (BSE) imaging combined with electron probe microanalyzer (EPMA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of magnetite from the Shuanglong Fe-Cu deposit, to characterize the factors controlling the formation of the various iron oxides and the evolution of the corresponding ore-forming fluids, to constrain the genesis of the regional Fe-Cu mineralization.

GEOLOGIC SETTING

Regional geology

The Central Asian Orogenic Belt (CAOB; Fig. 1a) is a complex collage of ophiolite suites, magmatic arc remnants, accretionary wedges, and continental fragments (Şengör 1996; Şengör et al. 1993; Windley et al. 2007), which formed during the evolution of the Paleo-Asian Ocean (PAO) through a long period from the Neoproterozoic to Neopaleozoic (Han and Zhao 2018; Şengör et al. 1993; Windley et al. 2007; Xiao et al. 2013). The Eastern Tianshan, situated to the north of the Tarim Basin in North Xinjiang (Fig. 1b), can be divided into the Dananhu-Tousuquan Island Arc Belt, Kangguer Shear Zone, and Aqishan-Yamansu Belt (from north to south) by the E-W-trending Kangguer and Yamansu faults (Fig. 1c).

The Dananhu-Tousuquan Island Arc Belt is situated to the north of the Kangguer shear zone and contains Devonian to Carboniferous volcanic and plutonic rocks, and hosts several porphyry copper deposits, including the Tuwu-Yandong deposit (Fig. 1c; Mao et al. 2005). The Kangguer Shear Zone is an important regional structure that separates the Junggar Block from the Tarim Block (Chen et al. 2019), and contains ductility deformed Carboniferous volcaniclastic rocks that have been metamorphosed to greenschist facies (Xiao et al. 2004) and Permian mafic-ultramafic intrusions (Qin et al. 2011). The shear zone hosts Au deposits in the west (e.g., Shiyingtan and Kangguer; Xiao et al. 2004) and Cu-Ni deposits in the east (e.g., Huangshan and Huangshandong; Fig. 1c; Qin et al. 2011).

The Aqishan-Yamansu Belt (Fig. 1c) contains mainly Carboniferous volcanic, volcaniclastic, and clastic rocks overlain by Permian clastic and volcanic rocks with local carbonate interbeds (Mao et al. 2005). The Carboniferous rocks consist of the Early Carboniferous Yamansu and Late Carboniferous Tugutubulak formations (Zhao et al. 2018b). Late Carboniferous to Early Triassic felsic intrusions intruded the Carboniferous Aqishan-Yamansu strata (Zhao et al. 2018b; Zhou et al. 2010) and are associated with Fe- and Fe-Cu deposits, including Hongyuntan, Bailingshan, Chilongfeng, Heijianshan, Yamansu, and Shaquanzi (Huang et al. 2018; Jiang et al. 2018; Zhao et al. 2017). Previous studies have proposed that the Aqishan-Yamansu belt represents an arc-related basin formed by southward subduction of the Kangguer oceanic plate beneath the Central Tianshan block during the Early Carboniferous (350-330 Ma), and the basin was then inverted during the Late Carboniferous (320-305 Ma; Zhang et al. 2020b).

Ore deposit geology

The Shuanglong Fe-Cu deposit is located ~260 km south of Hami city, NW China. The Shuanglong deposit is hosted in the Upper Carboniferous Tugutubulak Formation, which can be subdivided into three members: the lower member consisting of basalt, volcanic breccia, and volcanic tuff, which is volcanic explosive facies, and the middle member that is volcanic overflowing facies of volcanic tuff and rhyolitic ignimbrite, and the upper member that is volcano-sedimentary facies, comprising mainly andesitic tuff with carbonate interlayers. These volcanic rocks and volcaniclastic rocks all belong to the calc alkali series. Previous studies have shown that the volcanic tuff in the Shuanglong deposit has LA-ICP-MS zircon U-Pb ages of 319.1 ± 1.9 to 305.4 ± 1.6 Ma (Zhang et al. 2020b). The Tugutubulak Formation at Shuanglong was intruded by the Bailingshan intrusive complex, including diorite $(317.1 \pm 3.3 \text{ Ma}; \text{Zhang et al. } 2020a)$, monzogranite $(311.0 \pm 1.4 \text{ Ma}; \text{Zhang et al. } 2020\text{ b});$ granodiorite $(307.5 \pm 1.7 \text{ Ma}; \text{Zhao et al. } 2019)$, and minor granite and granite porphyry $(306.9 \pm 1.7 \text{ Ma}; \text{Fig. 2}; \text{Zhang et al. 2020b})$. Multiple faults have been recognized in the Shuanglong ore district, and the ore bodies are associated with the E-trending Shuanglong fault (Fig. 2).

Two ore zones have been defined in the Shuanglong district. The main Fe-Cu orebody (L3) occurs in the northern zone, extending for ~120 m in length with a width ranging from 9 to 27 m (Fig. 2). The orebody was controlled by the Shuanglong faults, and its dip direction is consistent with the fault dip and infilled in the fault. The host rocks of the orebody are Carboniferous Tugutubulak Formation volcaniclastic rocks and diorite intrusions. The ore minerals consist primarily of magnetite, hematite, and sulfides, including pyrite, pyrrhotite, and chalcopyrite. The wall rock alteration includes garnet (andradite), K-feldspar, epidote, amphibole (actinolite), quartz, calcite, and chlorite (pycnochlorite) alteration. Three hydrothermal alteration and mineralization stages can be identified at Shuanglong, namely (I) Skarn alteration, (II) Fe mineralization, and (III) Cu mineralization (Fig. 3).



FIGURE 1. (a) Simplified tectonic map of the Central Asian orogenic belt (CAOB), modified after Şengör (1996). (b) Tectonic map of north Xinjiang, modified after Chen et al. (2012). (c) Geological map of the Eastern Tianshan and distribution of the ore deposits, modified after Zhao et al. (2019). (Color online.)

Stage I skarn alteration contains abundant garnet occurring as euhedral to subhedral fine-grains in the magnetite ore and wall rock and is commonly replaced or cut by the Stage II K-feldsparmagnetite veins. The Stage II Fe mineralization mainly contains platy mushketovite that coexists with amphibole (Figs. 4a–4b), massive magnetite that occurs with amphibole, chlorite, quartz, and pyrite (Figs. 4c–4d), and disseminated magnetite with Kfeldspar, or epidote-amphibole in wall rocks that have undergone early K-feldspar alteration and secondary epidote-amphibole (-calcite) alteration (Figs. 4e–4f). In addition, residual hematite can be found in the cores of the mushketovite (Fig. 4b), indicating that hematite Stage occurred before the magnetite. Stage III Cu mineralization is dominated by veins or aggregates of quartz-hematite-chalcopyrite (Figs. 4g–4h) and epidote-calcitehematite-chalcopyrite, with locally minor chlorite.

SAMPLES AND ANALYTICAL METHODS

Representative samples of three types of magnetite from Stage II Fe mineralization were selected for this study. The magnetite samples include platy magnetite (MA Mag = SL16-6, SL16-8, SL17-157) and massive magnetite (MB Mag = SL17-116, SL17-118) collected from the ore bodies, as well as disseminated

FIGURE 2. Geological map of the Shuanglong Fe-Cu deposit [modified after Xinjiang Uygur Autonomous Region Geological Survey (2003)]. (Color online.)



magnetite (MC Mag = SL17-88, SL17-136, SL17-137) from the wall rocks. The chlorite and pyrite which coexist with magnetite were also selected for analysis in this study, including chlorite in platy magnetite sample (SL17-157) and massive magnetite sample (SL17-116, SL17-118), and pyrite in platy magnetite sample (SL17-157), massive magnetite sample (SL17-116) and disseminated magnetite sample (SL17-157), massive magnetite sample (SL17-116) and disseminated magnetite sample (SL17-88). All samples were prepared as standard polished thin sections and subsequently analyzed for their textural characteristics by scanning electron microscope (SEM) in backscattered electron (BSE) mode, magnetite, chlorite, and pyrite major chemistry by elser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The representative sample sections were carbon coated and then investigated with a Σ IGMA SEM in BSE mode at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). The major element geochemistry of magnetite, chlorite, and pyrite was analyzed using a JEOL JXA-8230 electron microprobe at the Shandong Analysis Center of China Metallurgical Geology Bureau. The operating conditions were 15 kV accelerating voltage, 20 nA beam current, 1 µm beam diameter, 10 s counting time, and ZAF correction procedure for the data reduction.



FIGURE 3. Alteration and mineralization paragenesis of the Shuanglong Fe-Cu deposit.

Zoning in magnetite grain was mapped using EPMA for Fe, Si, Ti, Al, Mn, and V, and zoning in chlorite grain was mapped for Si, Fe, Al, and Mg. The operating conditions were 20 kV voltage, 300 nA probe current, 0.5 to 4 μ m beam size, and a dwell time of 100 to 200 ms for each point used for mapping.

Magnetite trace element geochemistry was analyzed by LA-ICP-MS at the In Situ Mineral Geochemistry Lab, Ore Deposit and Exploration Centre (ODEC), Hefei University of Technology, Hefei, Anhui Province, China. The analyses were carried out on an Agilent 7900 Quadrupole ICP-MS coupled to a Photon Machines Analyte HE 193 nm ArF Excimer Laser Ablation system. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP (Ning et al. 2017; Wang et al. 2017). Each analysis was performed with a uniform spot size diameter of 30 mm at 8 Hz with an energy of ~4 J/cm² for 40 s after measuring the gas blank for 20 s. Standard reference materials NIST 610, NIST 612, BCR-2G, and MASS-1 were used as external standards to plot calibration curves using preferred element concentrations for the USGS reference glasses from the GeoReM database (http://georem.mpch-mainz.gwdg.de/). Off-line data processing was undertaken using the ICPMS Data Cal software package (Liu et al. 2008), and ⁵⁷Fe was used as internal standardization.

RESULTS

Petrography and texture of magnetite and chlorite

As mentioned above, magnetite in the Shuanglong deposit is composed of platy (MA), massive (MB), and granular (MC) types from the Stage II Fe mineralization stage. The MA magnetite commonly coexists with amphibole and shows three different zones in BSE images (central light, medium dark, and outer light; Figs. 5a-5b), indicating that it may have evolved through three generations. The light magnetite (MA-I) in the core is characterized by residual hematite, abundant porosity, and inclusions that commonly consist of tiny W-bearing minerals such as scheelite (Fig. 5b) and is commonly overgrown by the later dark MA-II magnetite that grows parallel to the contact interface of MA-I magnetite (Fig. 5b). Median dark magnetite (MA-II) is characterized by abundant silicate inclusions (i.e., amphibole) and weak to obvious oscillatory zoning including dark and light bands (MA-IID and MA-IIL; Fig. 5b). The outermost light magnetite (MA-III) lacks porosity and inclusions, and several dark bands occur within its rim (MA-III; Fig. 5b).

The MB magnetite occurs as aggregates of euhedral grains, coexisting with amphibole, minor chalcopyrite, and chlorite (Figs.



FIGURE 4. Photographs showing representative alteration/ mineralization paragenesis in the Shuanglong Fe-Cu deposit. (a) Platy MA magnetite. (b) Photomicrographs of platy MA magnetite. (c) Massive magnetite coexisting with amphibole, chlorite and chalcopyrite. (d) Photomicrographs of massive MB magnetite. (e) MC magnetite coexisting with K-feldspar, epidote, and amphibole in host rock of the Tugutubulak Formation. (f) Photomicrograph of granular MC magnetite coexisting with Kfeldspar and epidote. (g-h) Quartz-hematite-chalcopyrite vein cutting platy MA magnetite. Abbreviations: Mag = magnetite; Kfs = potassium feldspar; Cal = calcite; Ep = epidote; Amp = amphibole; Qtz = quartz; Hem = hematite; Ccp = chalcopyrite; Chl = chlorite. (Color online.)

4c–4d). It shows two generations, including primary dark magnetite, which is characterized by well-developed oscillatory zoning, and secondary light magnetite (Fig. 5d). In the primary dark magnetite with oscillatory zoning, the dark magnetite (MB-ID) has been overgrown by later light magnetite (MB-IL), and abundant porosity in the light magnetite (Fig. 5d). Complete MB-I magnetite grains have been replaced by secondary MB-II light magnetite, with abundant porosity and inclusions such as chlorite and chalcopyrite, distributed in the secondary MB-II magnetite at the interface between MB-I and MB-II magnetite (Figs. 5d and 5f). In addition, some MB-II also overgrew with primary dark magnetite grain and displayed oscillatory zoning with dark bands (Fig. 5d).

FIGURE 5. Photomicrographs (a, c, e, and g) and BSE images (b, d, f, and h) of the Shuanglong magnetite. (a) Platy magnetite (MA). (b) BSE images of platy magnetite, which shows three different zones. MA-I magnetite is light with abundant porosity and inclusions. MA-II magnetite is dark and shows chemical oscillatory zoning. MA-III magnetite is light and is lack of porosity and inclusions. (c) Massive magnetite (MB). (d) Two generations of magnetite in massive magnetite (MB). The first generation of magnetite (MB-I) shows oscillatory zoning composed of dark-gray (MB-ID) and light-gray (MB-IL) zones, and MB-ID magnetite was replaced by MB-IL magnetite, which contains abundant porosity and inclusions. The second generation of magnetite (MB-II) crosscuts MB-I magnetite and contains porosity and inclusions locally. (e) Massive magnetite (MB) and later mineral assemblage of chalcopyrite-sphalerite-chlorite. (f) BSE image of MB magnetite shows that the secondary magnetite (MB-II) contains chalcopyrite inclusions crosscutting the first generation of magnetite (MB-I). (g) Granular magnetite (MC) coexisting with K-feldspar and epidote, and K-feldspar was replaced by late epidote and calcite. (h) BSE image of MC magnetite, which shows two different zones. MC-I magnetite is dark and replaced by MC-II light magnetite. Abbreviations: Mag = magnetite; Kfs = potassium feldspar; Ep = epidote; Amp= amphibole; Qtz = quartz; Hem = hematite; Chl = chlorite; Sch = scheelite; Ccp = chalcopyrite; Sp = sphalerite; Cal = calcite. (Color online.)

The MB-II magnetite mainly coexists with chlorite, as shown in the micro-inclusions and cracks (Fig. 6a). The chlorite occurs as pseudo-uniaxial plates arranged in rosette-shaped aggregates (Figs. 6a and 6b). SEM images show that rosette chlorite displays oscillatory zoning pattern and mainly includes two zones (Figs. 6a and 6b). Zone 1 is composed of stacks of $20-80 \mu m$ thick layers, suggesting that the primary chlorite grew in an open space. Chlorite in zone 2 overgrows along the crystal in zone 1, and some also exist as euhedral to subhedral crystals. Chlorites in both zones show alternated dark and light bands, and the zone 2 chlorite coexists with the outermost layer of MB-II magnetite (Fig. 6a).

The MC magnetite commonly occurs as euhedral or subhedral granular magnetite in the wall rock, accompanied by two stages of alteration of an early K-feldspar(-calcite) phase and a late epidote-amphibole phase, where the K-feldspar is replaced by later epidote and calcite (Fig. 5g). These two phases of alteration may also be reflected in the textures of the magnetite, as the primary dark magnetite (MC-I) has been replaced by the secondary light magnetite (MC-II) which coexists with epidote (Figs. 5g–5h), and the MC-I magnetite probably formed with the early K-feldspar based on the sequence of alteration identified in wall rock.

Therefore, based on the petrography and texture of the different types of magnetite, they can be divided into three phases: an early MA-I mushketovite, a second phase including MA-II, MB-I, and MC-I magnetite, which occur as "dark bands" in BSE images; and the third phase of magnetite including MA-III, MB-II, and MC-II which occur as "light bands" in BSE images.



FIGURE 6. BSE images (**a** and **b**) of the MB magnetite and coexisting chlorite, and EMPA mapping of selected elements in chlorite. Abbreviations: Hem = hematite; Chl = chlorite. (Color online.)

EPMA

The EPMA elemental mapping shows that the three generations in MA magnetite including the first generation of MA-I magnetite transformed by precursor hematite, and the later phrases (MA-II and MA-III) are overgrown with it. The dark magnetite (MA-II) contains higher contents of Si, Al, but lower Fe content than the light magnetite (MA-I and MA-III; Fig. 7a). In the MB magnetite, the dark magnetite (MB-I) contains higher contents of Si, Al, but lower Fe and V contents than light magnetite (MB-II; Fig. 7b). For the dark and light bands in the oscillatory zoned MB-I magnetite, they display similar variation trend as the dark MB-ID magnetite which contains higher Si, Al, and lower Fe contents than light MB-IL magnetite (Fig. 7b). The EPMA elemental mapping shows that the dark zone in MC magnetite (MC-I) contains higher contents of Si and Al, but lower Fe contents than the light magnetite (MC-II; Fig. 7c).

A total of 201 EPMA spot analyses were completed on the magnetite, with 30 spots on MA-I, 29 on MA-IID, 21 on MA-IIL, 36 on MA-III, 27 on MB-ID, 11 on MB-IL, 17 on MB-II, 13 on MC-I, and 18 on MC-II. The full results of chemical contents of the Shuanglong magnetite are presented in Table 1. Figure 8a shows comparative box and whisker diagrams of major elements in the various magnetite generations.

The mushketovite (MA) contains three generations of magnetite, and the MA-II magnetite with oscillatory zoning has dark and light zones (MA-IID and MA-IIL), thus corresponding to four compositional groups (Fig. 7a). MA-I magnetite has the highest average Fe (72.9 wt%), the lowest Si (0.03 wt%), Al (0.02 wt%), Ca (0.03 wt%), Mn (0.08 wt%), and Ti (0.03 wt%), and the contents of Mg, V, Cr, and Ni are mostly below the detection limit; MA-IID magnetite has the lowest average Fe (68.5 wt%), the highest average Si (1.4 wt%), Al (0.43 wt%), Ca (0.68 wt%), Mg (0.08 wt%), Mn (0.13 wt%), Ti (0.03 wt%); MA-IIL magnetite contains moderate average Fe (67.0 wt%), and moderately high average Si (0.94 wt%), Al (0.22 wt%), Ca (0.42 wt%), Mg (0.06 wt%); MA-III magnetite has similar composition as MA-I, containing (average) contents of Fe (72.2 wt%), Si (0.19 wt%), Al (0.09 wt%), Ca (0.25 wt%), Mn (0.08 wt%), Ti (0.04 wt%), and Mg (0.02 wt%), with the contents of Cr and Ni mostly below the detection limit.

The MB magnetite contains two generations, and the primary generation (MB-I) contains obvious oscillatory zoning, including dark and light zones (MB-ID and MB-IL). MB-ID magnetite has the lowest average Fe (68.8 wt%), and the highest average Si (1.07 wt%), A1 (0.52 wt%), Ca (0.56 wt%), Mg (0.07 wt%), and Ti (0.11 wt%); MB-IL magnetite contains moderately low average Fe (70.0 wt%), and moderately high average Si (0.73 wt%), Al (0.33 wt%), Ca (0.40 wt%), Mg (0.05 wt%), and Ti (0.06 wt%); MB-II magnetite has the highest average Fe (72.1 wt%), and the lowest Si (0.11 wt%), Al (0.03 wt%), Ca (0.04 wt%), and Ti (0.05 wt%). All the MB magnetite subtypes contain similar Mn (0.072, 0.071, 0.058 wt%, respectively) and V (0.024, 0.024, 0.03 wt%, respectively). The concentrations of Ni and Cr are mostly below the detection limit. For the MC magnetite, MC-I magnetite has higher average Si (0.69 wt%), Al (0.16 wt%), Ca (0.36 wt%), Mg (0.04 wt%), Mn (0.14 wt%), Ti (0.04 wt%), V (0.06 wt%), and lower average Fe (70.0 wt%) compared to MC-II magnetite, which has lower average Si (0.18 wt%), Al (0.02 wt%), Ca (0.06 wt%), Mg (0.01



FIGURE 7. EMPA mapping of selected elements in magnetites from the Shuanglong deposit. (Color online.)

Magnetite type		Fe	Si	AI	Ca	Mg	Mn	Ti	V	Cr	Ni
MA-I (n = 30)	Mean	72.868	0.025	0.018	0.033	0.008	0.084	0.031	0.018	0.015	bdl
	Min	70.019	bdl								
	Max	73.711	0.097	0.037	0.090	0.011	0.154	0.037	0.020	0.023	bdl
MA-IID (n = 29)	Mean	68.488	1.400	0.428	0.675	0.081	0.130	0.034	0.024	0.017	0.026
	Min	67.238	1.014	0.209	0.417	0.061	0.026	bdl	bdl	bdl	bdl
	Max	69.885	1.646	0.597	0.855	0.125	0.197	0.052	0.044	0.027	0.032
MA-IIL (n = 21)	Mean	69.965	0.942	0.217	0.418	0.060	0.117	0.040	0.027	0.037	0.025
	Min	67.444	0.089	0.025	0.044	0.004	0.029	bdl	bdl	bdl	bdl
	Max	71.229	1.305	0.409	0.666	0.103	0.177	0.073	0.033	0.097	0.025
MA-III (n = 36)	Mean	72.171	0.192	0.087	0.253	0.022	0.083	0.036	0.022	0.025	bdl
	Min	69.058	0.014	bdl							
	Max	73.217	1.070	0.414	0.398	0.054	0.147	0.046	0.040	0.032	bdl
MB-ID (n = 27)	Mean	68.763	1.072	0.518	0.560	0.068	0.072	0.112	0.024	0.023	bdl
	Min	67.133	0.850	0.343	0.404	0.034	bdl	0.061	0.015	bdl	bdl
	Max	69.990	1.447	0.677	0.748	0.159	0.132	0.187	0.034	0.040	bdl
MB-IL (n = 11)	Mean	69.971	0.732	0.333	0.399	0.049	0.071	0.060	0.024	0.017	bdl
	Min	69.373	0.620	0.248	0.340	0.028	bdl	0.027	bdl	bdl	bdl
	Max	70.976	0.837	0.372	0.447	0.094	0.114	0.100	0.030	0.020	bdl
MB-II (n = 17)	Mean	72.101	0.113	0.030	0.040	0.010	0.058	0.049	0.030	0.024	bdl
	Min	71.138	0.043	0.006	bdl						
	Max	72.790	0.326	0.076	0.090	0.013	0.097	0.064	0.055	0.031	bdl
MC-I (n = 13)	Mean	70.018	0.691	0.175	0.361	0.039	0.140	0.041	0.061	0.023	0.037
	Min	69.165	0.364	0.066	0.151	0.023	0.092	0.002	0.004	bdl	bdl
	Max	71.273	0.858	0.268	0.539	0.055	0.170	0.069	0.088	0.037	0.037
MC-II (n = 18)	Mean	71.595	0.181	0.018	0.063	0.008	0.095	0.031	0.041	0.028	0.036
- (-)	Min	71.005	0.098	0.005	0.023	bdl	0.055	bdl	0.017	bdl	bdl
	Max	72.092	0.261	0.041	0.234	0.013	0.132	0.039	0.073	0.072	0.037

TABLE 1.	Mean, minimum,	, and maximum	contents (wt%)) of magnetite f	rom the Shuan	glong De	eposit b	y electron micro	probe analy	/ses
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wt%), Mn (0.1 wt%), Ti (0.03 wt%), V (0.04 wt%), and higher average Fe (69.2 wt%); and the concentrations in Ni and Cr of both subtypes are mostly below the detection limit.

lyzed by EPMA. However, due to their extremely small sizes, the obtained data seem to be a mixture of magnetite. Even so, the analyses reveal high Ca (5.4-6.4 wt%) and W (19.3-28.6 wt%) contents, with significant Mo (0.6-0.9 wt%); Online Materials¹ Table S1).

The tungsten inclusions in MA-I magnetite have also been ana-



FIGURE 8. Box diagram of major (a) and trace (b) element concentrations for the Shuanglong magnetite. (Color online.)

EPMA elemental mapping shows that the alternated dark and light bands in chlorite have compositional variations: the dark bands contain higher contents of Si, Mg, but lower Fe and Al contents than the light bands (Fig. 6). EPMA spot analysis shows that the oscillatory contrasts are mainly caused by FeO and MgO content variations. The average FeO and MgO contents in zone 1 exhibit variations from dark (21.7 wt%, 17.8 wt%; Online Materials¹ Table S1) to light bands (25.9 wt%, 14.7 wt%), and those in zone 2 vary from dark (19.5 wt%, 18.8 wt%) to light bands (24.8 wt%, 15.9 wt%). EPMA spot analysis shows that the pyrite, which coexists with magnetite has variable and high Co and Ni contents (0.19–1.54 wt%, 0.02–0.25 wt%).

LA-ICP-MS

Due to the small-scale oscillatory zoning in MA-II and MB-I magnetite, light and dark domains of magnetite could not be separately measured by LA-ICP-MS, and thus, analytical results of MA-II and MB-I magnetite represent the average composition of light and dark domains in oscillatory zoning. Full LA-ICP-MS analytical results and the corresponding detection limits are provided in Online Materials¹ Table S1 and illustrated in Figure 8b. Most of the data for Cu and rare earth elements (REE) are below detection limits. In general, the dark magnetites, including MA-II, MB-I, and MC-I have higher Mg, Al, Si, Ca, Ti, Zn, Ga, and Sr concentrations than those in the light magnetites that include MA-III, MB-II, and MC-I. The mushketovites, including MA-I and MA-II magnetite, have relatively high W (69–3311 ppm; 1–271 ppm), Sn (1.2–31.7 ppm; 1.1–14.6 ppm), and U (2.7–78.6 ppm; 0.2–1.9 ppm) concentrations than other magnetite subtypes, although the contents of these elements in other magnetite types are all below 1 ppm or below the detection limit (Online Materials¹ Table S1).

The statistical techniques (factor analysis) were used in this study to examine underlying relations among elements content obtained with LA-ICP-MS. We used a principal component extraction method with a Kaiser Varimax rotation (Kaiser 1958) and a Bartlett factor score (Bartlett 1937). Factors score coefficients for each analysis are derived from the factor loadings. The factor score represents the significance of a given factor for an analysis. The factor score line outside –0.5 to 0.5 indicates significant relations. The factor analysis results provide three multiple elements factors: factors 1 comprising Si, Al, Ca, Mg, Sr, Mn, and Co, factors 2 comprising Ti, Ga, and Zn, and factors 3 comprising V, Ni, Cr, and Sc (Fig. 9).

DISCUSSION

Controlling factors for magnetite composition

Magnetite has a general stoichiometry XY_2O_4 , where X is divalent cations such as Mg, Fe, Mn and Ni, and Y represents trivalent or tetravalent cations such as Si, Al, Fe and V. For the



FIGURE 9. Rotated component plot for magnetite showing factor analysis results from trace elements with significant contents. (Color online.)

EPMA results, positive correlations ($R^2 \ge 0.7$) are exhibited among Si, Al, Ca, Mg and Mn, and Ti positively correlates with Al ($R^2 =$ 0.6), whereas Ti and V do not correlate with any of the other trace elements. The factor analysis of LA-ICP-MS results also reveals three factors (Fig. 9), suggesting that some trace elements have underlying correlation, e.g., Si, Ca, Al, Mg, Mn, Sr, Sn and Co; Ti, Zn and Ga; V, Ni, Sc and Cr. These correlations of trace elements could probably be attributed to several reasons, such as the inclusions (amphibole) and partition coefficient. Fe3+ is negatively correlated with Si and Al (Fig. 10a), indicating that these elements were incorporated into the structural sites of magnetite by substitution of Si4+ and Al3+ for Fe3+. Si also positively correlates with Ca and Mg, indicating that these divalent elements play as a valence state balance species related to the substitution. Fe2+ is negatively correlated with Ca and Mg (Fig. 10b), indicating that Mg²⁺ and Ca2+ substitute for Fe2+. Micro-inclusions or nano-inclusions in magnetite can influence the magnetite geochemistry detected. For MA-I magnetite, the few anomalously high W and Ca signals may point to the presence of invisible W-bearing micro-inclusions (Figs. 11a and 11b), probably scheelite (CaWO₄), and few visible scheelite inclusions were also found in MA-I magnetite (Fig. 5b). Moreover, the positive correlate between W and Mn indicates the invisible wolframite [(Fe,Mn)WO₄] inclusions may occur (Fig. 12h). However, some spots show extremely high W content with stable signal, indicating W may also incorporate into the lattice of magnetite (Fig. 11c). For other magnetite, especially the trace element rich zone, our EPMA spot analyses can avoid the visible inclusions; however, most LA-ICP-MS analyses could not avoid nano-scale inclusions. For example, the positive correlation between Sr and Al, Ca may be caused by the silicate inclusions due to that Sr is highly incompatible for magnetite (Figs. 12f and 12g, Nielsen et al. 1994).

The composition of magnetite is mainly controlled by some factors including: (1) coprecipitating minerals (mainly Fesulfides); (2) fluid geochemistry and rock-water reaction; and (3) physicochemical conditions, including temperature and oxygen fugacity (Whalen and Chappell 1988; Lindsley and Frost 1991; Ghiorso and Sack 1991). The presence of other minerals within the mineral assemblage has significant effects on magnetite geochemistry. Minerals coprecipitated with magnetite can preferentially



FIGURE 10. Plots displaying negative correlations between (a) Si and Al vs. calculated Fe^{3+} in atom per formula unit (apfu) and (b) Mg and Ca vs. Fe^{2+} (apfu). (Color online.)

partition some certain elements; for instance, chalcophile (e.g., Cu, Co, Pb) and siderophile elements (e.g., Ni) preferentially partition into sulfides minerals (Cygan and Candela 1995; Fleet et al. 1996; Simon et al. 2008), whereas lithophile elements (e.g., Mg, Al, Si, Ti) partition into silicates minerals (Frost 1991; Toplis and Corgne 2002). The MA and MB magnetite produced from infilling coexist with similar minerals, primary dark magnetite with mainly amphibole and secondary light with mainly chlorite and few pyrite, whereas the MC magnetite was produced by K-Fe and subsequent Ca-Fe alteration. The MB and MC have similar low-Cu, -Pb, -Co, and -Ni contents (Fig. 8b); however, the rare coexisting pyrite has extremely high Co and high Ni contents (0.19-1.54 wt%, 0.02-0.25 wt%), indicating that coexisting sulfides effectively scavenge certain elements. Although there are some differences in lithophile elements (Fig. 8a, MA has higher Si, Al, Mg, Ca, Sr contents), it is difficult to know what caused them due to the influence of potential nano silicate inclusions, and such systematic differences were probably controlled by the fluid geochemistry or degree of rock-water reaction. Extensive fluid-host rock interaction commonly results in

hydrothermal magnetite enriching in Si, Al, Mg, and Mn (Carew

2004; Nadoll et al. 2014; Deditius et al. 2018). The MC magnetite

has low-Si, -Al, -Mg, and -Mn contents (Fig. 8a), reflecting a



FIGURE 11. Time-resolved analytical signal of LA-ICP-MS analysis for MA-I magnetite. CPS = counts per second. (Color online.)

low degree of fluid-rock interaction, and the MC has high-Mn content probably due to the recharge of Mn during K-Fe alteration (Corriveau et al. 2016). In addition, MA magnetite samples have significant W, Sn, Pb, and U contents which are basically below the detection line in MB and MC (Fig. 8b), and these elements are actually concentrated in MA-I (core of MA). Considering that MA-I was transformed from hematite, it may represent the compositional information of the original hematite.

Little experimental result is currently available on the partitioning efficiency of trace elements between magnetite and hydrothermal fluids (Chou and Eugster 1977; Ilton and Eugster 1989; Simon et al. 2004). It is generally considered that some factors such as temperature and oxygen fugacity control partitioning of trace elements in hydrothermal-derived magnetite like that in igneous system. For example, Al and Ti concentrations in igneous-derived magnetite are high positively correlative with temperature (Nielsen et al. 1994; Toplis and Carroll 1995), and these elements also decrease from high-temperature porphyry and skarn magnetite to low-temperature banded iron formation (BIF) (Nadoll et al. 2014). For the oscillatory zoning in MA-II and MB-I magnetite (Fig. 8a), it is clear that the light bands (MB-IL) have lower Ti contents than the dark bands (MB-ID, D, and



FIGURE 12. Binary diagrams of (**a**) Ga vs. Ti, (**b**) Zn vs. Ti, (**c**) Ni vs. V, (**d**) Cr vs. V, (**e**) Sc vs. V, (**f**) Sr vs. Al, (**g**) Sr vs. Ca and (**h**) W vs. Mn for the Shuanglong magnetite. (Color online.)

L mean dark and light bands); however, no obvious differences in Ti content were observed between dark (MA-IID) and light (MA-IIL) bands in MA-II magnetite (Fig. 8a), likely due to the very low abundances. Combined with the decrease of trace elements such as Al and Mg being related to temperature in MA-II and MB-I magnetite, it is likely that the oscillatory zoning in MA-II and MB-I magnetite was mainly controlled by changes in temperature. The above factor analysis result also shows that Ti, Ga, and Zn have correlations (Figs. 9, 12a, and 12b). Nadoll et al. (2014) proposed that Ga concentration follows the trend that the highest concentrations are in high-temperature igneous magnetite and the lowest in BIF magnetite. Previous studies also showed that Zn is more effectively fractionated into hydrothermal fluids than Fe with decreasing temperature (Ilton and Eugster 1989; Wu et al. 2019). Therefore, Ga and Zn in Shuanglong magnetite were also controlled by temperature. Nadoll et al. (2014) proposed the Ti+V vs. Al + Mn plot can reflect the variation in temperature, with high-temperature magnetite plotting at high values of Ti + V and Al + Mn values. The Shuanglong magnetite displays a descending temperature trend suggesting it formed from a fluid under middle to high-temperature conditions >200 °C (Fig. 13; Deditius et al. 2018; Nadoll et al. 2014). Some elements, such as V and Cr, can occur in various valence states (e.g., V3+, V4+, V5+), and therefore, their behavior is strongly linked to f_{O_2} (Nadoll et al. 2014; Toplis and Carroll 1995; Toplis and Corgne 2002). For example, Toplis and Corgne (2002) proposed vanadium partitioning is strongly dependent on oxygen fugacity, decreasing by approximately one order of magnitude with increasing f_{02} from NNO-0.7 to NNO+2.6 for magnetite at a constant temperature (1068 °C), and this behavior is inferred to be dominated by partitioning of V3+ due to the relative proportions of Vn+ (Toplis and Corgne 2002). However, it is less well constrained at cooler hydrothermal fluids (Nadoll et al. 2014). The MA magnetite has low V contents, reflecting a more oxidized fluid. For the dark zone and light zone in MA and MB magnetite, the contents of V were slightly increased, indicating the decreasing of oxygen fugacity in fluids, which is consistent with the coexisting pyrite in light magnetite. The Ni content also shows a strong positive correlation with V (Fig. 12c), probably also related to the oxygen fugacity. Moreover, the EPMA data



FIGURE 13. Plots of (Al + Mn) vs. (Ti + V), modified after Nadoll et al. (2014) and Deditius et al. (2018). (Color online.)

show that the V content of MC-II decreases obviously compared to MC-I (Fig. 8a), revealing an opposite trend.

Tungsten remobilization during mushketovitization

Previous studies have shown that platy magnetite (also call mushketovite) is common in IOCG deposits, such as the Heijianshan deposit in Eastern Tianshan and the Candelaria deposit in Chile (Marschik and Fontboté 2001; Zhao et al. 2018a). The mushketovite is interpreted to result from transformation of magnetite after hematite during reducing fluid reactions, a process called mushketovitization (Hu et al. 2020; Mücke and Cabral 2005; Ohmoto 2003). At Shuanglong, abundant platy magnetite (MA Mag) coexists with actinolite, pyrite, and chlorite. In fact, only the core of MA magnetite is the result of the reducing reactions according to the presence of residual hematite and abundant micro porosity probably formed by the volume shrinkage during the reactions (Hu et al. 2020; Mücke and Cabral 2005). Significantly, abundant scheelite inclusions occur in the MA-I magnetite, and the previous discussion revealed that the high W contents of MA-I were also attributed to invisible scheelite inclusions and lattice-tungsten. Measured partition coefficients for igneous magnetite indicate that W is highly incompatible (Klemme et al. 2006); however, some authors have reported the incorporation of W into magnetite at significant levels (up to dozens of ppm; Candela 1997; Carew 2004; Huang et al. 2019a). Thus, such high contents in mushketovite could have been inherited from the precursor hematite. Indeed, W-U-Sn-Mo enriched hematite is common in many hydrothermal deposits, such as the Olympic Dam Cu-U-Au-Ag deposit (Ciobanu et al. 2013; Verdugo-Ihl et al. 2017), and these elements were incorporated into the structural sites of magnetite by 2Fe3+ \leftrightarrow Me⁶⁺ + \Box , in which the Me could be U, W, and Pb (Ciobanu et al. 2013). Verdugo-Ihl et al. (2020) also proposed significant W can be released from hematite due to coupled dissolution-reprecipitation during interaction with fluids and was confirmed at the nanoscale. Therefore, when mushketovitization of hematite occurs, the reduction in volume results in abundant porosity and cracks, which provide pathways for fluid percolation and the release of W. In addition, the estimated values of f_{02} for many scheelite or wolframite deposits mostly lie between quartz-fayalite-magnetite (QFM) and Ni-NiO (NNO) buffers (Wood and Samson 2000 and reference therein), and no tungsten inclusions have been found in the hematite, indicating that these inclusions are not coexisting with the previous hematite. Therefore, these scheelite inclusions might be released from the previous hematite and precipitated in open spaces due to local supersaturation.

Origin of synchronous oscillatory zoning in magnetite-chlorite aggregates

Oscillatory zoning in MA and MB magnetite is very common in Shuanglong deposit and can be divided into two phases in MA-II, MB-I and MA-III, MB-II, respectively. They are composed of alternately dark and light bands under BSE imaging. The coexisting mineral chlorite occurring as a rosette shape can be divided into two oscillatory zones. Similar oscillatory zoning in magnetite is widely observed in Fe skarn deposit (Dare et al. 2014; Huang et al. 2018), IOCG deposit (Huang and Beaudoin 2019) and IOA deposit (Knipping et al. 2015b; Deditius et al. 2018). A common explanation for the oscillatory zoning in magnetite is that the changes in fluid compositions and/or physicochemical parameters (such as temperature and oxygen fugacity) during the crystal growth could also periodically change the partitioning behavior of trace elements into magnetite (Dare et al. 2012; Knipping et al. 2015b; Sievwright et al. 2017; Huang et al. 2019a). The oscillatory zoning is widely distributed in MA and MB magnetite, suggesting that oscillatory zoning is not due to ultra-local fluid disequilibrium. The sharp compositional boundaries between the dark and light zones within single magnetite grains imply preservation of the original oscillatory zoning, which requires the growth rate of the crystal to be higher than intracrystalline diffusion (Watson and Liang 1995). EPMA point analyses indicate the trace element-rich zones (MA-IID, MB-ID, and dark bands in MA-III and MB-II) involve all elements except V, and Ti for MA (Fig. 14), implying a relatively high temperature and stable oxygen fugacity. Therefore, oscillatory zoning in magnetite from MA and MB was probably caused by variation in temperature.

The rosette-like chlorite with similar oscillatory zoning was also observed from a green-schist facies fault zone in Spain (Trincal et al. 2015). Previous studies showed that chlorite chemistry can be a good indicator of the temperature of crystallization (Cathelineau and Nieva 1985; Inoue et al. 2009; Bourdelle et al. 2013; Lanari et al. 2014). In this study, we use the thermodynamic thermometer calibration of Lanari et al. (2014) based on the following equilibrium: 2 clinochlore + 3 sudoite = 4 amesite + 4 H_2O + 7 quartz. The ideal contributions of amesite, clinochlore, and sudoite are calculated using a site mixing model for chlorite end-members, and the ln(K) can be calculated using the following equation: ln(K) =ln(a⁴Ame/a²Clna³Sud). Chlorite temperatures were then calculated using: T_{Chl} (°C) = 172341/[-Rln(K) + 315.149] - 273.15. The average calculated temperature of the dark and light band was 243 and 444 °C in zone 1, and 430 and 212 °C in zone 2, which were consistent with the estimated temperature range of MA-III and MB-II magnetite (Fig. 13).

Texture features of MB magnetite reveal that the primary MB-I underwent a process of dissolution and precipitation according to the sharp boundaries with secondary magnetite, and the chlorite inclusions near the boundaries reveal that it occurred in a lower temperature than primary magnetite (Fig. 6a). Moreover, some MB-II magnetites also overgrow with primary MB-I grains (Fig. 5d), and these overgrowing MB-II magnetites usually have oscillatory zoning (Fig. 5d). It is reasonable to speculate that MB-II magnetite precipitated in two processes, including the early dissolution of massive MB-I magnetite, and subsequent precipitation of MB-II by two forms. For the coexisting chlorite, the zone 2 was synchronously formed with the MB-II magnetite overgrowing with the MB-I grains, and the zone 1 most likely formed during the early dissolution of MB-I magnetite. Previous studies have shown that increasing temperature, increasing chloride concentration, or decreasing pH are the most important controls on the dissolution of magnetite because these can enhance the solubility and result in undersaturation of iron (Crerar et al. 1978; Hemley et al. 1992). Experimental studies also revealed that additions of HCl could strongly enhance the solubility of magnetite in hydrothermal fluid (Holser and Schneer 1961; Chou and Eugster 1977; Whitney et al. 1985). External fluids such as basin brines or formation waters that dissolved evaporites, which will increase the salinity and Cl contents in ore-forming fluids, promoting the dissolution and reprecipitation process, have been identified as important components in many Fe skarn and IOCG deposits (Broughm et al. 2017; Bain et al. 2021; Hu et al. 2014; Huang and Beaudoin 2019). Therefore, the fluid composition, especially the Cl content in equilibrium with MB-I magnetite, could have changed, causing the dissolution of MB-I magnetite. Combined with the temperature variation in zone 1 of chlorite, it may indicate the incursion of a low-temperature external fluid, which caused the change in fluid composition. The composition of MB-II magnetite and chlorite, such as the higher Ti content in dark bands in MB-II magnetite (Fig. 14), and the decrease in temperature from dark band to light band in zone 2 of chlorite, all indicate that the decreasing temperature in the fluid may result in the precipitation of MB-II magnetite.

IMPLICATIONS

At Shuanglong, the MA-I magnetite represents a transformational mushketovite phase characterized by abundant porosity and extremely high W content, which mainly display as micro- and invisible scheelite inclusions probably caused by the W expulsion during mushketovitization. The sharp contacts between primary dark magnetite and later light magnetite suggest that they may have formed via coupled dissolution and reprecipitation. Moreover, the synchronous oscillatory zoning in light magnetite and coexisting chlorite was related to the

FIGURE 14. EPMA transects across the oscillatory zoning in dark and light magnetite. (Color online.)



variation of fluids temperature and was probably caused by the incursion of external low-temperature and high-salinity fluids, which can dissolve the primary dark magnetite.

ACKNOWLEDGMENTS

Our special thanks go to Peijun Lin and Haoran Dou for assisting with the EPMA analysis and Fangyue Wang for assisting with the LA-ICP-MS analysis. Pete Hollings is thanked for comments on an early version of the paper.

FUNDING

This work was supported by the National Natural Science Foundation of China (41725009, 42002083), and the Guangdong Major Project of Basic and Applied Basic Research (2019B03032013), and Science and Technology planning project of Guangdong Province (2017B030314175).

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Manuscript received April 25, 2021 Manuscript accepted January 12, 2022 Accepted manuscript online January 26, 2022 Manuscript handled by Matthew Steele-MacInnis

Endnote:

¹Deposit item AM-23-18400, Online Materials. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http:// www.minsocam.org/MSA/AmMin/TOC/2023/Jan2023_data/Jan2023_data.html).