Dissolution–reprecipitation process of magnetite from the Chengchao iron deposit: Insights into ore genesis and implication for *in-situ* chemical analysis of magnetite

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A B S T R A C T

Magnetite formed in different environments commonly has distinct assemblages and concentrations of trace elements that can potentially be used as a genetic indicator of this mineral and associated ore deposits. In this paper, we present textural and compositional data of magnetite from the Chengchao iron deposit, Daye district, China to provide a better understanding in the formation mechanism and genesis of the deposit and shed light on analytical protocols for *in-situ* chemical analysis of hydrothermal magnetite. Magnetite grains from the ore-related granitoid pluton, mineralized endoskarn, magnetite-dominated exoskarn, and vein-type iron ores hosted in marine carbonate intruded by the pluton were examined using scanning electron microscopy and analyzed for major and trace elements using electron microprobe. Back-scattered electron images reveal that primary magnetite from the mineralized skarns and vein-type ores were all partly reequilibrated with late-stage hydrothermal fluids, forming secondary magnetite domains that are featured by abundant porosity and have sharp contact with the primary magnetite. These textures are interpreted as resulting from a dissolution–reprecipitation process of magnetite, which, however, are mostly obscure under optically.

Primary magnetite grains from the mineralized endoskarn and vein-type ores contain high SiO_2 (0.92–3.21 wt.%), Al_2O_3 (0.51–2.83 wt.%), and low MgO (0.15–0.67 wt.%), whereas varieties from the exoskarn ores have high MgO (2.76–3.07 wt.%) and low SiO_2 (0.03–0.23 wt.%) and Al_2O_3 (0.54–1.05 wt.%). This compositional contrast indicates that trace-element geochemical composition of magnetite is largely controlled by the compositions of magmatic fluids and host rocks of the ores that have reacted with the fluids. Compared to its precursor mineral, secondary magnetite is significantly depleted in most trace elements, with SiO_2 deceasing from 1.87 to 0.47 wt.% (on average) and Al_2O_3 from 0.89 to 0.08 wt.% in mineralized endoskarn and vein type ores, and MgO from 2.87 to 0.60 wt.% in exoskarn ores. On the contrary, average content of iron is notably increased from 69.2 wt.% to 71.9 wt.% in the secondary magnetite grains. The results suggest that the dissolution–reprecipitation process has been important in significantly removing trace elements from early-stage magnetite to form high-grade, high-quality iron ores in hydrothermal environments. The textural and compositional data confirm that the Chengchao iron deposit is of hydrothermal origin, rather than being crystallized from immiscible iron oxide melts as previously suggested. This study also highlights the importance of textural characterization using various imaging techniques before *in-situ* chemical analysis of magnetite, as is the case for texturally complicated U–Th-bearing accessory minerals that have been widely used for U–Pb geochronology study.

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1. Introduction

Magnetite is a common oxide mineral in igneous, metamorphic, and sedimentary rocks. They also widely occur in a variety of iron ores, including BIF (banded iron formation), Kiruna-type, magmatic Fe–Ti oxide, and iron skarn deposits (Dupuis and Beaudoin, 2011; Huberty et al., 2012; Nadoll et al., 2012), as well as in other types of

hydrothermal deposits such as IOCG (iron oxide–copper–gold) and porphyry Cu–Au systems (Liang et al., 2009; Williams et al., 2005). Magnetite typically hosts a range of trace elements, such as Al, Ti, V, Si, Ca, Mn, and Mg (Dupuis and Beaudoin, 2011; Nadoll et al., 2012). Types and concentrations of trace elements in this mineral are largely dependent on physicochemical parameters of magnetite-forming system, including temperature, fO_2, fS_2, silica activity, and melt/fluid composition (Nadoll et al., 2012, and references therein). Existing studies have shown that trace elements in magnetite can be used as a provenance fingerprint of this mineral and a genesis indicator of associated ore deposits (Dare et al., 2012; Dupuis and Beaudoin, 2011; Nadoll

et al., 2012). For example, magnetite grains from skarn deposits commonly have lower Ti and V, but higher Ca, Al, and Mn, than those from Kiruna-type and magnetic Fe–Ti oxide deposits (Dupuis and Beaudoin, 2011).

Replacement of magnetite by hematite and vice-versa, forming mushketovite and martite, respectively, as well as chemical zoning in magnetite, has long been recognized (Ciobanu and Cook, 2004; Dupuis and Beaudoin, 2011; Shiga, 1988; Shimazaki, 1998; Westendorp et al., 1991). However, few studies have been conscious of the fact that magnetite can be altered by new generation of the same mineral during subsequent hydrothermal processes. Shcheka et al. (1977) first noticed replacement of early-stage magnetite with a subsequent phase in the Kovshunovskoye iron skarn deposit, Russia. Shimazaki (1998) showed similar textures in siliceous magnetite from the Yaguki Fe–Cu skarn deposits in Japan. More recently, Ciobanu and Cook (2004) reported hydrothermal overprint of magnetite from the Ocna de Fier-Dognecea Fe, Cu, and Zn–Pb skarn ore field. Although hydrothermal alteration or replacement of magnetite has been previously recognized, little attention has been paid to its effect on the trace-element geochemistry of this mineral, information critically important in the understanding of process and genesis of the mineral and related ore deposits.

In this paper, textural and compositional data for magnetite from the Chengchao iron deposit, China are presented to illustrate how magnetite was re-equilibrated with late stage fluids, leading to significant textural and chemical changes. The results are used to provide a better understanding in the genesis and evolution of magnetite and the Chengchao deposit. The findings from this study also highlight the utilization of textural characterization prior to *in-situ* chemical analysis of magnetite.

2. Geological setting

The Chengchao iron skarn deposit is located in the northern portion of the Daye Fe–Cu mineralizing district, western Middle-Lower Yangtze River Metallogenic Belt along the northeastern margin of the Yangtze Craton (Fig. 1a). This metallogenic belt contains more than 200 deposits and has been one of the most important Fe–Cu–Au producers in China in the last three decades (Pan and Dong, 1999; Zhai et al., 1996). The Daye district is well known for its resource endowment, with numerous Fe, Fe–Cu–(Au), Cu–Au, and Cu–Mo–(W) skarn or porphyry deposits (Fig. 1b; Li et al., 2008, 2009, 2010; Xie et al., 2011, 2012). Mineralization of these skarn deposits is mostly localized in contact zones between marine carbonates of the Lower Triassic Daye Formation and Early Cretaceous (143–127 Ma) intermediate to acidic intrusions (Li et al., 2008, 2010; Shu et al., 1992; Xie et al., 2012).

The Chengchao deposit represents the largest iron deposit in the Daye district, with a proven reserve of 280 Mt Fe at an average grade of 36–51 wt.% Fe (up to 61 wt.%; Xie et al., 2012). This deposit is related to a granite and quartz diorite plutons that intruded the lower members of the Daye Formation consisting of evaporate-bearing dolomitic limestones, limestones, and dolomites (Fig. 2). Laser ablation ICP-MS zircon U–Pb dating indicates that the granite and quartz diorite plutons were emplaced at 127 ± 2 and 129 ± 2 Ma, respectively (Xie et al., 2012). The Chengchao Fe deposit consists of seven large orebodies and 51 small varieties that are distributed along a northwest strike, forming a discontinuous mineralization zone approximately 2,300 m long and 800 m wide (Fig. 2). Some small orebodies are exposed to the surface, but most large ones occur at ca. 300–800 m below the surface (Fig. 2). No. II, III, and VI orebodies are economically most important, collectively accounting for 95% of the total reserve of the deposit (Shu et al., 1992; Xie et al., 2012).

The Chengchao deposit consists of two types of mineralization: (1) massive ores in the contact zone associated with typical skarn alteration (Fig. 3a–c) and (2) vein-type magnetite ores hosted within the granite or Triassic carbonate rocks with very thin or no alteration halos (Figs. 3d, 4e), with the former being economically much more

important. On the basis of field and textural relationships, five paragenetic stages of mineralization have been recognized: the prograde skarn stage, the retrograde alteration stage, the iron-oxide stage, the sulfide stage, and the carbonate stage. The ore minerals are predominantly magnetite, with lesser amounts of hematite. The gangue minerals consist mainly of prograde skarn minerals (garnet and diopside), anhydrite, calcite, and less significantly, retrograde skarn minerals (epidote, scapolite, tremolite, actinolite, phlogopite, serpentine, chlorite), quartz, pyrite, and chalcopyrite (Figs. 3–5; Ren, 2012; Yao et al., 1993; Zhai et al., 1992). Phlogopite separates extracted from a magnetite-bearing endoskarn sample yielded an $^{40}Ar/^{39}Ar$ plateau age of 132.6 ± 1.0 Ma (Xie et al., 2012), which is marginally consistent with zircon U–Pb age of the quartz diorite (Xie et al., 2012).

3. Samples and analytical methods

Five samples were collected for this study. Sample CC01-125 (Fig. 4a) is fresh granite collected from drill hole ZK01-105 at ~800 m depth. The granite consists of K-feldspar, plagioclase, quartz, biotite and hornblende, with accessory apatite, zircon, titanite, and magnetite (Fig. 5a). The other four samples are all from the major ore body No. III. Sample CC05 and CC81 were collected from intensively mineralized exoskarn (Fig. 4b, c), which comprises massive magnetite (>80 vol.%) and subordinate gangue minerals including pyrite, chalcopyrite, serpentine, phlogopite and calcite in sample CC05 and pyrite, chalcopyrite, phlogopite, chlorite in sample CC81 (Figs. 4b, c, 5b). Sample CC05 is much closer to the carbonate rocks of the Daye Formation than sample CC81. Sample CC102 is a mineralized endoskarn in close proximity of the least-altered quartz diorite, and consists of diopside, actinolite, and magnetite with minor albite, titanite, and pyrite (Figs. 4d, 5c). Sample CC28 is a magnetite-dominated vein filling fractures within carbonate rocks of the Daye Formation, with additional (<20 vol.%) calcite and traces of pyrite and hematite (Figs. 4e, 5d).

All samples were prepared as polished thin sections and subsequently examined using optical microscopy to characterize the mineralogical and textural relationships, with an emphasis on the occurrence, morphology, and texture of magnetite. The polished thin sections were then carbon-coated for scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The morphology and textures of magnetite were investigated using a FEI Quanta 200 environmental scanning electron microscope equipped with an energy dispersive spectrometer at the State Key Laboratory of Geological Process and Mineral Resources of the China University of Geosciences, Wuhan.

Electron probe microanalysis (EPMA) and X-ray mapping of magnetite consist of two sessions. Session 1 involved samples CC01-125, CC05, CC102, and CC28 and was conducted using a JXA-8230 Superprobe at the Center for Material Research and Analysis, Wuhan University of Technology (WUT). Standards and unknowns were analyzed with 1 μm beam diameter at an accelerating voltage of 20 kV and a beam current of 20 nA. Integration time for peaks of Al, Si and Mg are 30 s, and the remaining elements are 20 s. The following standards were used: Fe_3O_4 (Fe), $Mg_3Al_2Si_3O_{12}$ (Mg, Al and Si), $(Mn, Ca)SiO_3$ (Ca and Mn), $(ZnMn)_2SiO_4$ (Zn), TiO_2 (Ti), $FeCr_2O_4$ (Cr), vanadium metal (V), cobalt metal (Co) and Ni_2Si (Ni). Session 2 involved all five samples and was carried out using a JEOL JXA-733 Superprobe at University of New Brunswick (UNB), Canada. Standards and unknowns were analyzed with 1 μm beam diameter at 20 kV and 120 nA current. The peak counting time for Fe was 30 s, Ca was 400, Mn was 120, Co, Ni and Zn were 150, and the remaining elements were 200. The following standards were used: Fe_3O_4 (Fe), $Mg_3Al_2Si_3O_{12}$ (Mg, Al and Si), $(Mn, Ca)SiO_3$ (Ca and Mn), $ZnAl_2O_4$ (Zn), $FeTiO_3$ (Ti), $FeCr_2O_4$ (Cr), vanadium metal (V), cobalt metal (Co) and NiO (Ni). Oxygen was calculated from cation stoichiometry, and the chemical formula was normalized to 32 O atoms.