Textural and compositional evolution of iron oxides at Mina Justa (Peru): implications for mushketovite and formation of IOCG deposits

Xia Hu1,2,3,4, Huayong Chen1,5*, Georges Beaudoin3,4, Yu Zhang6

1. Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
2. University of Chinese Academy of Sciences, Beijing 100049, China
3. Département de Géologie et de Génie Géologique, Université Laval, Québec, QC G1V 0A6, Canada
4. Research Center on the Geology and Engineering of Mineral Resources (E4m), Université Laval, Québec, QC G1V 0A6, Canada
5. Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou 510640, China
6. School of Geosciences and info-Physics, Central South University, Changsha 410083, China

*Corresponding author: huayongchen@gig.ac.cn

Address: Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, P.O. Box 1131, Tianhe District, Guangzhou 510640, Guangdong PRC
ABSTRACT

Magnetite is a common mineral in many ore deposits and their host rocks. It contains a wide range of trace elements that can be used to fingerprint deposit type and hydrothermal processes. In this study, we present detailed textural and compositional data on magnetite of the Mina Justa deposit in southern Perú to constrain the formation of iron oxides in the Iron oxide Cu-Au (IOCG) deposit type.

Two types of magnetite, i.e., mushketovite (\(T_1\)) and granular (\(T_2\)) magnetite are identified based on their morphology. Mushketovite shows three different zones (central bright, dark and outer bright) in BSE (backscattered electron) images. The central bright part (\(T_1-1\)), characterized by abundant porosity and inclusions, was intensively replaced by dark magnetite of the median rim (\(T_1-2\)). The outer rim (\(T_1-3\)) is also bright but lacks porosity and inclusions. Granular magnetite (\(T_2\)) is anhedral and shows two different brightness (dark and bright) in BSE images. The dark (\(T_2-1\)) and bright (\(T_2-2\)) domains are intergrown, with irregular boundaries. In general, the dark zones of both magnetite types (\(T_1-2\) and \(T_2-1\)) are characterized by higher Si, Ca, Al and lower Fe contents than the bright zones. Additionally, the lattice parameters of the two types of magnetite are similar and slightly lower than that of pure magnetite, indicating that some cations (e.g., Si\(^{4+}\), Al\(^{3+}\)) whose ionic radii are smaller than Fe\(^{2+}\) or Fe\(^{3+}\) entered into the magnetite structure by simple or coupled substitutions.

Our study shows that oxygen fugacity and temperature change are the dominant mechanisms leading to the formation of different types of magnetite at Mina Justa.
Primary hematite, identified by Laser Raman analysis, was transformed into magnetite ($T_{M1}$-1) due to a sharp decline of $fO_2$ and then replaced by $T_{M1}$-2 magnetite during temperature increase, followed by formation of $T_{M1}$-3 due to decreasing temperature, eventually forming the mushketovite with different zones. The granular magnetite may have originally precipitated from hydrothermal fluid which crystallized $T_{M2}$-1 and also $T_{M1}$-2 magnetite, and was then modified by changing temperature and $fO_2$ to form $T_{M2}$-2.

Even though the iron oxides in IOCG deposits may have formed in the same alteration stage, they could undergo a very complicated evolution process. Therefore, it is very important to combine texture and mineral chemistry to investigate the origin and evolution history of iron oxides.

**Keywords:** Iron oxides, mushketovite, texture, mineral chemistry, hydrothermal fluids, IOCG deposit
INTRODUCTION

Magnetite is a common mineral in many igneous, metamorphic and sedimentary rocks, as well as in various Fe-containing deposit-types, including Kiruna-type, BIF (banded iron formation), magmatic Fe-Ti oxide, Fe-skarn, IOCG and porphyry deposits (Williams et al., 2005; Liang et al., 2009; Groves et al., 2010; Sillitoe et al., 2010; Dupuis and Beaudoin, 2011; Huberty et al., 2012; Nadoll et al., 2012; Hu et al., 2015; Hu et al., 2017; Wen et al., 2017; Yin et al., 2017; Huang et al., 2018). Magnetite has an inverse spinel structure and typically incorporates a variety of minor and trace elements such as Mg, Al, Ti, V, Cr, Ni, Si, Ca, and Mn into its structure (Dupuis and Beaudoin, 2011; Dare et al., 2012; Nadoll et al, 2014). Previous studies have shown that compositional variety in magnetite can be used to fingerprint various deposit types or ore-forming processes (Carew 2004; Singoyi et al., 2006; Rusk et al., 2009; Dupuis and Beaudoin, 2011; Dare et al., 2012; Nadoll et al., 2012; Knipping et al., 2015). However, other studies (e.g., Hu et al., 2015; Wen et al., 2017; Yin et al., 2017) have also shown that the chemical composition of magnetite can be significantly modified or reequilibrated by hydrothermal fluid.

The iron oxide-copper-gold mineralization, characterized by Cu-sulfides±Au hydrothermal mineralization with abundant magnetite and/or hematite, has been a major exploration and research target since the discovery of the giant Olympic Dam Cu-U-Au (-REE) deposit (Hitzman et al., 1992). Magnetite and hematite from IOCG deposits have
proven to be characterized by different trace elements, i.e., magnetite is characterized by higher Sn and Mn and lower V, Ti, Mg, Si, Cr, and Zn concentrations whereas hematite is characterized by higher As, Ga, Sb, and W concentrations (Carew, 2004). Huang et al. (2018) used trace element compositions of magnetite and hematite from 16 well-studied IOCG and IOA (iron oxide apatite) deposits to investigate the links between the chemical composition of iron oxides, hydrothermal processes and deposit subtypes. The above studies mainly focused on presenting geochemical data of iron oxides or using trace elements in iron oxides to constrain the formation of IOCG. However, it is equally important to investigate the textural evolution of iron oxides in IOCG deposits. In addition, magnetite in IOCG deposits commonly occurs as two different forms, i.e., mushketovite (a kind of platy magnetite which is formed by replacing specular hematite.) and granular magnetite (Marschik and Fontboté, 2001; Simard et al., 2006; Chen et al., 2010; Apukhtina et al., 2017). Previous studies commonly did not distinguish the two magnetite types and used their combined compositional data for deposit type discrimination (e.g. Zhibo and Chagangnuoer deposits, Günther et al., 2017). Most importantly, many researchers working in IOCG deposits usually immediately catalogue “platy magnetite” as mushketovite without detailed mineralogical studies (Chen et al., 2010; Apukhtina et al., 2017). However, some studies reported that platy magnetite may be originally magnetite which is crystallized from rapid cooling of fluid (Nystrom, 1994).

In this study, we use the Mina Justa deposit as an example to investigate magnetite
mineralization in IOCG deposit. We present compositional data coupled with detailed texture anatomy of two textural types of magnetite. We provide powerful mineralogical evidence to support that platy magnetite in IOCG systems should be mushketovite. In addition, we discuss the factors controlling the magnetite chemistry and the links between the texture and chemical compositions of magnetite, to constrain the formation of iron oxides in the IOCG deposit based on these textural and geochemical analyses.

GEOLOGIC SETTING

The Mina Justa Cu deposit, with an indicated open pit resource of 346.6 Mt at an average grade of 0.71% Cu, 3.83 g/t Ag and 0.03 g/t Au (Chen et al., 2011), is located in the IOCG metallogenic belt in southern Peru (Fig. 1a). The deposit is hosted by the mid-late Jurassic Upper Río Grande Formation, which is dominated by plagioclase-phyric andesite and andesitic volcaniclastic units with minor sandstone, siltstone and limestone lenses (Fig. 1b; Caldas, 1978; Hawkes et al., 2002; Baxter et al., 2005).

Two primary areas of Cu orebodies have been delimited at Mina Justa, namely the main and upper orebodies, both of which are spatially associated with nearly parallel, NE-trending and shallowly SE-dipping faults, ranging from 10 m to 200 m in vertical extent (Fig. 1b; Chen et al., 2010; Baxter et al. 2005). The main mineralized body crops out as a 400 m long, discontinuous belt of Cu oxides with albite-K-feldspar-actinolite alteration (Fig. 1b), which dips 10° to 30° to the southeast. The similarly
northeast-trending, but northwest-dipping magnetite lenses are also exposed on surface
(Fig. 1b). They commonly contain minor Cu oxides and were locally cut by the
southeast-dipping Mina Justa normal faults.

Four stages of hydrothermal alteration and mineralization were recognized at Mina
Justa based on the detailed petrological studies: (I) an early alteration stage; (II) the
hematite stage; (III) the magnetite-pyrite stage; and (IV) the Cu mineralization stage (Fig.
2, Chen et al., 2010). Stage I alteration mainly contains albite, microcline, diopside, and
actinolite. The main stages associated with iron oxides at Mina Justa are stage II and
stage III. Therefore, we will describe these two stages in details as follows. Stage II
alteration is an obliterated hematite-dominant stage inferred from the existence of
“mushketovite”, magnetite unambiguously pseudomorphous after specular hematite
(Chen et al., 2010). The hematite may have originally formed fractured plates.

Anhedral-to-subhedral, and medium- to coarse-grained calcite is intergrown with the
pseudomorphs, and was replaced by quartz and magnetite (Chen et al., 2010). This stage
temporally separates the early alteration and the main magnetite alteration in andesite
host. Stage III mainly contains magnetite, pyrite, quartz and chlorite. Pyrite is medium- to
crude grained and locally cut by chalcopyrite veins (Fig. 3a). Magnetite can be divided
into two different types based on its morphology. One is mushketovite associated with
pyrite and quartz (Fig. 3a). Chalcopyrite commonly occurs interstitially in mushketovite
(Fig. 3a). The second is anhedral granular magnetite which has planar grain boundaries
with pyrite and quartz (Fig. 3b). The Cu mineralization stage mainly contains Cu sulfides
(e.g. chalcopyrite, bornite, chalcocite).

**SAMPLING AND ANALYTICAL METHODS**

Representative samples of two different types of magnetite from Stage III were selected for our study. All samples were prepared as standard polished thin sections and subsequently examined using the following analytical methods to determine the textural and compositional relationships.

Polished thin sections were carbon-coated and then investigated with a ΣIGMA scanning electron microscope (SEM) in BSE mode, at the School of Earth Science and Geological Engineering, Sun Yat-sen University (SYSU).

In situ micro-X-ray diffraction (XRD) experiments were conducted with a Rigaku D/max Rapis IIR micro-XRD system at the Central South University, Changsha, China. All measurements were carried out at 40 kV and 250 mA (CuKa) with a collection time of 22 min. The X-ray beam is ~40 μm in diameter and was focused on the selected spots on the thin sections. The software of MDI Jade 6.0 was used to analyze the obtained XRD patterns. We used this software to carry out whole pattern fitting refinement of the measured spectrum and then calculated lattice parameter. Because magnetite has a cubic structure, cell length “a” is the only parameter needed to be determined.

To identify whether hematite residue occurred in the platy magnetite, Raman spectra of magnetite were collected using a RM2000 laser micro-Raman spectrometer at the Key Laboratory of Mineralogy and Metallogeny of Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences (GIGCAS), Guangzhou, China. A 514.5 nm Ar laser was used and the laser spot is 2 μm in diameter. The scanning range was between 100 and 1500 cm\(^{-1}\). The laser power reaching the sample surface was 10mW and the typical acquisition time was 60 s to avoid laser-induced thermal effects and oxidation.

The software of Adobe Photoshop CS4 was used to estimate the proportion of pore volume (approximately represented by area percentage) in the whole magnetite. The smallest unit of an image is a pixel and thus the area percentage can be represented by the pixel percentage. The pixels of pore area and whole magnetite area can be calculated by software, respectively. Therefore, the ratio of pixels in pore area and whole area is the proportion of pore volume in the whole magnetite.

The chemical composition of magnetite was analyzed using a JEOL JXA-8230 electron probe micro-analyzer (EPMA) at GIGCAS. The analyses were carried out with 15 kV voltage, 20 nA beam current and 1μm spot size. In addition, zoning in magnetite grains was mapped using EPMA for Fe, Si, Ca and Al. The operation conditions of an accelerate voltage of 20 kV, a probe current of 300 nA, a beam size of 1 to 4 μm and a dwell time of 100 to 200 ms for each point were used for mapping.

**RESULTS**

**Morphology and texture of magnetite**

Magnetite in the Mina Justa deposit can be classified into mushketovite (T\(_{M1}\)) and
granular (T$_{M2}$) types. The T$_{M1}$ magnetite commonly coexists with pyrite, quartz and chalcopyrite (Fig. 3a, b). It shows three different zones (central bright, median dark and outer bright rims) based on the SEM observation in BSE mode (Fig. 4 b-d). The central bright part (T$_{M1}$-1 Mag) is characterized by abundant porosity and inclusions, and was replaced by the dark median rim (T$_{M1}$-2 Mag). Inclusions in T$_{M1}$-1 magnetite commonly consist of tiny W-bearing minerals such as scheelite (Fig. 4d). The outer rim (T$_{M1}$-3 Mag) is also bright but lacks porosity and inclusions. The T$_{M2}$ magnetite is usually intergrown with pyrite and quartz. It is commonly anhedral and shows two different brightness in BSE images. The dark (T$_{M2}$-1 Mag) and bright (T$_{M2}$-2 Mag) domains in this magnetite are intergrown with irregular boundaries (Fig. 4f).

**Structural characteristics of magnetite**

XRD analysis results show that T$_{M1}$ magnetite has cell parameter $a = 8.3894 (0.00022)$ Å, which is slightly lower than that of pure magnetite (PDF No. 19-0629, $a = 8.396$ Å). The cell parameter (a) of the T$_{M2}$ magnetite is 8.3909 (0.00019) Å, which is within error equal to that of T$_{M1}$ magnetite. The full-width at half maximum (FWHM) of $\{311\}$ peak of T$_{M1}$ magnetite is 0.205°, and that of T$_{M2}$ magnetite is 0.228° (Fig. 5). Hence, T$_{M1}$ magnetite may have higher crystallinity than T$_{M2}$ magnetite (Crepaldi et al. 2003).

All samples exhibit Raman bands characteristic of magnetite (Wang et al., 2004), including a weak peak at ~298 and two stronger ones at ~540 and ~667 cm$^{-1}$ (Fig. 6). The central bright zone (T$_{M1}$-1 mag, Fig. 4c,d) also exhibits Raman bands indicative of
hematite at ca. 225, 406, and 1320 cm$^{-1}$ (Giarola et al., 2012; Tan et al., 2015), implying that there are still hematite residue in the $T_{M1}$-1 magnetite (Fig. 6).

**Chemical composition of magnetite**

The EMPA elemental mapping provided information on major and trace element distribution patterns within individual $T_{M1}$ and $T_{M2}$ magnetite crystals from the Mina Justa deposit (Fig. 7). Of the three main zones (one dark and two bright zones) in $T_{M1}$ magnetite, the dark zone contains the highest contents of Si, Ca, Al but the lowest Fe content (Fig. 7a). $T_{M2}$ magnetite displays a similar variation trend as $T_{M1}$ magnetite, in which the dark domain of magnetite is characterized by higher contents of Si, Ca, Al and lower Fe content than the bright domain (Fig. 7b).

The average, minimum, and maximum chemical contents of the Mina Justa magnetite are presented in Table 1. Mushketovite forms three compositional groups, corresponding to three different zones (Fig. 8). $T_{M1}$-1 magnetite has the lowest average SiO$_2$ (0.072 wt.%), Al$_2$O$_3$ (0.047 wt.%), MgO (0.016 wt.%), and the highest average total FeO (92.448 wt.%), whereas CaO is mostly below the detection limit (b.d.l). $T_{M1}$-2 magnetite has the highest average SiO$_2$ (1.582 wt.%), CaO (0.233 wt.%), Al$_2$O$_3$ (0.324 wt.%), MgO (0.12 wt.%), and the lowest average total FeO (90.28 wt.%). $T_{M1}$-3 magnetite contains moderately high average SiO$_2$ (0.505 wt.%), CaO (0.077 wt.%), Al$_2$O$_3$ (0.072 wt.%), MgO (0.036 wt.%), and moderately low average total FeO (91.938 wt.%). These three subtypes of magnetite contain similar MnO (0.047 wt.%, 0.064 wt.%,...
0.039 wt.%, respectively), $V_2O_3$ (0.033 wt.%, 0.033 wt.%, 0.026 wt.%, respectively) and $TiO_2$ (0.012 wt.%, 0.031 wt.%, 0.014 wt.%, respectively) contents. The concentrations in $NiO$ and $Cr_2O_3$ are mostly below the detection limit.

The granular magnetite forms two compositional groups, corresponding to two different zones (Fig.8). $T_{M2-1}$ magnetite has the higher average $SiO_2$ (1.365 wt.%), $CaO$ (0.247 wt.%), $Al_2O_3$ (0.4 wt.%), $MgO$ (0.221 wt.%), $MnO$ (0.094 wt.%), $TiO_2$ (0.146 wt.%) and lower average total $FeO$ (89.817 wt.%), $V_2O_3$ (0.256 wt.%). $T_{M2-2}$ magnetite is characterized by lower average $SiO_2$ (0.297 wt.%), $Al_2O_3$ (0.108 wt.%), $MgO$ (0.041 wt.%), $MnO$ (0.057 wt.%), $TiO_2$ (0.075 wt.%) and higher average total $FeO$ (90.186 wt.%), $V_2O_3$ (0.424 wt.%). The contents of $NiO$, $CaO$ and $Cr_2O_3$ are mostly below the detection limit. In general, the element contents (e.g., Si, Ca, Al) of the $T_{M1-2}$ and $T_{M1-3}$ magnetite are similar to those of the $T_{M2-1}$ and $T_{M2-2}$ magnetite, respectively. Whereas the concentration of $V_2O_3$ in $T_{M1}$ is lower than $T_{M2}$ magnetite (Fig.8).

**DISCUSSION**

**Elemental substitution mechanisms in magnetite**

Magnetite has an inverse spinel structure with a general formula $XY_2O_4$, where $X$ represents a divalent cation such as $Fe^{2+}$, Mg, Mn, Ni, Co and Zn, and $Y$ represents a trivalent or tetravalent cation such as $Fe^{3+}$, Al, V, Cr, Si and Ti (Wechsler et al., 1984; Nadoll et al., 2014). Tetrahedral sites in the magnetite structure are exclusively occupied...
by the ferric (Fe$^{3+}$) iron atoms, whereas octahedral sites are randomly occupied by ideally
equal numbers of ferric (Fe$^{3+}$) and ferrous (Fe$^{2+}$) iron atoms (Lindsley, 1976; Wechsler et
al., 1984; Nadoll et al., 2014). As reviewed by Nadoll et al. (2014), divalent cations such
as Mg$^{2+}$, Mn$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, and Ni$^{2+}$ may enter into the magnetite structure by
substituting Fe$^{2+}$, whereas Fe$^{3+}$ can be replaced by some trivalent cations such as Al$^{3+}$,
V$^{3+}$ and Cr$^{3+}$. In addition, some tetravalent cations such as Ti$^{4+}$, Si$^{4+}$ may enter into the
magnetite structure when coupled with the substitution of a divalent cation (Wechsler et
al., 1984; Newberry et al., 1982; Westendorp et al., 1991; Xu et al., 2014).

The lattice parameter of T$_{M1}$ magnetite (8.389 Å) is subequal to that of T$_{M2}$
magnetite (8.390 Å), which are somewhat lower than that of the standard/pure magnetite
(8.396 Å, Fukasawa et al., 1993). For magnetite at Mina Justa, the concentration of Fe$^{3+}$
is negatively correlated with those of Si$^{4+}$, Fe$^{2+}$, Al$^{3+}$ and Ca$^{2+}$ (Fig. 9a, c, d, e) whereas
the Fe$^{2+}$ content is positively correlated with Si$^{4+}$ (Fig. 9b), which may indicate that these
elements were incorporated into the structural sites of magnetite by following
substitution:

$$\text{ⅣSi}^{4+} + \text{Ⅵ}(\text{Fe}^{2+}, \text{Ca}^{2+}) \rightarrow \text{ⅣFe}^{3+} + \text{ⅥFe}^{3+} \quad (1)$$

$$\text{ⅤAl}^{3+} \rightarrow \text{ⅥFe}^{3+} \quad (2)$$

In these substitutions, both Si$^{4+}$ and Al$^{3+}$ have smaller ionic radii than Fe$^{3+}$
(Shannon, 1976), which may result in the lower lattice parameters of magnetite in Mina
Justa compared to that of the standard magnetite. In addition, above correlations between
those ions may be resulted from the presence of small inclusions of different minerals
although they were not directly observed.

**Genesis of mushketovite: transformation of hematite to magnetite**

According to the Raman spectra (Fig. 6), T_{M1-1} magnetite (central bright zone, Fig. 4c) exhibits characteristic Raman bands of residual hematite, which indicates that original hematite was transformed to magnetite. Such observation also provides convincing mineralogical evidence that platy magnetite should be mushketovite in previous studies at Mina Justa (Chen et al., 2010) and other IOCG deposits (such as Candelaria, Chile; Marschik and Fontboté, 2001).

There are two different transformation mechanisms of hematite to magnetite (Ohmoto, 2003; Mücke and Cabral, 2005). One is a redox reaction in which the Fe^{3+} ions in hematite are reduced to Fe^{2+} ions:

\[
3\text{Fe}^{3+}_2\text{O}_3 (\text{Hem}) + \text{H}_2 = 2\text{Fe}^{2+}_2\text{Fe}^{3+}_2\text{O}_4 (\text{Mag}) + \text{H}_2\text{O} \quad (3)
\]

Another is a nonredox reaction in which the conversion of hematite to magnetite by a simple addition of Fe^{2+} ions:

\[
\text{Fe}^{3+}_2\text{O}_3 (\text{Hem}) + \text{Fe}^{2+} + \text{H}_2\text{O} = \text{Fe}^{2+}_2\text{Fe}^{3+}_2\text{O}_4 (\text{Mag}) + \text{2H}^+ \quad (4)
\]

In reaction (3), the amount of Fe atoms remains constant and there is only removal of oxygen. According to the cell volumes of magnetite (592.704 Å^3; Mücke and Cabral, 2005) and hematite (302.279 Å^3; Mücke and Cabral, 2005) and the amount of Fe atoms in them (24 in magnetite and 12 in hematite), it can be calculated that the replacement of hematite by magnetite causes a volume decrease of 1.64%. In contrast, in reaction (4),...
the amount of Fe atoms is not constant. The reaction has an iron ratio of 2:3 between the initial and the final products, which will cause an obvious increase in volume of 47.55%. According to Ohmoto (2003), this reaction may occur in many sedimentary iron formations. For magnetite from the Mina Justa deposit, the BSE images show that the central part of mushketovite (T\textsubscript{M1-1} Mag) contains abundant microporosity and inclusions (Fig. 4 c, d). The pore volume was estimated by the software of Adobe Photoshop CS4. As shown in Figure 10a, we mark out the pore area along its contour with Polygonal Lasso Tool of Adobe Photoshop CS4, i.e. white dashed circles, and attain the pixels of pore area and whole area, respectively (Fig. 10b, c). As a result, the ratio of pixels in pore area and whole area is the proportion of pore volume in the whole T\textsubscript{M1-1} magnetite grain, i.e. 1.61%, which is very close to the theoretic decreased volume (1.64%) in the reaction (3). This statement suggests that the abundant micropores in T\textsubscript{M1-1} magnetite resulted from the decrease in volume during transformation of hematite to magnetite, which means the reaction (3) may have occurred under a relative reduced environment.

**Factors controlling magnetite composition**

The composition of magnetite deposited from hydrothermal fluids is controlled by a number of factors, such as fluid composition, nature of co-crystallizing minerals, temperature (T) and oxygen fugacity ($f$O$_2$) during mineral formation (Nadoll et al., 2014). At Mina Justa, most magnetite precipitated during stage III, indicating that the two
magnetite textures formed from similar hydrothermal fluids. The mushketrovite and granular magnetite in Mina Justa deposit co-crystallized with the same assemblage, i.e., sulfides (pyrite and minor chalcopyrite) and quartz (with minor chlorite), suggesting the partitioning with co-crystallizing minerals had limited control on the composition of magnetite. Thus, the major controlling factors of distinct magnetite compositions at Mina Justa may be the temperature and oxygen fugacity.

Temperature is considered to be a major controlling factor for hydrothermal magnetite since element partition coefficients are temperature dependent (McIntire, 1963; Sievwright et al., 2017). High-temperature porphyry and skarn magnetite shows relatively high trace element contents, whereas un-metamorphosed magnetite from banded iron formation (BIF) has the lowest trace element contents (Nadoll et al., 2014). Titanium in Fe oxides is regarded to be positively correlated with temperature (Dare et al., 2012; Nadoll et al., 2012). In addition, according to Nadoll et al. (2014), to some extent, the Ti +V vs. Al+Mn plot can reflect the variation in temperature, with high temperature magnetite plotting at high Ti + V and Al + Mn values field. T_{M1}-2 magnetite has the highest Ti + V and Al + Mn contents (Fig.11a), indicating that temperature increased from T_{M1}-1 to T_{M1}-2, but then declined from T_{M1}-2 to T_{M1}-3 magnetite. T_{M2}-1 magnetite also has slightly higher Ti + V and Al + Mn contents than T_{M2}-2 magnetite, indicating that temperature declined from T_{M2}-1 to T_{M2}-2 magnetite. In general, T_{M2} may have formed in relatively higher temperatures than T_{M1}.

Oxygen fugacity can also impact the composition of magnetite by controlling
element partition coefficients. Some elements, such as V, can occur in various valence
states and therefore their behavior is strongly linked to $f_{O_2}$ (Nielsen et al., 1994; Righter
et al., 2006). The oxidation state of V in natural environments varies from +3 to +5.
Among these species, $V^{3+}$ has the highest compatibility with the spinel structure of
magnetite (Balan et al., 2006; Righter et al., 2006). Vanadium is incompatible at high
oxygen fugacity levels due to its $5^+$ oxidation state. Therefore, the partition coefficient of
magnetite/liquid for V decreases with increasing $f_{O_2}$ because $V^{3+}$ is less stable under
these conditions. For Mina Justa magnetite, the box and whisker plot of V (Fig. 11b)
shows that the V contents of $T_{M1}$ magnetite are lower than that of $T_{M2}$ magnetite,
indicating that the $f_{O_2}$ of $T_{M1}$ magnetite is higher than that of $T_{M2}$ magnetite. This is
consistent with mushketovite which is formed by replacing hematite. In addition, there
are no significant variation of V contents in $T_{M1}$-1, $T_{M1}$-2 and $T_{M1}$-3 magnetite,
suggesting that there was no significant changes in $f_{O_2}$ among different zones of
mushketovite (Fig. 11b). The $T_{M2}$-1 magnetite has slightly lower V content, indicating
that $f_{O_2}$ slightly decreased from the $T_{M2}$-1 to $T_{M2}$-2 magnetite.

**Evolution process of iron oxides at Mina Justa**

Based on above discussion, the primary hematite (Figure 12), which may have
crystallized from an early-stage magmatic-hydrothermal fluid, was replaced by $T_{M1}$-1
magnetite after a sharply drop of $f_{O_2}$ with abundant microporous and mineral inclusions
due to shrinking of volume. Then $T_{M1}$-1 magnetite was replaced by hydrothermal fluids
with increasing temperature that formed $T_{M1-2}$ magnetite with lower Fe and higher Si, Al, Ca concentrations. As the temperature decreased, less Si, Al, Ca entered into magnetite lattice to form $T_{M1-3}$ magnetite which lacks micropores and mineral inclusions. Hydrothermal fluids, likely the same that formed $T_{M1-2}$, directly precipitated granular magnetite ($T_{M2}$) with sulfides and quartz, supported by the higher temperature for $T_{M2}$ compared to $T_{M1}$ (Fig. 11a, 12). As the temperature decreased, together with a slight decrease in $fO_2$ (Fig. 11b), $T_{M2-2}$ magnetite precipitated with lower Si, Al, Ca and higher Fe and replaced $T_{M2-1}$ magnetite (Fig. 12).

**IMPLICATIONS**

This study provided mineralogical evidence to support that the platy magnetite in IOCG systems is mushketovite. In addition, textural and compositional data on magnetite from the Mina Justa deposit provide new insights into genetic mechanism of iron oxides in IOCG deposits. Oxygen fugacity and temperature changes are the dominant mechanisms leading to the formation of different types of magnetite. The primary hematite transformed into magnetite ($T_{M1-1}$) due to a decline in $fO_2$ and then replaced by $T_{M1-2}$ magnetite with increased temperature. Meanwhile, granular $T_{M2-1}$ magnetite directly precipitated from hydrothermal fluid. With the decrease of temperature, $T_{M1-2}$ and $T_{M2-1}$ magnetite are replaced by $T_{M1-3}$ and $T_{M2-2}$ magnetite, respectively. This study shows that even though the iron oxides may have formed from the same alteration stage in hydrothermal deposits, they could undergo a very complicated process of evolvement.
ACKNOWLEDGEMENTS

This study was funded by the National Natural Science Foundation of China (41572059 and U1603244) and the China Scholarship Council Fund (201804910485). We would like to thank prof. Xiangping Gu (Central South University) and Dr. Changming Xing (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences) for their help in the XRD and EMPA analyses. Discussion with Xiaoliang Liang and Wei Tan (Guangzhou Institute of Geochemistry, Chinese Academy of Sciences) improved the understanding of the structure of magnetite and hematite. We also acknowledge constructive comments and suggestions from Irene del Real Contreras and an anonymous reviewer, and editorial handling by Melinda Dyar.
REFERENCES CITED


Caldas, V.J. (1978) Geología de los cuadrángulos de San Juan, Acarí y Yauca: hojas, (31-m, 31-n, 32-n). Instituto de Geología y Minería, Lima, Peru.


Nyström, J.O., and Henríquez, F., 1994, Magmatic features of iron ores of the Kiruna type in Chile and...
Sweden; ore textures and magnetite geochemistry: Economic Geology, 89, 820–839.


layered intrusion (SW China). American Mineralogist, 100, 2348–2351.


Yin, S., Ma, C.Q., Robinson, P.T. (2017) Textures and high field strength elements in hydrothermal
magnetite from a skarn system: Implications for coupled dissolution-reprecipitation reactions.

American Mineralogist, 102, 1045–1056.

Figure captions

**Fig.1.** (a) The position of the Mina Justa deposit within the IOCG metallogenic belt of southern Perú. 
(b) Geological map of the Mina Justa deposit, hosted by the Middle Jurassic Upper Río Grande Formation (modified after Chen et al., 2011). Ab = albite, Act = actinolite, Kfs = K-feldspars.

**Fig.2.** Alteration and mineralization paragenesis of the Mina Justa deposit. (Modified after Chen et al., 2011).

**Fig.3.** Photomicrographs of magnetite from the Mina Justa deposit. (a) Mushketovite intergrown with pyrite and locally cut by chalcopyrite veins; (b) Granular magnetite is usually anhedral and has planar grain boundaries with pyrite.


**Fig.4.** Photomicrographs (a, e) and BSE images (b, c, d, f) of the Mina Justa magnetite. (a) Mushketovite (T\textsubscript{M1}) with interstitial chalcopyrite. (b-d) BSE images of mushketovite, which shows different zones. T\textsubscript{M1}-1 magnetite is bright with abundant porosity and inclusions. T\textsubscript{M1}-2 magnetite is dark and replacing T\textsubscript{M1}-1 magnetite with sharp contact between them. T\textsubscript{M1}-3 magnetite is also bright but lack of porosity and inclusions. (e) Granular magnetite (T\textsubscript{M2}). (f) T\textsubscript{M2}-1 magnetite is replaced by T\textsubscript{M2}-2 magnetite.


**Fig.5.** In situ XRD patterns of magnetite from the Mina Justa deposit compared with standard
magnetite (19-0629). In addition to magnetite, the XRD pattern also shows the characteristic peaks of other minerals coexisting with magnetite, such as chalcopyrite ($T_{M1}$) and apatite ($T_{M2}$). The circles are 40 μm in diameter and represent the test area.

**Fig.6.** Raman spectra of different magnetite textures in the Mina Justa deposit. All samples displayed the characteristic peaks of magnetite, including a weak peak at ~298 cm$^{-1}$ and two stronger at ~540 and ~667 cm$^{-1}$. But characteristic vibrations of hematite at ~225, ~406 and ~1320 cm$^{-1}$ (Giarola et al., 2012) also observed in the central bright zone of platy magnetite, which indicates that it transformed from hematite and still contains hematite residue.

**Fig.7.** EMPA mapping of selected elements in different magnetite from the Mina Justa deposit. (a) Mushketovite; (b) Granular magneite. All color scales are in weight percent.

**Fig.8.** Multi-element variation diagram of the average trace element concentrations in magnetite from the Mina Justa deposit.

**Fig.9.** Binary plots of magnetite from the Mina Justa deposit indicating that trace elements entered into magnetite by substitution of divalent, trivalent and/or tetravalent cations for iron. (a) Si$^{4+}$ vs. Fe$^{3+}$; (b) Si$^{4+}$ vs. Fe$^{2+}$; (c) Fe$^{2+}$ vs. Fe$^{3+}$; (d) Al$^{3+}$ vs. Fe$^{3+}$; (e) Ca$^{2+}$ vs. Fe$^{3+}$; (f) Si$^{4+}$+Al$^{3+}$ vs. Fe$^{2+}$+Ca$^{2+}$.

**Fig.10.** The estimation of pore volume (manipulate by the software of Adobe Photoshop CS4). The smallest unit of an image is a pixel and thus the area percentage can be represented by the pixel percentage. (a) $T_{M1}$ magnetite with abundant porosity and inclusions. White dashed circles are the pore identified by the Polygonal Lasso Tool of software. (b-c) The pixels of pore area and whole $T_{M1}$ magnetite area calculated by software, respectively. Therefore, the ratio of pixels in pore area and whole area, i.e. 1.61%, is the proportion of pore volume in the whole $T_{M1}$ magnetite.
Fig. 11. (a) Plot of (Al+Mn) vs. (Ti+V) for Mina Justa magnetite. The high temperature magnetite usually plotted into the high Ti + V and Al + Mn values field (Nadoll et al., 2014). (b) Plot of V concentration for Mina Justa magnetite. $V^{3+}$ has the highest compatibility with the spinel structure of magnetite and $V^{5+}$ is incompatible at high oxygen fugacity levels (Balan et al., 2006; Righter et al., 2006). Therefore, higher V concentration may indicate lower $f_{O_2}$.

Fig. 12. Schematic evolution-textural and chemical of iron oxides from the Mina Justa deposit. (a1-a4) primary hematite was replaced by $T_{M1-1}$ magnetite with the decrease of $f_{O_2}$. Then $T_{M1-1}$ magnetite was replaced by hydrothermal fluids with increasing temperature that formed $T_{M1-2}$ magnetite. Finally, $T_{M1-3}$ magnetite was formed on the outside of $T_{M1-2}$ magnetite with the decrease of temperature. (b1-b2) Granular magnetite ($T_{M2-1}$) directly precipitated from hydrothermal fluids and then replaced by $T_{M2-2}$ magnetite with the decrease of temperature and $f_{O_2}$. 

28
<table>
<thead>
<tr>
<th>Minerals</th>
<th>Early alteration Stage I</th>
<th>Hematite Stage II</th>
<th>Magnetite-pyrite Stage III</th>
<th>Cu mineralization Stage IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albité</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microcline</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diopside</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actinolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hématite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apatite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Allanite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopryrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bornite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcocite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphalerite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrollite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epidote</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinozoisite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prehnite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Legend:
- Abundant
- Local
- Trace
Fig. 3

(a) Q, Ccp, Tm1 Mag, Py

(b) Q, Ccp, Tm2 Mag
Fig. 5

<table>
<thead>
<tr>
<th></th>
<th>a(Å)</th>
<th>V(Å³)</th>
<th>2θ(°)</th>
<th>FWHM(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19-0629</td>
<td>8.396</td>
<td>591.858</td>
<td>35.422</td>
<td></td>
</tr>
<tr>
<td>T_{M1}</td>
<td>8.3894(0.00022)</td>
<td>590.46</td>
<td>35.455</td>
<td>0.205</td>
</tr>
<tr>
<td>T_{M2}</td>
<td>8.3909(0.00019)</td>
<td>590.78</td>
<td>35.411</td>
<td>0.228</td>
</tr>
</tbody>
</table>

Intensity

2θ(°)

T_{M2} magnetite

T_{M1} magnetite

Magnetite (19-0629)
Fig. 8

Concentration (wt.%) vs Elements: Si, Ca, Ni, Mg, Al, Mn, Cr, V, Ti

Lines and markers represent:
- $T_{M1-1}$
- $T_{M1-2}$
- $T_{M1-3}$
- $T_{M2-1}$
- $T_{M2-2}$

Concentration values for each element vary across the graph.
Fig. 10

Pore Vol. % = 2859 / 177152 ≈ 1.61 Vol. %
Table 1 Mean, minimum and maximum contents of electron microprobe analyses (wt.%) for magnetite from the Mina Justa deposit.

<table>
<thead>
<tr>
<th>Magnetite type</th>
<th>SiO₂</th>
<th>CaO</th>
<th>NiO</th>
<th>MgO</th>
<th>FeO</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>Cr₂O₃</th>
<th>V₂O₃</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T_M1-1 (n=13)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.072</td>
<td>b.d.l</td>
<td>0.011</td>
<td>0.016</td>
<td>92.448</td>
<td>0.047</td>
<td>0.047</td>
<td>0.009</td>
<td>0.033</td>
<td>0.012</td>
</tr>
<tr>
<td>Min</td>
<td>0.010</td>
<td>b.d.l</td>
<td>b.d.l</td>
<td>0.010</td>
<td>91.964</td>
<td>0.020</td>
<td>0.019</td>
<td>b.d.l</td>
<td>b.d.l</td>
<td>b.d.l</td>
</tr>
<tr>
<td>Max</td>
<td>0.294</td>
<td>b.d.l</td>
<td>0.045</td>
<td>0.102</td>
<td>93.294</td>
<td>0.100</td>
<td>0.089</td>
<td>0.054</td>
<td>0.079</td>
<td>0.048</td>
</tr>
<tr>
<td><strong>T_M1-2 (n=18)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.582</td>
<td>0.233</td>
<td>0.005</td>
<td>0.120</td>
<td>90.280</td>
<td>0.324</td>
<td>0.064</td>
<td>0.011</td>
<td>0.033</td>
<td>0.031</td>
</tr>
<tr>
<td>Min</td>
<td>0.984</td>
<td>0.035</td>
<td>b.d.l</td>
<td>0.010</td>
<td>88.834</td>
<td>0.132</td>
<td>0.014</td>
<td>b.d.l</td>
<td>b.d.l</td>
<td>b.d.l</td>
</tr>
<tr>
<td>Max</td>
<td>2.612</td>
<td>0.588</td>
<td>0.026</td>
<td>0.321</td>
<td>92.266</td>
<td>0.723</td>
<td>0.106</td>
<td>0.030</td>
<td>0.085</td>
<td>0.106</td>
</tr>
<tr>
<td><strong>T_M1-3 (n=22)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.505</td>
<td>0.077</td>
<td>0.009</td>
<td>0.036</td>
<td>91.938</td>
<td>0.072</td>
<td>0.039</td>
<td>0.017</td>
<td>0.026</td>
<td>0.014</td>
</tr>
<tr>
<td>Min</td>
<td>0.036</td>
<td>0.010</td>
<td>b.d.l</td>
<td>0.010</td>
<td>90.072</td>
<td>0.016</td>
<td>b.d.l</td>
<td>b.d.l</td>
<td>b.d.l</td>
<td>b.d.l</td>
</tr>
<tr>
<td>Max</td>
<td>0.940</td>
<td>0.420</td>
<td>0.035</td>
<td>0.086</td>
<td>94.291</td>
<td>0.184</td>
<td>0.079</td>
<td>0.065</td>
<td>0.083</td>
<td>0.075</td>
</tr>
<tr>
<td><strong>T_M2-1 (n=21)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.365</td>
<td>0.247</td>
<td>0.004</td>
<td>0.221</td>
<td>89.817</td>
<td>0.400</td>
<td>0.094</td>
<td>0.013</td>
<td>0.256</td>
<td>0.146</td>
</tr>
<tr>
<td>Min</td>
<td>1.031</td>
<td>0.115</td>
<td>b.d.l</td>
<td>0.082</td>
<td>87.324</td>
<td>0.233</td>
<td>0.022</td>
<td>b.d.l</td>
<td>0.046</td>
<td>0.075</td>
</tr>
<tr>
<td>Max</td>
<td>1.898</td>
<td>0.383</td>
<td>0.045</td>
<td>0.437</td>
<td>91.236</td>
<td>0.690</td>
<td>0.155</td>
<td>0.060</td>
<td>0.561</td>
<td>0.237</td>
</tr>
<tr>
<td><strong>T_M2-2 (n=45)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.297</td>
<td>0.011</td>
<td>0.008</td>
<td>0.041</td>
<td>90.186</td>
<td>0.108</td>
<td>0.057</td>
<td>0.015</td>
<td>0.424</td>
<td>0.075</td>
</tr>
<tr>
<td>Min</td>
<td>0.013</td>
<td>b.d.l</td>
<td>b.d.l</td>
<td>0.01</td>
<td>88.259</td>
<td>0.025</td>
<td>0.015</td>
<td>b.d.l</td>
<td>0.102</td>
<td>0.01</td>
</tr>
<tr>
<td>Max</td>
<td>0.99</td>
<td>0.092</td>
<td>0.022</td>
<td>0.229</td>
<td>94.426</td>
<td>0.338</td>
<td>0.148</td>
<td>0.085</td>
<td>0.786</td>
<td>0.193</td>
</tr>
</tbody>
</table>

Abbreviation: n = numbers of analyses; b.d.l = below detection limits.