### Determination of Fe<sup>2+</sup>/Fe<sup>3+</sup> Ratios of Magnetite using Different Methods: A Case Study from the Qimantag Metallogenic Belt



YI Liwen<sup>1, 2, \*</sup>, LI Qiuping<sup>1</sup>, LU Anhuai<sup>3</sup>, GU Xiangping<sup>2</sup> and CHI Guoxiang<sup>4</sup>

<sup>1</sup> School of Geographical Sciences, Hunan Normal University, Changsha 410081, China

<sup>3</sup> School of Earth and Space Sciences, Peking University, Beijing 100871, China

<sup>4</sup> Department of Geology, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Abstract: Determination of  $Fe^{2+}/Fe^{3+}$  ratios from metallogenic belts to explore controlling physical and chemical conditions of rock formation is of great significance. In order to explore magnetite  $Fe^{2+}/Fe^{3+}$  ratios of the Qimantag metallogenic belt, part of the Eastern Kunlun orogenic belt in the northeastern margin of the Qinghai-Tibetan plateau, western Central Orogenic Belt of China, and overcome the limitation of the traditional electronic probe, five different measurement methods are proposed and their respective advantages and disadvantages evaluated, with the composition data of the magnetite obtained using electron probe microanalysis (EPMA). The direct oxygen measurement method has a significant impact on the determination results of FeO and Fe<sub>2</sub>O<sub>3</sub>, but the accuracy and uniformity of the results are low. The valence method (Flank method) based on the spectral intensity ratio of La to LB for iron is also unreliable for FeO and Fe<sub>2</sub>O<sub>3</sub> measurements because it is difficult to establish a relationship between LB/La, the spectral intensity ratio, and the Fe<sup>2+</sup>/Fe<sup>3</sup> content ratio. In comparison, the charge difference method, the surplus-oxygen method and the Mössbauer spectrum method are still the most favorable. Mössbauer spectroscopy, with its isomer movement particularly sensitive to the oxidation state of iron, yields results closer to 0.5, which is relatively reliable. Earlier magnetite deposits are located in intrusions or contact zones and formed by magmatic fluids with high Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios, whereas later magnetite deposits are farther away from intrusions and have low  $Fe^{2^+}/Fe^{3+}$  ratios. The transformation mechanism of hematite and magnetite in the Qimantage metallogenic belt is also studied. No large volume changes, such as pore filling and shrinkage fracture, were detected in the metallogenic belt, and the transformation mechanism is more similar to a reoxidation and reduction mechanism.

Key words: iron, magnetite, direct oxygen measurement, flank-charge difference-surplus-oxygen methods, Mössbauer spectra, Qimantage

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### **1** Introduction

The speciation of transition metals in solids is of relevance to many scientific fields (e.g., petrology, material sciences, atmospheric sciences). Iron, the fourth most abundant element in the Earth, usually presents in two valence states,  $Fe^{2+}$  and  $Fe^{3+}$ , and even in one mineral. The knowledge of  $Fe^{2+}/Fe^{3+}$  ratios of minerals is essential for the determination of  $e^{2+}/Fe^{3+}$ for the determination of physicochemical conditions of rock formation, such as temperature and oxygen fugacity (Frost, 1991). The electron probe is a means of analysis of characteristic X-ray of elements, but it only reflects the transition of the inner layer electrons and is less affected by the valence electrons, and so the conventional method of electron probe analysis cannot distinguish the  $Fe^{2+}$  from the  $Fe^{3+}$  (Yang et al., 2007). In order to overcome this limitation of the electron probe and analyze the contents of FeO and Fe<sub>2</sub>O<sub>3</sub> in minerals, direct oxygen measurement (Chen et al., 1992), the charge difference and surplusoxygen methods (Zheng, 1983) and the flank method (Höfer et al., 1994) have all been put forward. All of these methods have been adopted by scholars; unfortunately, the actual results have been unsatisfactory.

Traditionally, the ferric iron content is estimated from elemental analyses by indirect means, i.e., by stoichiometric calculation. These calculated  $\rm Fe^{2+}/Fe^{3+}$ ratios are extremely sensitive to error because the analytical errors of the measurements of all other elements are combined in their calculation (Spear, 1995). The  $Fe^{2+}/$ ratios of magnetite estimated in electron probe Fe<sup>3+</sup> microanalysis (EPMA) using calculation procedures that optimize the mineral formula in terms of site occupancy and charge balance are only applicable with some confidence to minerals with tight constraints on stoichiometry and in the absence of other cations with a variable oxidation state (Canil and O'Neill, 1996); despite progress of determining  $Fe^{2+}/Fe^{3+}$  ratios in the electron microprobe (Höfer et al., 1994), accuracy and spatial resolution remain limited. Mössbauer spectroscopy is an important and accepted tool for geosciences to determine

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<sup>&</sup>lt;sup>2</sup> School of Geosciences and Info-Physics, Central South University, Changsha 410083, China

<sup>\*</sup> Corresponding author. E-mail: yilw@hunnu.edu.cn

the iron oxidation state in minerals. However, Mössbauer spectroscopy is also limited in spatial resolution to ca. 200 mm, obliterating potential zonations in  $Fe^{2+}/Fe^{3+}$  ratios.

Therefore, in this study, through the determination of  $Fe^{2+}/Fe^{3+}$  ratios of magnetite from the Qimantag metallogenic belt in the western Central Orogenic Belt (COB), China, the quality of all these methods is evaluated. In this study, we report the major element compositions of magnetite from the Qimantag metallogenic belt deposits. Compositional data of magnetite was obtained by EPMA and display regular variations among Kendekeke, No. 2 ore body of the Hutouya deposit, and other deposits (Fig. 1).

### 2 Geological Setting and Sampling

The Qimantag metallogenic belt is located in the western portion of the Eastern Kunlun orogenic belt (EKOB), and contains more than 10 large and mediumsized deposits; it has significant potential to be one of the most important Fe-Cu mineralizing districts in China in the near future (Zhao et al., 2013). Tectonically, the EKOB is in the northeastern margin of the Qinghai– Tibetan plateau, the western part of the COB (Bian et al., 2002), and near the intersection of the Kunlun–Qaidam and Bayan Har–Songpan–Qiangtang terranes (Yin, 2001). The EKOB is bounded by the Qaidam basin in the north,



Fig. 1. (a) Paleozoic tectonic framework of the Altun–Qilian–East Kunlun composite terrane characterized by multiple subterranes and arcs in the western part of the Central Orogenic Belt, China (after Xu et al., 2006), showing the location of the Qimantag ore district; (b) geological sketch map of the Qimantag area showing distribution of major Fe-Cu-polymetallic deposits (after Feng et al., 2011).

(a) Inset is a tectonic map of the Qinghai–Tibetan plateau; dotted pattern indicates the distribution of the Altyn Tagh–Qilian–East Kunlun composite terrane on the northeastern margin of the Qinghai–Tibetan plateau. the Bayankala mountains in the south, and the NEtrending Altun strike-slip fault in the west (Fig. 1a). Four NWW-trending deep faults divide it into five tectonic belts, from north to south: northern Kunlun, central Kunlun, southern Kunlun, Anyemagen, and northern Bayankala; most deposits of the Qimantag area are located in the North Kunlun terrane (Fig. 1b).

The basement of the North Kunlun terrane is the Proterozoic Jinshuikou Group, which is dominated by paragneisses of variable compositions, with minor marble, amphibolites, migmatite, and locally granulite and eclogite (Wang and Chen, 1987; Wang et al., 2004; Chen et al., 2006; Wang et al., 2007; Lu et al., 2009; Chen et al., 2011; Meng et al., 2013). Archean to Cenozoic strata are exposed in the Qimantag area. Of these, the carbonate and clastic rocks of the Mesoproterozoic Jixian System, carbonate and other sedimentary rocks of the Ordovician–Silurian Tanjianshan Group, and carbonate rocks of the Tanjianshan Group are the most important hosts of Femineralization.

Tremendous Indosinian granitoids with whole-rock K-Ar dates of 207-227 Ma and Variscan granitoids with whole-rock K-Ar and Rb-Sr dates of 257-376 Ma, intrude the northern Kunlun belt, forming a nearly EW-trending magmatic belt (Gu et al., 1996). Numerous studies indicate that the East Kunlun is a multiple orogen that underwent a complicated evolutionary process; four major tectonic cycles are recognized, of which the early Paleozoic and late Paleozoic to early Mesozoic are the most important cycles of polymetallic mineralization in the region (Pan et al., 1996; Yin and Zhang, 1997; Jiang et al., 2000). During late Paleozoic-early Mesozoic, numerous Fe-polymetallic deposits in the Qimantag area were formed in the late stage of collision, with zircon U-Pb dates of 218–239 Ma (Liu et al., 2006; Li et al., 2008; Wang et al., 2009; Song et al., 2010; Xi et al., 2010; Feng et al., 2011; Zhao et al., 2013). It is particularly noteworthy that metallogenic specialization is obvious in the Oimantag area; Fe-mineralization is closely associated with diorite, granodiorite and monzonitic granite, while Cu-mineralization is mainly associated with granodiorite and monzonitic granite; Pb-Zn-mineralization is only associated with monzonitic granite (Zhao et al., 2013).

The Kaerqueka Cu-Fe-Mo-Pb-Zn deposit is located in the western portion of the Qimantag area, which represents the most important copper deposit in the belt, with a proven reserve of 0.38 Mt Cu at an average grade of 0.15-3.28 wt% Cu (Zhao et al., 2013). This deposit is related to a porphyritic monzonite granite and granodiorite plutons that intruded the Tanjianshan Group (Li et al., 2011). SHRIMP zircon U-Pb dating indicates that the porphyritic monzonite granite and granodiorite plutons were emplaced at 227  $\pm$  2 and 237  $\pm$  2 Ma, respectively (Wang et al., 2009). The Hutouya Cu-Fe-Pb-Zn deposit is located in the western part of the North Kunlun terrane, found by the Qinghai Geological Survey Institute in 1980. After years of geological exploration by many geological units, Hutouya has been identified as a large-scale Cu-Fe-Pb-Zn polymetallic deposit (Zhao et al., 2013). This deposit is also related to a porphyritic monzonite granite and granodiorite plutons that intruded the Jixian System, the Tanjianshan Group, and Dagangou and Diaosu groups (Zhang et al., 2013). Laser ablation ICP-MS and SHRIMP zircon U-Pb dating indicate that the porphyritic monzonite granite and granodiorite plutons were emplaced at  $219.4 \pm$ 1.4 and  $235.4 \pm 1.8$  Ma, respectively (Feng et al., 2011). The Kendekeke Fe-Co-Bi-Ag deposit represents the largest iron deposit in the Qimantag area, with a proven reserve of 74.06 Mt Fe, 9.5 t Au, 482.7 t Co and 4457.7 t Bi at an average grade of 4.43 g/t Au, 0.095 wt% Co, 0.95 wt% Bi (Xiao et al., 2005; Zhao et al., 2013). The host lithologies at Kendekeke include Ordovician, Silurian and Carboniferous sedimentary rocks. The Galinge Fe-Pb-Zn deposit is located in the eastern part of the North Kunlun terrane and also represents a most important Fe deposit in the Qimantag area, with a proven reserve of 15 Mt Fe (Zhao et al., 2013). Sedimentary and other strata in this area are the Ordovician-Silurian Tanjianshan Group that consists of marbles, limestones, slates and andesites. Laser ablation ICP-MS zircon U-Pb dating indicates that the diorite and adamellite were emplaced at  $228.3 \pm 0.5$  and  $234.4 \pm 0.6$  Ma, respectively (Gao et al., 2012).

Field work in these deposits and the vicinity included examination and mapping of surface outcrops, trenches, and adits in ore blocks and 18 samples were collected for this study. Samples KQ012 and KQ072 were collected from major Cu-Mo ore body No. 7 and peripheral Fe ore body No. 18 of the Kaerqueka deposit, respectively. Sample H4100-25 was collected from major Pb-Zn ore body No. 7 of the Hutouya deposit. Samples HT09, HT10, HT13 and HTX were all collected from Fe-Cu ore body No. 2 of Hutouya deposit near granite. Magnetite is rare in major Pb-Zn ore body No. 7, which is further from the granite; sample H4100-25 was the only magnetite sample we found in this ore body (Fig. 2). Six samples from the Kendekeke Fe deposit (KD01, KD02, KDF01, KDF04, KDF13 and KDF22) were all collected from the major ore body. Samples ZK26005-09, ZK26005-10, ZK26005-13, ZK26005-15 and ZK26005-15 were collected from drill hole ZK26005 at ~200 m depth in the Galinge deposit.

There are massive, disseminated and brecciated ores in the metallogenic belt. Disseminated ores occur along the ends of the lenticular ore bodies. Massive ores generally occur in the center of Fe ore bodies, such as in samples KQ072, HT09, HT10, HT13, HTX, KD01, KD02, KDF01, KDF04, KDF13 and KDF22 (Fig. 3).

#### **3** Petrography and Texture of Sequence

The magnetite samples have been generally classified according to their occurrences in massive, disseminated and banded ores. Massive ores generally occur in Kendekeke, Galinge, Kaerqueka, and the Hutouya No. 2 ore body, whereas disseminated ores occur in the Hutouya No. 7 ore body or the edge of the ore bodies in Kendekeke and Galinge deposits. Banded ores only occur in the Kendekeke deposit. Ore minerals include magnetite, pyrrhotite, pyrite, chalcopyrite, galena, sphalerite, molybdenite, arsenopyrite, and minor cassiterite. Gangue minerals are dominated by pyroxene, garnet, hornblende,



Fig. 2. Geological sketch map of the Hutouya deposit (after Third Geological Exploration Institute of Qinghai Province, 2009). 1–Quaternary; 2–Upper Triassic Elashan Formation and Member; 3–Upper Carboniferous Diaosu Formation and Member; 4–Lower Carboniferous Dagangou Formation and Member; 5–Ordovician–Silurian Tanjianshan Group; 6–Jixian System Langyashan Formation and Member; 7–moyite; 8–mozonitic granite; 9–granodiorite; 10–diorite; 11–skarn alteration zone; 12–ore body and its number; 13–fault.

and vesuvianite with minor plagioclase, biotite, chlorite, quartz, calcite, and epidote. Massive ores from Kendekeke, Galinge and Hutouya No. 2 ore bodies have similar mineral assemblages of magnetite  $\pm$  pyrite  $\pm$ pyrrhotite  $\pm$  chalcopyrite. Disseminated and banded ores from Kaerqueka and the Hutouya No. 7 ore bodies have similar mineral assemblages of magnetite  $\pm$  chalcopyrite  $\pm$ galena  $\pm$  sphalerite  $\pm$  molybdenite.

Magnetite from massive ores occurs as anhedral to euhedral grains generally larger than 100  $\mu$ m in diameter, and gray to dark black (Fig. 3b, c). Magnetite from disseminated ores occurs as subhedral to euhedral grains scattered associated with calcite and galena (Fig. 3a, f). Radialis assemblages of magnetite and ludwigite occur in the edge of ore bodies in the Galinge deposit (Fig. 3b). Pyrite occurs as veins or interstitial infilling in fractures of magnetite grains (Fig. 3c) or subhedral to euhedral crystals associated with magnetite. Chalcopyrite assumes gridded or ring-like exsolution in bomite or sphalerite (Fig. 3d, e).

Two distinct generations of magnetite, hereinafter termed as early-stage (Mag1) and later-stage (Mag2), have been recognized in the Kendekeke deposit. Mag1 magnetite is homogeneous and dark black, with fairly fine porosity (Fig. 3f); the grains are mostly subhedral to euhedral and 50 to 500  $\mu$ m across, whereas Mag2 magnetite surrounds in the early phase and occurs as irregular patches or veinlets (Fig. 3f). Unlike at Kendekeke, Mag1 magnetite in the Hutouya deposit is typically euhedral to anhedral and ranges in size from 100 to 500  $\mu$ m. It occurs as massive grains in the ore body between adamellite and the Carboniferous Diaosu Group (No. 2 ore body). Mag2 magnetite in the Hutouya deposit occurs as disseminated grains or veins in calcareous rock between the Carboniferous Dagangou Group and the

Jixian System (No. 7 ore body) (Fig. 3a).

# 4 Analytical Methods and Results of Fe<sup>2+</sup>/Fe<sup>3+</sup> Ratios of Magnetite

#### 4.1 Direct oxygen measurement

Magnetite from the different deposits was studied petrographically and analyzed by EPMA. All samples were prepared as polished thin sections and subsequently examined by optical microscope to characterize the mineralogical and textural relationships, with an emphasis on the occurrence, morphology, and texture. The polished thin sections were then carbon-coated for scanning electron microscopy (SEM) and EPMA. The morphology and textures of magnetite were investigated in a LEICA DM2500p microscope, and the microprobe quantitative analyses was carried out on a Shimadzu EPMA-1720 equipped with an EDAX Genesis energy dispersive system at the Key Laboratory of Metallogenic Prediction of Nonferrous Metals, Ministry of Education, Beijing. The analysis was carried out at an accelerating voltage of 15 kV and beam current of 10 mA.

Results of EPMA direct oxygen measurement for various types of magnetite are presented in Table 1. Magnetite in the ores close to a granite body such as the Kaerqueka No. 7 ore body and Hutouya No. 2 ore body have high contents of Ti (up to 0.19 wt%) and Mn (0.21–1.41 wt%), with minor Mg (0.01–0.18 wt%). Contents of Ti and Mn are significantly lower in the magnetite from the ores in surrounding rocks, such as Kaerqueka No. 18 ore body (Ti: 0 wt%, Mn: 0.15 wt%) and Hutouya No. 7 ore body (Ti: 0.02 wt%, Mn: 0.27 wt%). Mag1 magnetite in the Kendekeke deposit is enriched in Mg (0.11 wt%) and Ti (2.45 wt%), Mn (0.35 wt%), which is significantly



Fig. 3. Photomicrographs and EPMA-BSE images of the ore samples (under reflected light) from the Qimantag metallogenic belt deposits.

(a) Subhedral to euhedral magnetite grains from No. 7 ore body of the Hutouya deposit scattered associated with calcite; (b) radialis magnetite (Mag1) from the Galingge deposit associated with radialis ludwigite (Lud); (c) vein-type pyrite (Py) infills fracture of magnetite (Mag1) from the Kendekeke deposit; (d) chalcopyrite (Ccp/ Cv) assuming gridded exsolution in bomite (Bn) from No. 7 ore body of the Kaerqueka deposit; (e–f) EPMA-BSE images showing typical magnetite grains from the Kendekeke deposit sample KD01, accompanied with analysis positions.

higher than the values of Mag2 (0.04 wt% Mg and 0.04 wt% Ti, 0.13 wt% Mn).

The determination of the oxidation state of transition metals by EPMA is of long-standing interest in geological and technical problems. For ultra-light elemental oxygen, the electron probe can only use its K $\alpha$  spectrum for quantitative analysis. On the one hand, the position and

shape of the peak will transform along with the difference of the state of combination, so the calculation of the concentration by the ratio of peak intensity is uncertain. On the other hand, the overlapping interference of the L line of heavy elements, the contamination of the surface of the sample, the smoothness and finish of the sample, and the difficulty of selecting similar standard samples all

Deposits	Samples		Fe	0	Mg	Mn	Ca	Ti	Al	Total	Fe/O	Fe <sup>2+</sup> /Fe <sup>3+</sup>	Туре
No. 7	1 -012	$Avg (n = 3)^a$	69.28	28.60	0.59	0.97	0.03	0.02	0.09	99.58	2.42	0.25	Mag2
ore body Kaerqueka No. 18 ore body Kaerqueka	Kq012	stdev	0.61	0.43	0.04	0.03	0.00	0.02	0.05	0.86	0.03	0.06	
	kq072	Avg(n = 4)	67.80	28.85	2.55	0.15	0.02	0.00	0.11	99.48	2.35	0.29	Mag2
		stdev	0.67	0.84	0.18	0.03	0.02	0.01	0.05	1.09	0.06	0.15	
	ht07	Avg(n = 4)	69.52	29.05	0.09	0.55	0.05	0.03	0.17	99.45	2.39	0.14	Magl
		stdev	0.28	0.29	0.08	0.09	0.05	0.03	0.13	0.40	0.02	0.03	
	ht07-2	Avg(n = 4)	69.30	30.02	0.16	0.62	0.18	0.01	0.11	100.41	2.32	0.09	Magl
		stdev	2.55	2.47	0.25	0.05	0.22	0.01	0.01	0.72	0.25	0.28	
No. 2	ht10	Avg(n = 4)	71.63	28.63	0.02	0.37	0.01	0.04	0.15	100.83	2.50	0.31	Magl
ore body Hutouva		stdev	0.20	0.10	0.01	0.04	0.01	0.02	0.03	0.16	0.01	0.03	
ore body flutouya	ht13	Avg(n=4)	69.77	28.86	0.01	0.21	0.01	0.01	0.05	98.91	2.42	0.15	Magl
		stdev	0.24	0.82	0.01	0.02	0.01	0.01	0.02	0.90	0.06	0.10	
	ht13-2b	Avg(n=4)	69.96	28.28	0.13	1.41	0.03	0.09	0.09	100.00	2.47	0.32	Magl
		stdev	0.90	0.53	0.14	0.31	0.02	0.08	0.11	1.27	0.03	0.04	
	ht17	Avg(n=4)	71.23	29.03	0.13	0.70	0.05	0.01	0.17	101.32	2.45	0.25	Magl
		stdev	0.25	0.06	0.03	0.07	0.08	0.01	0.09	0.20	0.01	0.02	
No. 7	4100-25	Avg(n = 4)	66.80	32.56	0.19	0.27	0.33	0.02	0.21	100.39	2.06	-0.25	Mag2
ore body Hutouya	1100 20	stdev	1.99	1.73	0.15	0.13	0.13	0.01	0.08	2.57	0.12	0.10	
	kd01	Avg(n = 3)	71.18	29.55	0.39	0.27	0.07	0.05	0.06	101.55	2.41	0.18	Mag2
		stdev	0.24	1.15	0.07	0.02	0.07	0.02	0.01	1.05	0.10	0.15	
	kd02-		67.15	26 53	0.11	0.35	0.00	2.45	0.15	96 74	2.53	0.80	Mag1
	massive												
Kendekeke	kd02-diss-		71.48	27.46	0.04	0.13	0.00	0.04	0.14	99.30	2.60	0.51	Mag2
	eminated		(		1.00	0.55	0.02	0.10	1.40	04.04		0.00	
	kdf04	Avg $(n = 4)$	65.17	28.21	1.39	0.55	0.03	0.13	1.48	96.96	2.31	0.29	Mag2
		stdev	2.68	0.54	0.38	0.09	0.02	0.06	1.30	1.79	0.08	0.13	
	kdf22	Avg(n=3)	69.09	28.38	0.58	0.51	0.17	0.02	0.12	98.87	2.43	0.26	Mag2
		stdev	1.09	0.43	0.11	0.03	0.08	0.02	0.09	1.68	0.01	0.02	
	zk26005-09	Avg $(n = 4)$	66.15	28.80	2.84	0.19	0.00	0.06	0.62	98.66	2.31	0.32	Mag2
Galingge		stdev	5.71	1.86	2.54	0.07	0.00	0.08	0.82	1.82	0.33	0.29	
	zk26005-10	Avg $(n = 2)$	67.35	29.39	1.//	0.4/	0.00	0.00	0.14	99.12	2.29	0.11	Mag2
		stdev	0.17	0.10	0.27	0.02	0.00	0.00	0.06	0.46	0.00	0.01	
00	zk26005-14 zk26005-15	Avg $(n = 8)$	06.44	28.65	1.55	1.03	0.00	0.58	0.70	98.74	2.32	0.28	Mag2
		stdev	2.82	0.43	0.93	0.34	0.00	0.16	0.63	1.08	0.13	0.09	M 2
		Avg $(n = 3)$	0/.10	29.9/	1.32	0.51	0.00	0.02	0.28	99.20	2.24	0.02	Mag2
		stdev	0.94	0.96	0.55	0.07	0.00	0.01	0.03	1.21	0.09	0.09	

Table 1 EPMA direct oxygen measurement results for major elements in magnetite from the Qimantag metallogenic belt deposits (in wt%)

Abbreviation: Avg = average, stdev = standard deviation. <sup>a</sup> Numbers in parenthesis represent the number of analyzed spots.

have a very high impact on the analysis results (Xu et al., 1988) and, therefore, the accurate measurement of oxygen is actually very difficult (Xu, 1990). Nash (1992) reported a very accurate measurement method, which uses a standard sample similar to the sample, with an appropriate sample preparation method used for both; the relative deviation of oxygen can be raised to 0.6%. However, this method has strict conditions of the standard samples and measurement, and is difficult to be applied in practice. On the basis of the evaluation for measurement uncertainty, Yang et al. (2007) found that the measurement uncertainty of oxygen will be expanded approximately 10 times, because uncertainty and sensitivity coefficients of FeO and Fe<sub>2</sub>O<sub>3</sub>, derived from the super light element oxygen, are 8.981 and 9.981, respectively. Thus it can be seen that the direct oxygen measurement method is not suitable for FeO and Fe<sub>2</sub>O<sub>3</sub> measurements because of the transfer of oxygen measurement uncertainty. According to the  $Fe^{2+}/Fe^{3+}$ ratios diagram (Fig. 4), results of direct oxygen measurement have a wide range and far away from 0.5 (variance 0.05995-0.56662). It shows that the accuracy and uniformity of the results are low.

#### 4.2 Flank method

The principle of  $Fe^{2+}/Fe^{3+}$  quantification using the flank

method microprobe is based on the soft FeL X-ray emission shift phenomenon; there is a distinct peak shift of FeLa and FeL $\beta$  spectra lines to lower energies with increasing Fe<sup>3+</sup>, as well as a noticeable change in the intensity (counts) ratio with the iron's oxidation state. The basic principle is that in X-ray emission spectra of transition metals, the L $\alpha$  and L $\beta$  peaks and also the L $\alpha$ /L $\beta$ intensity ratios shift with a change in the oxidation states (Fischer, 1965). Andersen (1966) pointed out that the relative intensities of Fe L $\alpha$  and L $\beta$  X-ray emission peaks differ significantly with the valence state in metallic Fe, FeS<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub>. Tossell et al. (1974) showed that for iron this is due to a shift of the empty 4 s states in the conduction band from lower energies in compounds containing divalent iron to higher energies in compounds containing trivalent iron. This reduces the intensity of the FeL $\beta$  peak preferentially to the FeL $\alpha$  peak due to selfabsorption. In an attempt to use these effects for quantitative analysis, Albee and Chodos (1970) determined  $L\beta/L\alpha$  intensity ratios in Fe– and Mn-bearing oxides and silicates, but were only able to derive a semiquantitative application.

In the past, many attempts have been made to determine the iron oxidation state by electron microprobe. Yet, only semiquantitative  $Fe^{2+}/Fe^{3+}$  estimations were achieved so far (Pavićević, 1989).



Fig. 4. Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios diagram for samples from the Qimantag metallogenic belt.

Based on these experiences, Höfer et al. (1994) developed a new method they termed the flank method, which allows accurate measurement of the critical X-ray intensities related to the iron oxidation state in solid samples. This method has been successfully applied to sodic amphiboles by Enders et al. (2000) and Höfer et al. (2000). According to the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios diagram (Fig. 4), results of the L $\beta$ /L $\alpha$  ratios method also have a wide range, but compare to the results of the direct oxygen measurement (Variance 0.01669–0.23892), are closer to 0.5 and the results of Mössbauer spectroscopy.

# 4.3 Charge difference method and surplus-oxygen method

EPMA results without oxygen measurement for various types of magnetite are presented in Table 2. Magnetite in the ores near a granite body such as the Kaerqueka No. 7 ore body and Hutouya No. 2 ore body have high contents of TiO<sub>2</sub> (up to 0.12 wt%), MnO (0.83–1.12 wt%) and Fe<sup>2+/</sup> Fe<sup>3+</sup> value (0.462–0.515), with minor MgO (0.85–1.04 wt%). Contents of TiO<sub>2</sub>, MnO and Fe<sup>2+</sup>/Fe<sup>3+</sup> value are significantly lower in the magnetite from the ores in surrounding rocks, such as Kaerqueka No. 18 ore body (TiO<sub>2</sub>: 0-0.01 wt%, MnO: 0.13-0.22 wt%, 0.384) and Hutouya No. 7 ore body (TiO<sub>2</sub>: 0-0.03 wt%, MnO: 0.13-0.42 wt%, 0.496). Mag1 magnetite in the Kendekeke deposit is enriched in MgO (0.8-2.17 wt%) and TiO<sub>2</sub> (0.59 -4.07 wt%), Al<sub>2</sub>O<sub>3</sub> (0.31-3.36 wt%) MnO (0.53-1.25 wt%), which are significantly higher than the values of Mag2 (0.42-0.53 wt% MgO and 0.02-0.16 wt% TiO<sub>2</sub>, 0-0.03 wt% Al<sub>2</sub>O<sub>3</sub> 0.31–0.35 wt% MnO).

Using EPMA analysis data without oxygen measurement is the traditional way to calculate  $Fe^{2+}/Fe^{3+}$  ratios of minerals. Mysen and Griffin (1973), Neumann (1976) and Carpenter (1979) calculated and updated  $Fe^{2+}/Fe^{3+}$  ratios from pyroxene using such EPMA data; Stout (1972) calculated  $Fe^{2+}/Fe^{3+}$  ratios from amphibole also

using this EPMA method. Zheng (1983) systematically discussed the principle, applicable conditions and existing problems of calculating FeO and  $Fe_2O_3$  contents in minerals by the charge difference method and the surplus-oxygen method, and made correction and simplification. According to the method of Zheng (1983), the  $Fe^{2+}/Fe^{3+}$  ratios of magnetite from the different deposits of the charge difference method (Variance 0.00002–0.01356) and the surplus-oxygen method (Variance 0.00005–0.01351) is very close to 0.5 and the results of Mössbauer spectroscopy (Fig. 4).

#### 4.4 Mössbauer spectra

Mössbauer spectra analysis of magnetite was determined using a Bench MB-500 Mössbauer spectra by WissEl (Radioactive source Co-57, Strength:  $9.25 \times 10^8$ Bga, Test temperature: room temperature 22°C) at the Geochemistry Department, Lanzhou Center of Oil and Gas Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences. About 20 mg of freshly powdered sample was gently pressed into a sample holder for 57Fe Mössbauer spectroscopy analysis. The Mössbauer spectra were acquired with a Bench MB-500 Mössbauer spectrometer using a y-ray source of 0.925 GBq 57Co/Rh at room temperature (about 290 K). The obtained spectra were fitted to the Lorentzian line-shapes using standard line-shape fitting routines. The isomer shifts (IS) were expressed with regard to the centroid of the spectrum of metallic iron foil (Ma et al., 2016).

Magnetite has a spinel structure, which has two cation sites containing vacancies; the spinel structure is stable in the case of large deviations from stoichiometry. Fe<sub>3</sub>O<sub>4</sub> has a phase transition at 120 K, and physical properties at room temperature can be very different from those at liquid nitrogen temperature; at room temperature it is magnetic, and so can easily be separated magnetically from any mineral of which it belongs. For these reasons,

Deposits	Samples	FeLa	FeLβ	FeLa/FeLβ
	G0901	1019.22	352.58	2.89
	G0902	1036.61	344.34	3.01
	G0903	1032.52	344.47	3.00
	G0904	1055.78	338.68	3.12
	G1021	1001.26	342.82	2.92
	G1022	1003.04	335.53	2.99
	G1031	958.19	315.78	3.03
Galingge	G1301	912.83	284.04	3.21
0	G1302	916.68	318 51	2.88
	G10101	1037 74	354.27	2.00
	G10102	1052.20	349.38	3.01
	G15011	1048.43	330.64	3.00
	G15012	1046.45	224.40	3.07
	G15012	1010.57	221.40	3.04
	G15021	970.96	331.40	2.93
	G15022	1018.61	349.21	2.92
	HI32BI	1035.52	356.75	2.90
	H132B2	1078.41	351.76	3.07
	H107-2	1077.21	365.73	2.95
	H0722	1027.30	335.51	3.06
No. 2 ore body	H13011	1093.65	358.40	3.05
Hutouya	H13012	928.06	343.38	2.70
	H17201	1048.75	359.28	2.92
	H17202	1080.23	348.43	3.10
	HX01	1036.37	352.46	2.94
	HX02	1016.83	358.84	2.83
	H132B1	1035.52	356.75	2.90
	H132B2	1078.41	351.76	3.07
	HT07-2	1077.21	365.73	2.95
	H0722	1027.30	335.51	3.06
No. 2 ore body	H13011	1093.65	358.40	3.05
Hutouya	H13012	928.06	343.38	2.70
	H17201	1048.75	359.28	2.92
	H17202	1080.23	348.43	3.10
	HX01	1036.37	352.46	2.94
	HX02	1016.83	358.84	2.83
	H-251	1179.12	364.32	3.24
No. 7 ore body	H-252	1210.78	367.94	3.29
Hutouya	H-253	1142.08	353.19	3.23
	H-254	1125.75	367.46	3.06
	K01011	1093.41	360.77	3.03
	K01012	1076.22	341.74	3.15
	K01021	10/4.43	355.37	3.02
Kendekeke	K01022	1062.80	34/.10	3.06
	KF0401 KE0402	949.44	329.02	2.89
	KF0402	1009.00	338.20	2.99 2.07
	KF0403	1021.31 007.68	344.40	2.97
No. 7 ore body	K01201	085.22	378.67	2.00
Kaerqueka	KQ1201	905.52	320.04	2.00
No. 18 oro hody	KQ1202	1047.70	220.52	2.70
Kaerowska	KQ/201	1009.45	339.32	3.13
кастчиска	NQ/202	1000.97	331.47	5.05

Table 2 FeLα/FeLβ ratios of magnetite from the Qimantag metallogenic belt deposits (cps)

Fe<sub>3</sub>O<sub>4</sub> seems an ideal substance for fingerprinting minerals by Mössbauer spectroscopy, since it is capable of exhibiting large variations in its physical properties.

Magnetite from the Qimantag metallogenic belt produces two sextuples in the Mössbauer spectra: one is due to Fe(III) in tetrahedral oxygen sites, and the other, in octahedral sites, is due to an average spectrum of Fe(II) and Fe(III), which are able to exchange electrons (Fig. 5). When obvious isomorphous replacement occurs in magnetite, the area of the B peak will be relatively reduced, for example in KQ072, KQ073 and KQ074 (Table 3). Mössbauer parameters show that the parameters of magnetite from Qimantag are constant, particularly the quadrupole splitting. The latter of  $Fe^{2+}$  and  $Fe^{3+}$  has values from -0.013 to 0.044 mm/s, practically without variation; the quadrupole splitting of  $Fe^{3+}$  has values from -0.033 to 0.004 mm/s. Likewise, the isomer shifts of  $Fe^{2+}$  and  $Fe^{3+}$  vary in small ranges from 0.637 to 0.661 mm/s; those of  $Fe^{3+}$  vary from 0.276 to 0.333 mm/s.

During the past five decades, Mössbauer spectroscopy has become an increasingly important analytical tool for characterization of synthetic and natural Fe-containing materials, such as soils, sediments, oxides and oxyhydroxides (Da Costa et al., 1998) Since Bauminger et al. (1961) first used Mössbauer spectroscopy to discuss magnetite, many researchers have used this method to further study magnetite (Singhvi et al., 1986; Persoons et al., 1990; Helgason et al., 1994; Peev, 1995; Peev et al., 1995; Rodriguez et al., 2007; Silva et al., 2014). The isomer shift of Mössbauer spectroscopy is particularly sensitive to the oxidation state of iron. Therefore, Mössbauer spectroscopy has become the most commonly used method to determine the oxidation state of iron. The isomer shift is determined by the density of the *s* electrons in the nucleus, but the increase or decrease of the electrons of p or d will also affect the isomer shift. For the most common valence state  $Fe^{2+}$  and  $Fe^{3+}$  in minerals, their d electron shells are  $3d^6$  and  $3d^5$ , respectively. Because the number of d electrons in the shell is different, this will affect the density of s electrons in the nucleus, so that  $Fe^{2+}$ and  $Fe^{3+}$  can have different isomer shifts. In this way, the valence state of iron can be determined according to the isomer shift. Base on the method of Da Costa (1998), the  $Fe^{2+}/Fe^{3+}$ ratios of magnetite from the Qimantag metallogenic belt (0.30-0.49) are close to 0.5 (Variance 0.00012-0.03058) and also to the results of the charge difference and surplus-oxygen methods.

#### **5** Discussion

# 5.1 Comparison of five methods to determine Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios and two types of magnetite

After calculating five different methods for determining Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios in magnetite, based on the results of variance analysis, the most accurate methods are Mössbauer spectroscopy, the charge difference method and the surplus-oxygen method. These three methods have relatively small variance results (Fig. 4), and give results of close to 0.5 and are more convergent. However, Mössbauer spectroscopy is limited in spatial resolution to ca. 200 mm, obliterating potential zonations in Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios; it is not an in situ analysis method and has defects in its scope of application. Therefore, the most reliable in situ methods are the charge difference and surplus-oxygen methods. Because of the difficulty of exact measurement of O<sub>2</sub>, the direct oxygen measurement method is inaccurate. The relationship between  $L\beta/L\alpha$  ratios and the  $Fe^{2+}/Fe^{3+}$  ratios is still uncertain, which leads to the conclusion that the flank method is also inaccurate.

Comparing texture, occurrence, and chemical composition, two types of magnetite can be distinguished: Type 1 consists of the magmatic Mag1 magnetite near the ore-related granite in the Hutouya No. 2 ore body and



Galingge

8

6

4 2 0 2 4 6

Fig. 5. The Mössbauer absorption spectrum of magnetite from the Qimantag metallogenic belt.

4

6 8 10-10

2

Velocity(mm/s)

Mag1 magnetite in the Kendekeke deposit; Type 2 is represented by Mag2 magnetite in the Kendekeke deposit and magnetite widespread in mineralized endoskarn, exoskarn ores, and vein-type ores of the other three deposits.

1

0.98

0.96

0.94

0.92

0.9

1

0.98

0.96

0.94

0.92

0.9

Absorption (%)

-10 -8

Hutouya

Kaerqueka

8

10

6 4 -2 0

Absorption (%)

Combined with the petrographic features of magnetite from the Kendekeke deposit, our research and previous work (Yi et al., 2015) show that Mag1 appears in massive ores, and the major associated mineral is pyrite, which is formed by early-stage magmatic iron fluids. Mag2 appear in disseminated ores, and the major associated mineral are galena and chalcopyrite, indicating hydrothermal fluid mineralization. EPMA results of magnetite indicate that the TiO<sub>2</sub> content of the Hutouya No. 2 ore body (Mag1) is higher than the Hutouya No. 7 ore body (Mag2). Most magnetite grains from the No. 2 ore body (Mag1) plot in the magmatic associated field in both the (MgO + MnO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> diagram and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO diagram; on the other hand, most magnetite grains from the No. 7 ore body (Mag2) plot in the hydrothermal associated field (Yi et al., 2015). Based on the spatial distribution of orebodies in Hutouya deposit, the No. 2 ore body is located in the contact zones of the Carboniferous Diaosu Group and the porphyritic monzonite granite, while the No. 7 ore body is located between the Mesoproterozoic Jixian System and the Carboniferous Dagangou Group. According to the  $Fe^{2+}/Fe^{3+}$  ratios diagram (Fig. 4), magnetite in the Hutouya No. 2 ore body and Kaerqueka No. 7 ore body (Mag1) have higher  $Fe^{2+}/Fe^{3+}$  ratios than magnetite in the Hutouya No. 7 ore body and Kaerqueka No. 18 ore body (Mag2).

Velocity(mm/s)

Raw data

 $Fe_{3}O_{4}(A)$ 

 $Fe_{3}O_{4}(B)$ 

8 10

Sum

Deposits	Samples		MgO	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO	Total	CDM	SOM	Type
No. 7 ore body	KO12	$Avg(n=8)^a$	0.95	0.07	0.25	0.15	1.00	90.00	92.41	0.462	0.462	Mag2
Kaerqueka	RQ12	stdev	0.05	0.03	0.11	0.13	0.11	1.40	1.39	0.005	0.005	111452
No. 18 ore body	KO72	Avg(n=6)	4.19	0.01	0.24	0.08	0.16	88.39	93.07	0.384	0.384	Mag2
Kaerqueka		stdev	0.21	0.01	0.06	0.15	0.03	0.77	0.67	0.006	0.006	
No. 7 ore body	H4100-25	Avg(n = 11)	0.16	0.00	0.35	0.05	0.20	87.21	87.97	0.498	0.496	Mag2
Hutouya		stdev	0.13	0.01	0.21	0.03	0.08	1.59	1.44	0.007	0.003	U
	HT09	Avg(n = 7)	0.01	0.03	0.10	0.05	0.18	92.83	93.28	0.499	0.499	Mag1
		stdev	0.01	0.04	0.12	0.03	0.06	1.15	1.17	0.001	0.001	
	HT13	Avg(n = 19)	0.03	0.02	0.37	0.36	0.25	92.13	93.15	0.503	0.503	Mag1
No. 2 ore body		stdev	0.08	0.02	0.68	0.75	0.07	2.36	1.59	0.013	0.013	
Hutouya	HT10	Avg(n = 9)	0.01	0.07	0.58	0.25	0.50	92.18	93.58	0.502	0.502	Mag1
		stdev	0.01	0.03	0.40	0.22	0.09	1.06	1.10	0.006	0.006	
	HTX	Avg(n = 14)	0.17	0.24	1.25	0.02	0.17	90.71	92.56	0.515	0.514	Mag1
		stdev	0.16	0.20	1.16	0.02	0.09	3.06	2.34	0.013	0.013	
	KD01-disse- minated	Avg $(n = 3)$	0.47	0.09	0.02	0.03	0.34	92.31	93.26	0.484	0.484	Mag2
		stdev	0.06	0.07	0.02	0.04	0.02	0.72	0.65	0.001	0.001	
	KD01- massive	Avg $(n = 6)$	1.61	2.44	2.47	0.03	0.99	86.82	94.36	0.542	0.542	Magl
		stdev	0.47	1.14	1.17	0.03	0.26	3.08	1.25	0.031	0.031	
	KD01-2	Avg(n = 6)	0.87	0.09	0.22	0.03	0.34	90.57	92.12	0.475	0.475	Mag2
		stdev	0.36	0.04	0.18	0.03	0.05	0.91	1.04	0.008	0.008	U
77 11 1	KD02	Avg(n = 8)	0.12	0.38	0.39	0.07	0.18	93.15	94.29	0.510	0.510	Mag1
Kendekeke		stdev	0.16	0.42	0.22	0.04	0.12	1.57	0.97	0.009	0.009	U
	KDF01	Avg(n = 8)	3.14	0.02	0.33	0.02	1.33	87.83	92.67	0.394	0.394	Mag2
		stdev	1.41	0.04	0.51	0.04	0.33	2.78	1.43	0.041	0.041	U
	KDF04	Avg(n = 16)	1.74	0.27	1.84	0.13	0.84	89.17	93.99	0.466	0.466	Mag2
		stdev	0.67	0.20	1.29	0.18	0.23	1.67	1.66	0.018	0.018	U
	KDF13	Avg $(n = 20)$	1.73	0.74	1.09	0.06	0.87	90.14	94.63	0.470	0.470	Mag1
		stdev	0.70	0.33	0.63	0.07	0.41	1.93	1.33	0.024	0.024	-
	KDF22	Avg(n = 6)	0.93	0.05	0.19	0.04	0.67	91.46	93.33	0.467	0.466	Mag2
		stdev	0.16	0.03	0.14	0.03	0.12	1.16	1.20	0.002	0.002	-
Galingge	ZK26005-09	Avg(n = 16)	2.07	0.06	0.11	0.02	0.15	88.08	90.50	0.441	0.440	Mag2
		stdev	0.51	0.06	0.08	0.02	0.06	1.49	1.57	0.015	0.015	
	ZK26005-10	Avg(n = 16)	2.75	0.04	1.57	0.03	0.52	87.86	92.76	0.431	0.431	Mag2
		stdev	0.74	0.03	0.59	0.02	0.09	1.45	0.75	0.019	0.019	-
	ZK26005-13	Avg(n = 10)	1.31	0.24	0.86	0.04	0.31	89.36	92.13	0.474	0.473	Mag2
		stdev	0.84	0.42	0.80	0.07	0.15	2.34	1.45	0.024	0.024	-
	ZK26005-14	Avg $(n = 13)$	2.61	0.38	0.63	0.07	0.89	85.56	90.14	0.427	0.427	Mag2
		stdev	1.52	0.31	0.69	0.11	0.23	3.37	1.60	0.034	0.034	-
	ZK26005-15	Avg(n = 18)	2.76	0.02	0.51	0.07	0.60	88.28	92.24	0.418	0.418	Mag2
		stdev	1.42	0.02	0.26	0.09	0.13	2.27	1.06	0.039	0.039	-

Table 3 EPMA results for  $Fe^{2+}/Fe^{3+}$  of the charge difference method and the surplus-oxygen method (in wt%)

Abbreviation: Avg = average, stdev = standard deviation.<sup>a</sup> Numbers in parenthesis represent the number of analyzed spots. CDM, Charge difference method; SOM, Surplus-oxygen method.

## 5.2 Probable precipitation mechanisms of oxidized and reduced mineral sequences

Reasons for the decrease of Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios from Mag1 to Mag2 are related to the mutual replacement of hematite and magnetite. An oxidized mineral association is found in most of the IOCG (Iron Oxide-Copper-Gold Deposits) deposits in the Andes, and the replacement of hematite by magnetite records a drop in the redox state of the fluid (Marschik and Fontboté, 2001). Interestingly, the same sequence is also widely documented in skarns (e.g., Boni et al., 1990; Dünkel, 2002; Ciobanu and Cook, 2004; Prendergast et al., 2005) and in some porphyry copper deposits, all of which are notoriously of magmatic hydrothermal origin (e.g., Frikken et al., 2005).

Magnetite pseudomorphous after hematite or hematite pseudomorphous after magnetite is controlled by the redox reaction:

$$3Fe_2O_3(hm) + H_2(aq) = 2Fe_3O_4(mt) + H_2O,$$
 (1)

which is equivalent to

$$2Fe_3O_4(mt) + 1/2O_2(aq) = 3Fe_2O_3(hm).$$
 (2)

As already pointed out by Giggenbach (1987), the second reaction is conceptually correct but has no meaning in terms of real reactions because fluids near the hematite–magnetite stability boundary at temperatures less than 500°C contain virtually no  $O_2$ . The hematite–magnetite pairing therefore relates to the H<sub>2</sub> content of the fluid, as in Reaction (1). Ohmoto (2003) and Otake et al. (2007). Proposed a non-redox mechanism for the transformation of magnetite and hematite in hydrothermal systems based on the following Reactions:

$$Fe_2O_3(hm) + Fe^{2+} + H_2O = Fe_3O_4(mt) + 2H^+, \quad (3)$$
  

$$Fe_3O_4(mt) + 2H^+ = Fe_2O_3(hm) + Fe^{2+} + H_2O. \quad (4)$$

Reaction (3) can realize the transformation from hematite to magnetite simply by adding  $Fe^{2+}$  to the solution, and Reaction (4) can realize the transformation from magnetite to hematite by leaching  $Fe^{2+}$ . Since there is no change in the valence of Fe in Reactions (3) and (4), it is called a non-redox reaction.

In the main deposits of the Qimantag metallogenic belt, the early magnetite deposits are located in intrusions or

 Table 4 Mössbauer parameters of magnetite from the Qimantag metallogenic belt

Deposits Sample ID Iron species $\frac{\text{Relative}}{\text{content}} = \frac{\text{IS}}{(\%)} = \frac{\text{QS}}{(\text{mm/s})} = \frac{\text{HW}}{(\text{mm/s})} = \frac{\text{HW}}{(\text{mm/s})} = \frac{\text{Fe}^{2+}}{(\text{mm/s})}$	/Fe <sup>3+</sup>
$\frac{1}{10000000000000000000000000000000000$	i/T         B/A $Fe^{2+}/Fe^{3+}$ ratios $\pm 0.03$ 1.32         0.40 $\pm 0.02$ 0.85         0.30 $\pm 0.02$ 0.86         0.30 $\pm 0.02$ 0.86         0.30 $\pm 0.02$ 0.96         0.32 $\pm 0.01$ 1.91         0.49 $\pm 0.01$ 1.96         0.49 $\pm 0.01$ 1.96         0.49 $\pm 0.02$ 1.9         0.49 $\pm 0.01$ 1.33         0.40 $\pm 0.01$ 1.66         0.45 $\pm 0.01$ 1.66         0.44 $\pm 0.01$ 1.66         0.44 $\pm 0.01$ 1.67         0.44 $\pm 0.01$ 1.83         0.48
$KQ071 \qquad \text{mag} = \frac{1}{100} \left( \frac{1}{100} + \frac{1}{100} $	
$\max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.304 \pm 0.002 \qquad 0.004 \pm 0.004 \qquad 0.224 \pm 0.004 \qquad 40.22 \pm 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.304 \pm 0.002 \qquad 0.004 \pm 0.004 \qquad 0.221 \pm 0.004 \qquad 40.22 \pm 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.304 \pm 0.002 \qquad 0.004 \pm 0.004 \qquad 0.221 \pm 0.004 \qquad 40.22 \pm 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.304 \pm 0.002 \qquad 0.004 \pm 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.002 = 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.002 \pm 0.002 \qquad 0.004 \pm 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.002 \pm 0.002 \qquad 0.002 \pm 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.002 \pm 0.002 \qquad 0.004 \pm 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.002 \pm 0.002 \qquad 0.002 \pm 0.002 \qquad 0.002 \pm 0.004 \qquad 0.002 \pm 0.002 \qquad 0.002 \pm 0.002 = 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.002 \pm 0.002 \qquad 0.004 = 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.002 \pm 0.002 = 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.002 \pm 0.002 \qquad 0.004 = 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.002 \pm 0.002 = 0.002 \\ \max_{n=0} F_{n=0}^{2^{n+1}}(\Lambda) = 54.2 \qquad 0.002 \pm 0.002 \qquad 0.004 = 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.004 \qquad 0.002 \pm 0.002 \qquad 0.002 = 0.002 \qquad 0.002 $	
No. 18 ore KQ072 mag $E_{2}^{-2}(E_{3}^{-3}+R)$ 45.8 0.641 + 0.004 0.008 + 0.007 0.240 + 0.006 45.72 + 0.04 0.85 0.2	
body $m_{22} = c_{1}^{2+}(A) = 52.6$ $0.232 \pm 0.004 \pm 0.004 \pm 0.007 = 0.242 \pm 0.005 \pm 0.005 \pm 0.004 \pm 0.004$	
Kaerqueka KQ073 $\max_{\alpha} E_{\alpha}^{-2+} E_{\alpha}^{-3+}(D)$ 46.28 $0.635 \pm 0.003 = 0.004 \pm 0.003$ $0.225 \pm 0.003 = 47.505 \pm 0.002$ $0.86$ $0.505 \pm 0.002$ $0.250 \pm 0.007$ $0.577 \pm 0.02$ $0.86$ $0.575 \pm 0.002$ $0.56$	0.30 0.32
$\lim_{m \to \infty} \sum_{i=1}^{m} (A_i) = 51 + 5 = 0.236 \pm 0.004 \pm 0.004 \pm 0.004 \pm 0.007 \pm 0.007 \pm 0.077 \pm 0.02$	
KQ074-A $mag = re (A)$ 51.15 0.226 ± 0.004 = 0.014 ± 0.005 0.206 ± 0.004 49.5/ ± 0.02 0.96 0.57	
mag-re re (B) $48.85$ $0.057 \pm 0.004$ $0.014 \pm 0.007$ $0.238 \pm 0.005$ $45.84 \pm 0.04$	
HT10-2 mag Fe <sup>+</sup> (A) 34.39 $0.278 \pm 0.001 - 0.004 \pm 0.001 0.127 \pm 0.002 49.19 \pm 0.01 1.91 0.64$	0.49
No 2 ore mag- Fe <sup>2+</sup> Fe <sup>2+</sup> (B) 65.61 $0.649 \pm 0.001 - 0.010 \pm 0.002 0.175 \pm 0.003 45.91 \pm 0.01$	
bdy HT13-1 mag- Fe <sup>3</sup> (A) 33.83 $0.276 \pm 0.001 - 0.019 \pm 0.002 0.123 \pm 0.003 49.29 \pm 0.02$ 1.96 0.4	0.49
$ \begin{array}{c} \text{out} y \\ \text{Hubburg} \end{array} \qquad \text{mag-} \ \mathrm{Fe}^{2+} \mathrm{Fe}^{3+} (\mathrm{B}) \qquad 66.17 \qquad 0.658 \pm 0.001 \qquad 0.015 \pm 0.003 \qquad 0.181 \pm 0.003 \qquad 45.93 \pm 0.01 \qquad 1.70 \qquad 0.181 \pm 0.003 \qquad 0.003$	
$mag-Fe^{3+}(A = 34.52 = 0.278 \pm 0.004 = -0.016 \pm 0.008 = 0.149 \pm 0.006 = 49.21 \pm 0.03 = 10 = 0.043 \pm 0.006 = 0.016 \pm 0.008 =$	0.49
$mag-Fe^{2+}Fe^{3+}(B) \qquad 65.48 \qquad 0.656 \pm 0.004 \qquad -0.013 \pm 0.005 \qquad 0.210 \pm 0.006 \qquad 45.85 \pm 0.02 \qquad 1.9 \qquad 0.966 $	
mag-Fe <sup>3+</sup> (A) 38.61 $0.298 \pm 0.002 - 0.033 \pm 0.014 - 0.162 \pm 0.007 - 49.19 \pm 0.01 + 22 = 0.01$	0.40
KD001 mag- $Fe^{2+}$ · $Fe^{3+}(B)$ 51.39 0.658 ± 0.002 0.025 ± 0.002 0.214 ± 0.004 45.84 ± 0.01 1.33 0.425	
mag-Fe <sup>3+</sup> (A) 37.63 $0.303 \pm 0.002 - 0.015 \pm 0.003 0.159 \pm 0.002 49.21 \pm 0.01$	0.45
Kendekeke KDF06 mag- $Fe^{2+}Fe^{3+}(B)$ 62.37 0.649 ± 0.001 0.033 ± 0.003 0.233 ± 0.003 45.78 ± 0.01 1.66 0.4	
mag-Fe <sup>3+</sup> (A) 38 43 $0.290 \pm 0.001 - 0.016 \pm 0.002 0.151 \pm 0.002 49.15 \pm 0.01$	0.44
KDF07 $mag - Fe^{2+} \cdot Fe^{3+}(B)$ 61 57 0 656 ± 0.001 0.021 ± 0.003 0.211 ± 0.002 45.81 ± 0.01 1.6 0.4	
$\max_{a} = Fe^{3+}(A) \qquad 39.18 \qquad 0.291 + 0.001 = -0.012 + 0.002 \qquad 0.159 + 0.005 \qquad 49.29 + 0.05$	
ZK26005-10 mag. $E_{2}^{-2}$ , $E_{3}^{-3+}$ (B) 60.82 0.652 + 0.001 0.012 + 0.003 0.195 + 0.005 45.83 + 0.01 1.55 0.4	0.44
Galingge $a_{1,2} = a_{1,2} = a_{1,$	0.48
ZK26005-13 mag $12^{-2}$ (A) 53.50 0.607 0.007 0.024 0.002 0.157 0.002 4.7.52 0.01 1.83 0.4	
$\lim_{n \to \infty} \frac{1}{10} \int \frac{1}{10} \int$	

Abbreviation: IS-Isomer shift; QS-Quadruple splitting; HW-Half-width. Despectral software: WinNoroms-for-Igor.

contact zones and formed from magmatic fluids with high  $Fe^{2+}/Fe^{3+}$  ratios, whereas the late magnetite deposits are far away from intrusions and have low  $Fe^{2+}/Fe^{3+}$  ratios. Whether the reason for this special phenomenon is the redox reaction or the non-redox reaction in the mutual transformation of magnetite and hematite is still unclear. Our research holds that all ore veins are produced at similar altitudes and not far from the surface weathered layer, so there should be no great difference in the degree of leaching. In addition, more importantly, according to the water repellent mineral chlorite found in the Kalqueka deposit (Yi et al., 2017), combined with the study of paleogeography in this area, and except for a few humid periods, the Qimantag area has been in a condition of extreme drought and little rain for a long time, especially with the uplift of the Oinghai Tibet Plateau, which has exacerbated the arid climate in this region, and so there should have been no massive leaching. Although this reaction is valid at the redox boundary between the fields of hematite and magnetite, its extension to higher or lower redox conditions (i.e., in the fields of hematite or magnetite stability) would imply metastable transformations not documented in natural mineral assemblages. Additionally, Mücke and Cabral (2005) pointed out that a non-redox magnetite-hematite transformation implies important volume changes (>30%). In contrast, the redox transformation of hematite and magnetite (Reaction 1) implies that the volume change is less than 2 percent. Since there is no evidence of great changes of volume in the Qimantag metallogenic belt, such as pore filling structure or shrinkage fissures, the reaction between magnetite and hematite should be redox. This may indicate that the skarn hydrothermal solution forming the veins in the surrounding rock had a high oxygen fugacity.

### **6** Conclusions

In conclusion, massive magnetite ores (Mag1) are located near intrusions or contact zones, and were formed from magmatic fluids with high  $Fe^{2+}/Fe^{3+}$  ratios. Disseminated-scattered magnetite ores (Mag2) are far away from intrusions, formed from hydrothermal fluids that have low  $Fe^{2+}/Fe^{3+}$  ratios. These features indicate a magmatism-hydrothermalism process of magnetite in origin from intrusions to layers of the Qimantag metallogenic belt deposits.

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#### About the first and corresponding author



YI Liwen, male; born in 1988 in Hunan; Ph.D. in Geology; associate professor of Hunan Normal University; mainly engaged in genetic mineralogy and deposit geochemistry research; E-mail: yilw@ hunnu.edu.cn.