Redox reactions control Cu and Fe isotope fractionation in a magmatic Ni–Cu mineralization system

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Received 12 January 2018; accepted in revised form 27 December 2018; Available online 8 January 2019

Abstract

Copper and Fe are redox-sensitive metals, and their isotopic compositions may potentially record changes of oxidation conditions in high-temperature magmatic Ni–Cu mineralization systems. High-precision Cu and Fe isotope data for sulfides (chalcopyrite) and whole-rock samples of the Tulaergen magmatic Ni–Cu system (NW China) were analyzed to evaluate redox-induced fractionation during segregation of sulfide melt from silicate melt and internal fractionation within segregated sulfide melt. Sulfide mineralization includes disseminated and massive types, with massive sulfides being further divided into Cu- and Fe-rich ores. Numerical modeling using mass-balance and Rayleigh equations indicate that disseminated sulfide mineralization was generated from a common parental magma, and massive sulfides were formed by monosulfide solid-solution (MSS)–residual sulfide liquid fractionation. During segregation of sulfide melt from silicate melt, crystallization of olivine and pyroxenes with sulfide segregation, in an Fe2+-dominated phase, led to the incorporation of lighter Fe isotopes in these minerals. The residual silicate melt became progressively more oxidized, with δ56Fe whole-rock values increasing as melts evolved. The disseminated chalcopyrite formed in early stages has lighter Cu and heavier Fe isotopic compositions than the disseminated sulfides formed in later stages due to charge-balance effects. Minor accumulated Ni–Cu sulfide melt was fractionated into an Fe-rich MSS cumulate and a Cu-rich sulfide liquid. MSS crystallization caused the oxygen fugacity of the evolved sulfide liquid to increase, which was accompanied by increasing δ65Cu and decreasing δ56Fe values in chalcopyrite. Iron isotopic compositions of the whole system were shifted towards heavier values from MSS cumulate to the evolved sulfide melt. Numerical modeling using the Rayleigh equation indicates that the fractionation factors α65Cu residual sulfide melt–MSS and α56Fe residual sulfide melt–MSS are ~1.0011 and ~1.0005, respectively, during internal fractionation within segregated sulfide melt. This study demonstrates that redox reactions play a key role in Cu and Fe isotope fractionation in high-temperature magmatic Ni–Cu mineralization systems. Furthermore, Cu and Fe isotopes can be used to trace concealed orebodies. Elevated δ65Cu and δ56Fe whole-rock values may indicate Cu-rich mineralization potential, while light Cu and Fe isotopic compositions imply favorable hosts for disseminated and Fe-rich orebodies in mafic–ultramafic intrusions.

Keywords: Copper and Fe isotope fractionation; Redox reactions; Magmatic Ni–Cu mineralization system; Tulaergen deposit

1. INTRODUCTION

Redox reactions occur in various geological processes, with some being recorded by Cu and Fe isotopic compo-
ations due to their redox-sensitive affinities. For example, Fe isotopes have been applied to tracing Archean and Paleoproterozoic ocean oxidation states (Rouxel et al., 2005), biogeochemical cycling (Johnson et al., 2008), mantle oxidation states (Williams et al., 2004), mantle melting (Weyer, 2008), magma oxidation conditions (Teng et al., 2008; Sossi et al., 2012; Dauphas et al., 2014), and continental weathering (Thompson et al., 2007; Fernandez and Borrok, 2009; Liu et al., 2014a). Copper isotope fractionation has been widely observed due to continental weathering (Fernandez and Borrok, 2009; Mathur et al., 2012; Liu et al., 2014a; Lv et al., 2016), supergene leaching (Mathur et al., 2005), and segregation of sulfide melt from silicate melt (Zhao et al., 2017).

Mantle melting and crystallization of basaltic magma cause no detectable Cu isotope fractionation (Liu et al., 2015; Savage et al., 2015; Huang et al., 2016). Iron isotope behavior at high temperatures seems to be more complex than that of Cu due to multiple Fe-bearing phases. Mantle partial melting generates limited Fe isotope fractionation in basaltic magma (~0.1‰ for δ56Fe; Dauphas et al., 2017). Measurable Fe isotope fractionation has been observed during basaltic magma differentiation (~0.15‰ for δ56Fe; Teng et al., 2008; Sossi et al., 2012; Dauphas et al., 2014, 2017). Experimental (Shahar et al., 2008) and theoretical (Mineev et al., 2007; Polyakov et al., 2007) considerations indicate measurable redox-related Fe isotope fractionation between fayalite and magnetite at magmatic temperatures. Schuessler et al. (2007) conducted an experimental study of pyrrhotite and silicate melt under magmatic conditions and found that the Fe oxidation state is highly correlated with the magnitude of Fe isotope fractionation. It seems that electron transfer under high-temperature magmatic conditions may contribute to Fe isotopic variations.

The formation of magmatic Ni–Cu deposits commonly involves large volumes of magma in dynamic systems (Barnes and Lightfoot, 2005). Oxygen fugacity is a key parameter controlling the petrogenesis of mafic–ultramafic rocks and their associated sulfide mineralization (Mao et al., 2017). Magmatic Ni–Cu mineralization systems generally experience two processes: immiscible segregation of sulfide melt from silicate melt and internal fractionation within segregated sulfide melts (Barnes and Lightfoot, 2005; Naldrett, 2010). The oxidation state of the whole system is hypothesized to have changed in these processes (Naldrett et al., 2000; Wohlgemuth-Uebewasser et al., 2013; Zhao et al., 2017). The factors contributing to Cu and Fe isotope fractionation in magmatic Ni–Cu systems are still a matter of debate. For example, the large Cu isotopic variations (~2‰ for δ65Cu) in magmatic Ni–Cu mineralization systems (Malitch et al., 2014; Ripley et al., 2015; Zhao et al., 2017) have been attributed to multiple mantle sources, different magmatic processes, crustal contamination, and/or redox reactions. In contrast, Fe isotopic compositions in magmatic Ni–Cu sulfide deposits have a narrow range (~0.6‰ for δ56Fe; Fiorentini et al., 2012; Hiebert et al., 2013) as a result of magmatic processes. Copper and Fe isotopic variations observed in magmatic Ni–Cu systems may therefore result from multiple geological processes, and isotopic systematics may fingerprint the role of each process in magmatic Ni–Cu mineralization systems. In addition, the comparison of Cu and Fe isotopic compositions of sulfide mineralization formed in different oxidation states may directly indicate the degree of redox-induced fractionation.

This study focuses on the Tulaergen magmatic Ni–Cu mineralization system, NW China. We present new platinum-group element (PGE) data for the Tulaergen intrusion to constrain mineralization processes. Redox-induced Cu and Fe isotope fractionation during segregation of sulfide melt from silicate melt and internal fractionation within segregated sulfide melt are also discussed. In addition, fractionation factors (δ65Cu residual sulfide melt–MSS and δ56Fe residual sulfide melt–MSS; MSS = monosulfide solid-solution; see Section 5.3) are calculated using the Rayleigh equation. These results demonstrate that Cu and Fe isotope fractionation is primarily controlled by redox reactions in magmatic Ni–Cu mineralization systems, and has implications for tracing concealed orebodies.

2. GEOLOGICAL BACKGROUND AND SAMPLE DESCRIPTIONS

The Central Asian Orogenic Belt (CAOB) is one of the longest and largest accretionary orogenic belts on Earth, extending for more than 5000 km between the Siberian, North China and Tarim cratons (Fig. 1a; Zonenshain et al., 1990; Sengör et al., 1993). The Tianshan Orogenic Belt, in the southernmost part of the CAOB, is separated from the Tarim Craton and Beishan terrane in the south by the North Tarim and Xingxingxia faults, respectively (Fig. 1b). The Tianshan Orogenic Belt can be divided into the North, Middle, and South Tianshan terranes from north to south (Fig. 1b). The North Tianshan terrane is separated from the Middle Tianshan terrane by the Shaquanzi fault (Fig. 1c). The Middle Tianshan terrane comprises mainly Precambrian basement complexes, while the North Tianshan terrane contains abundant Paleozoic volcanic and sedimentary rocks (Gao et al., 2013). The Tulaergen intrusions were emplaced along the eastern part of the North Tianshan terrane (Fig. 1b, c). The NE-trending Kangguer–Huangshan shear zone in the North Tianshan terrane was the dominant conduit for sulfide-bearing mafic–ultramafic intrusions (Qin et al., 2006; Yannick et al., 2012; Zhao et al., 2018), which occur as small NE-oriented sills or dikes (Fig. 1c; Mao et al., 2008).

The Tulaergen deposit contains 120,000 tonnes (t) of Ni and 100,000 t of Cu with average grades of 0.6 and 0.4 wt. %, respectively (San et al., 2007, 2010; Liu et al., 2012), hosted by Carboniferous strata composed of dacitic or andesitic breccia tuff and flaggy tuffaceous sandstone (Fig. 1d). The Tulaergen intrusion can be divided into four lithofacies: hornblende lherzolite, hornblende olivine websterite, hornblende websterite, and hornblende gabbro. Adjacent lithofacies have gradational relationships. Sulfide mineralization in the Tulaergen deposit includes disseminated (1–30 wt.% sulfide; Fig. 2a, c) and massive ores (generally > 50 wt.% sulfide; Fig. 2a, b, d, e). Massive sulfides can be further divided into Fe-rich (Fig. 2a, d) and
Cu-rich (Fig. 2b, e) types. The Fe-rich massive orebodies occur as dikes between disseminated sulfide and country rocks (Fig. 2a), while Cu-rich massive orebodies were emplaced into country rocks (Fig. 2b). The disseminated sulfide ores comprise pyrrhotite, pentlandite and chalcopyrite with minor violarite, Ni-cobaltite and Co-gersdorffite. Iron-rich massive sulfides consist of pyrrhotite, pentlandite, and minor chalcopyrite (Fig. 2f), while Cu-rich sulfides contain large amounts of chalcopyrite with minor pentlandite and pyrrhotite (Fig. 2g).

The samples for this study, including disseminated and massive sulfides, were collected from underground adits in the Tulaergen magmatic Ni–Cu mineralization system (Table 1). The disseminated sulfides hosted by hornblende lherzolite, hornblende olivine websterite, hornblende websterite, and hornblende gabbro were collected from the 1100 m, 1148 m, and 1170 m levels. In each adit, more than two samples were collected in order to obtain representative coverage of the mineralized part of the Tulaergen intrusion. These disseminated samples contain >6 wt.% sulfide, which ensures that chalcopyrite is included. The Fe-rich massive samples were collected from the 1058 m and 1100 m levels, with >70 wt.% sulfide. The Cu-rich massive samples were collected from the 1058 m level, containing >85 wt.% sulfide.

Fig. 1. (a) Major tectonic units of the Central Asian Orogenic Belt (modified from Jahn, 2004). (b) Ni–Cu deposits associated with mafic–ultramafic intrusions in the Tianshan terrane (modified from Sun et al., 2013). (c) Simplified geological map of the Tulaergen intrusion (modified from San et al., 2007).
3. METHODS

3.1. PGE, Cu, Ni, and S analyses

Whole-rock chalcophile element (PGE, Cu, and Ni) compositions and S contents of sulfide ores were determined at the National Research Center of Geoanalysis, Beijing, China. Copper and Ni contents were determined by digestion of samples in HF + HNO$_3$ in steel-jacketed Teflon bombs, followed by analysis using a Finnigan MAT ELEMENT high-resolution inductively coupled plasma mass spectrometry (ICP-MS), using the methods of Balaram et al. (1995) and Wu et al. (1996). Reproducibility was estimated to be better than 2–10% in terms of
Table 1
Chalcophile elements (PGE, Cu, and Ni) and S contents of whole-rock samples from the Tulaergen deposit.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Mineralization types</th>
<th>Elevation (m)</th>
<th>Pt (ppb)</th>
<th>Pd (ppb)</th>
<th>Os (ppb)</th>
<th>Ir (ppb)</th>
<th>Ru (ppb)</th>
<th>Rh (ppb)</th>
<th>Cu (ppm)</th>
<th>Ni (ppm)</th>
<th>S (wt.%)</th>
</tr>
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<td>2T-3</td>
<td>Disseminated</td>
<td>1148</td>
<td>11.6</td>
<td>14.1</td>
<td>0.22</td>
<td>0.14</td>
<td>0.13</td>
<td>0.27</td>
<td>3210</td>
<td>3293</td>
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</tr>
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<td>5094</td>
<td>10,748</td>
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<td>46,220</td>
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<td>35,390</td>
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<td>37,930</td>
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<td>14,505</td>
<td>42,110</td>
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<td>204</td>
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<td>0.13</td>
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<td>0.63</td>
<td>23.1</td>
<td>302,000</td>
<td>5408</td>
<td>34.25</td>
</tr>
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</table>

* Data from Zhao et al. (2017).
relative standard deviation (RSD), and the accuracy was better than ±10%. Whole-rock S contents were determined using a high-frequency infrared carbon sulfur analyzer (HIR 944) following the established methods of Yu et al. (2016). Detection limits of S content analysis are 0.005 wt.%, and the reproducibility and accuracy of S content analysis was estimated to be better than 10% RSD and ±5%, respectively. PGE contents were determined by nickel sulfide fire assay and Te co-precipitation followed by ICP-MS, using a method similar to that of Asif and Parry (1991). Accuracy as demonstrated by analysis of reference materials (UMT-1 and WPR-1) was better than ±10%, and the reproducibility was estimated to be better than 10% RSD.

3.2. Cu isotopes

Sulfide ores were crushed to minus-80-mesh, from which chalcopyrite was separated using conventional heavy liquid techniques, and then hand-picked under a binocular microscope. Sample digestion, column chemistry, and instrumental analysis followed established methods (Liu et al., 2014a, 2014b, 2015; Li et al., 2015) modified from Maréchal et al. (1999), and as summarized here.

About 1 mg of chalcopyrite separates and 25 mg of basalt standard BHVO-2 (US Geological Survey) were digested in double-distilled HF + HNO3 + HCl. After complete dissolution, 1 mL of 8 N HCl + 0.001% H2O2 was added and then heated to dryness at 80 °C. This process was repeated three times to ensure that all cations were converted to chloride species prior to ion-exchange separation. The purity of chalcopyrite separates was assessed by determining the Cu/Fe ratios of solutions analyzed for Cu isotopes. The sample solution was loaded onto AG-MP-1M ion exchange resin as described by Liu et al. (2014a,b), to separate Cu from the matrix. The Cu eluate was evaporated and re-dissolved as above, and passed through a second column of the same resin for further purification. Copper recovery was >99.7%, and total Cu procedural blank was <2 ng. Copper fractions were evaporated to dryness and re-dissolved in 3% HNO3 twice to remove all Cl− before isotope analysis.

Copper isotopic ratios were determined using a Thermo Scientific Neptune plus multi-collector ICP-MS instrument (MC–ICP–MS) at the Isotope Geochemistry Laboratory, China University of Geosciences, Beijing, China. The standard–sample bracketing method was used to correct for instrumental mass fractionation (Zhu et al., 2002). For each measurement, data were collected in two blocks of 40 cycles with ~8 s integration. Copper isotopic data are reported in standard per mil (δ) notation relative to the standard reference material NIST 976:

\[
\delta^{65}\text{Cu} = \left( \frac{^{65}\text{Cu}}{^{63}\text{Cu}} \right)_{\text{sample}} / \left( \frac{^{65}\text{Cu}}{^{63}\text{Cu}} \right)_{\text{NIST976}} \times 1000
\]

Long-term external reproducibility for δ65Cu determinations was better than ±0.05‰ (2SD), based on repeated analyses of natural samples and synthetic solutions (Liu et al., 2014a,b). In our analytical session, standard BHVO-2 yielded δ65Cu = 0.12 ± 0.05‰ (2SD), which is within the published ranges for this standard (e.g., δ65Cu = 0.10 ± 0.10‰; Weinstein et al., 2011; δ65Cu = 0.15 ± 0.05‰; Liu et al., 2014a,b). The Cu/Fe ratios of chalcopyrite separates were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), with an analytical precision better than ±5% at element concentrations of >0.1 mg L−1.

3.3. Fe isotopes

Whole-rock Fe isotope measurements were conducted at the China University of Geosciences, Beijing, China, and chalcopyrite Fe isotopic compositions were analyzed at Pennsylvania State University, USA. Procedures for sample dissolution, column chemistry, and mass spectrometry were as described by Dauphas et al. (2009), He et al. (2015), and Yesavage et al. (2016), and as summarized here.

Fresh, unaltered, and mineralized rock and chalcopyrite samples were crushed and milled to produce a powder for Fe isotope analysis. Whole-rock sample (1–5 mg) and peridotite standard JP-1 (20 mg) powders were dissolved in double-distilled HF + HNO3 + HCl, and chalcopyrite powder in aqua regia. After dissolution, the solutions were evaporated to dryness and converted to chloride form. Iron was purified using AG1X-8 resin in HCl media for rocks, and AGMP-1 resin for chalcopyrite. Column procedures were performed twice to ensure complete matrix elimination. The final Fe eluate was acidified with 100 μL of concentrated HNO3, re-evaporated to dryness, and re-dissolved in 3% HNO3 to remove all Cl− before isotope determination. The total procedural Fe blank was <10 ng, or <0.01% of the sample Fe.

Whole-rock and chalcopyrite Fe isotopic compositions were determined using Thermo Scientific Neptune plus and Neptune MC–ICP–MS instruments, respectively. Whole-rock Fe isotope analyses were performed in high-resolution mode, with a standard–sample bracketing approach (Dauphas et al., 2009; He et al., 2015). Analytical conditions for chalcopyrite were as described by Yesavage et al. (2016). Samples were introduced using a quartz dual cyclonic spray chamber and 50 or 100 μL/min nebulizer flow rate. The instrument was operated at 1200 W power, with standard Cu-cored Ni cones, and in high-resolution mode. Instrumental mass fractionation was corrected by standard–sample bracketing.

The Fe isotopic compositions are expressed in the usual per mil (δ) notation, relative to the reference material IRMM-014:

\[
\delta^{56}\text{Fe} = \left( \frac{^{56}\text{Fe}}{^{54}\text{Fe}_{\text{sample}}} \right) / \left( \frac{^{56}\text{Fe}}{^{54}\text{Fe}_{\text{IRMM-014}}} \right) - 1 \times 1000
\]

The long-term external reproducibility of δ56Fe determinations was better than ±0.03‰ (2SD), based on repeated analyses of natural samples and synthetic solutions. Peridotite standard JP-1 (analyzed at the China University of Geosciences, Beijing) yielded δ56Fe = 0.00 ± 0.04‰ (2SD), which is within the published range for this standard (e.g., δ56Fe = 0.006 ± 0.011‰; He et al., 2015). Two internal standards were analyzed at Pennsylvania State Univer-
sity: HPS-UW yielded $\delta^{65}$Fe = 0.57 ± 0.04‰ and NIST SRM-312a yielded $\delta^{56}$Fe = 0.35 ± 0.04‰. Both values are within published ranges for these standards (e.g., Beard et al., 2003; Yesavage et al., 2016).

4. RESULTS

Whole-rock chalcophile element (PGE, Cu, and Ni) compositions and S contents, and chalcopyrite and whole-rock Cu and Fe isotopic compositions, are given in Tables 1 and 2.

All disseminated samples have similar IPGE (Ir-group: Os, Ir, and Ru) and PPGE (Pt-group: Rh, Pt, and Pd) contents (Fig. 3). Iron-rich massive sulfides are characterized by higher Cu and Ni and more variable PGE contents than disseminated sulfide ores. Copper-rich massive sulfides have high Cu contents, with depletion in IPGEs and enrichment in PPGEs relative to the Fe-rich massive and disseminated sulfide ores, except for Pt depletion in some massive sulfides (Fig. 3). Iron-rich massive and disseminated sulfide ores have similar PGE, Ni, and Cu tenors (in 100% sulfides) (Fig. 3). Copper-rich massive sulfides have low Ir and Ni tenors and high Cu and Rh tenors (Fig. 3).

The Cu/Fe ratios of chalcopyrite samples in the Tulaergen deposit show a restricted range from 0.96 to 1.16, consistent with the Cu/Fe ratio of stromatolitic chalcopyrite (~1). The $\delta^{65}$Cu values have an overall range from −0.83‰ to +0.53‰, and the $\delta^{56}$Fe values of chalcopyrite and whole-rock samples vary from +0.35‰ to +1.31‰ and −0.20‰ to +0.38‰, respectively. Chalcopyrite in disseminated sulfides has $\delta^{65}$Cu and $\delta^{56}$Fe values of −0.83‰ to +0.04‰ and +0.35‰ to +0.92‰, respectively (Fig. 4), with whole-rock $\delta^{56}$Fe values of −0.20‰ to +0.27‰. Chalcopyrite in Cu-rich massive sulfides has a relatively narrow range of $\delta^{65}$Cu values from +0.48‰ to +0.53‰, and $\delta^{56}$Fe values are from +0.77‰ to +1.37‰. Whole-rock $\delta^{56}$Fe values of Cu-rich massive sulfides have a narrow range from +0.28‰ to +0.38‰ (Fig. 4). In Fe-rich massive ores, $\delta^{65}$Cu and $\delta^{56}$Fe values of chalcopyrite vary from −0.26‰ to −0.53‰ and +1.25‰ to +1.29‰, respectively. Whole-rock $\delta^{56}$Fe values of Fe-rich massive ores have a relatively narrow range of +0.04‰ to +0.15‰ (Fig. 4).

5. DISCUSSION

5.1. Mineralization processes in the Tulaergen system

The formation of magmatic Ni–Cu mineralization systems commonly involves two processes: (1) immiscible segregation of sulfide melt from silicate melt; and (2) internal fractionation within segregated immiscible sulfide melts (Barnes and Lightfoot, 2005; Naldrett, 2010). In process (1), sulfide droplets segregated from parental magma accumulate in a limited space to form disseminated sulfides. In some cases, the accumulated sulfide liquid may fractionate into an Fe-rich monosulfide solid-solution (MSS) cumulate and a Cu-rich sulfide liquid (Barnes and Lightfoot, 2005). In process (2), internal fractionation within segregated sulfide melt leads to the concentration of compatible elements (Os, Ir, Ru, and Rh) in the MSS cumulate. In contrast, Cu, Pt, Pd, and Au are incompatible in the MSS and concentrate in the Cu-rich sulfide liquid (Li et al., 1996; Barnes and Lightfoot, 2005; Naldrett, 2010, 2011). In most deposits, sulfide liquids exhibit a combination of fractional and equilibrium crystallization, depending on whether the fractionated liquid can escape from the accumulating MSS (Naldrett, 2010). In the Tulaergen deposit, massive sulfides have more variable Cu, Ni, and PGE tenors than disseminated sulfide mineralization. In detail, Cu-rich sulfides show relatively high Cu and Pd and low Ir and Ni tenors, and disseminated sulfides exhibit low Cu and Pd and high Ir and Ni tenors (Fig. 3). Iron-rich massive sulfide ores have the lowest Pd tenors, but their Ir, Cu, and Ni tenors are similar to those of disseminated ores (Fig. 3).

The mass–balance equation of Campbell and Naldrett (1979) was used to simulate segregation of sulfide melt from silicate melt (Fig. 5), and the Rayleigh equation (Neumann et al., 1954) was used to model internal fractionation within segregated sulfide melts. Modeling results indicate that Ir and Pd tenors of disseminated sulfide ores may be accounted for by a parental magma containing ~0.003 ppb Ir and ~0.25 ppb Pd, with R factors (mass ratio of silicate-to-sulfide-melts; Campbell and Naldrett, 1979) from ~500 to ~1000. The formation of massive sulfide ores has experienced fractionation between the MSS and residual sulfide liquid (forming Fe- and Cu-rich massive ores, respectively; Figs. 5–7). The Ir and Pd contents of the Tulaergen mineralization system are similar to those of high-Mg basaltic parental magmas of the Hunagshannan (herzolite ~0.02 ppb Ir and ~0.4 ppb Pd; websterite ~0.009 ppb Ir and ~0.75 ppb Pd; Zhao et al., 2016a), Huangshandong (~0.01 ppb Ir and ~0.1 ppb Pd; Sun et al., 2013), and Hulu (~0.08 ppb Ir and ~0.4 ppb Pd; Zhao et al., 2016b) deposits in the North Tianshan terrane (Fig. 1b), but much lower than those in the parental magma of the Jinchuan deposit (~0.36 ppb Ir and ~2.9 ppb Pd; Chen et al., 2013). To summarize, the Tulaergen magmatic Ni–Cu mineralization system was generated from a common parental magma, which involved a combination of segregation of sulfide melt from silicate melt and internal fractionation within segregated sulfide melt.

5.2. Copper and Fe isotopes record redox reactions during segregation of sulfide melt from silicate melt (disseminated sulfides)

Disseminated sulfides have not undergone hydrothermal overprinting or internal fractionation within sulfide melt (Barnes and Maier, 1999), and their isotopic compositions most likely reflect those of the parental magma. Zhao et al. (2017) evaluated possible mechanisms of Cu isotope fractionation during formation of disseminated sulfides in the Tulaergen deposit, including crustal contamination, hydrothermal overprinting, diffusion, mantle sources or magmatic processes, and oxidation states. Redox reactions were considered as the main factor in producing the large $\delta^{65}$Cu variations (~2‰) observed in the disseminated sulfides (Zhao et al., 2017).

The difference in redox sensitivity between Cu and Fe is indicated by the isotopic compositions of disseminated
Table 2
Copper and Fe isotopic compositions and Cu/Fe ratios of chalcopyrite separates, and whole-rock Fe isotopic compositions from the Tulaergen magmatic Ni–Cu mineralization system.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>δ⁶⁵Cu (%)</th>
<th>2SD</th>
<th>Cu/Fe of chalcopyrite</th>
<th>δ⁵⁶Fe_{chalcopyrite} (%)</th>
<th>2SD</th>
<th>δ⁵⁷Fe_{chalcopyrite} (%)</th>
<th>2SD</th>
<th>δ⁵⁶Fe_{whole-rock} (%)</th>
<th>2SD</th>
<th>δ⁵⁷Fe_{whole-rock} (%)</th>
<th>2SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2T-3</td>
<td>-0.25</td>
<td>0.05</td>
<td>1.03</td>
<td>0.46</td>
<td>0.03</td>
<td>0.70</td>
<td>0.02</td>
<td>0.27</td>
<td>0.04</td>
<td>0.36</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-4</td>
<td>0.04</td>
<td>0.05</td>
<td>0.97</td>
<td>0.35</td>
<td>0.03</td>
<td>0.62</td>
<td>0.03</td>
<td>0.27</td>
<td>0.04</td>
<td>0.36</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-10</td>
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<td>0.05</td>
<td>n.d.</td>
<td>0.78</td>
<td>0.03</td>
<td>1.18</td>
<td>0.02</td>
<td>0.07</td>
<td>0.04</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-11</td>
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<td>1.08</td>
<td>0.57</td>
<td>0.07</td>
<td>0.88</td>
<td>0.02</td>
<td>-0.02</td>
<td>0.04</td>
<td>-0.03</td>
<td>0.06</td>
</tr>
<tr>
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<td>n.d.</td>
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<td>0.07</td>
<td>1.35</td>
<td>0.02</td>
<td>-0.01</td>
<td>0.04</td>
<td>-0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-14</td>
<td>-0.55</td>
<td>0.10</td>
<td>1.16</td>
<td>0.90</td>
<td>0.08</td>
<td>1.36</td>
<td>0.08</td>
<td>-0.12</td>
<td>0.04</td>
<td>-0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-15</td>
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<td>n.d.</td>
<td>0.92</td>
<td>0.08</td>
<td>1.36</td>
<td>0.02</td>
<td>0.01</td>
<td>0.04</td>
<td>-0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>tleg-13</td>
<td>-0.24</td>
<td>0.05</td>
<td>1</td>
<td>0.42</td>
<td>0.04</td>
<td>0.69</td>
<td>0.05</td>
<td>0.08</td>
<td>0.04</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>tleg-25</td>
<td>-1.05</td>
<td>0.05</td>
<td>1.01</td>
<td>0.80</td>
<td>0.04</td>
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<td>-0.12</td>
<td>0.04</td>
<td>-0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>tleg-14</td>
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<td>0.97</td>
<td>0.75</td>
<td>0.04</td>
<td>1.13</td>
<td>0.02</td>
<td>-0.07</td>
<td>0.04</td>
<td>-0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>tleg-24</td>
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<td>0.05</td>
<td>0.88</td>
<td>0.85</td>
<td>0.05</td>
<td>1.28</td>
<td>0.02</td>
<td>-0.20</td>
<td>0.04</td>
<td>-0.29</td>
<td>0.06</td>
</tr>
<tr>
<td>tleg-31</td>
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<td>0.05</td>
<td>n.d.</td>
<td>1.29</td>
<td>0.01</td>
<td>1.88</td>
<td>0.02</td>
<td>0.06</td>
<td>0.03</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-24</td>
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<td>0.07</td>
<td>n.d.</td>
<td>1.30</td>
<td>0.06</td>
<td>1.91</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-25</td>
<td>-0.42</td>
<td>0.05</td>
<td>n.d.</td>
<td>1.31</td>
<td>0.06</td>
<td>1.92</td>
<td>0.02</td>
<td>0.15</td>
<td>0.03</td>
<td>0.24</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-27</td>
<td>-0.26</td>
<td>0.05</td>
<td>1</td>
<td>1.31</td>
<td>0.06</td>
<td>1.93</td>
<td>0.02</td>
<td>0.11</td>
<td>0.03</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
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<td>0.05</td>
<td>1.09</td>
<td>1.25</td>
<td>0.11</td>
<td>1.93</td>
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<td>0.03</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-34</td>
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<td>0.05</td>
<td>1.08</td>
<td>0.92</td>
<td>0.02</td>
<td>1.37</td>
<td>0.02</td>
<td>0.28</td>
<td>0.04</td>
<td>0.38</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-35</td>
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<td>0.05</td>
<td>1</td>
<td>0.82</td>
<td>0.06</td>
<td>1.23</td>
<td>0.02</td>
<td>0.38</td>
<td>0.03</td>
<td>0.56</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-37</td>
<td>0.50</td>
<td>0.05</td>
<td>1.02</td>
<td>0.71</td>
<td>0.01</td>
<td>1.19</td>
<td>0.02</td>
<td>0.28</td>
<td>0.03</td>
<td>0.41</td>
<td>0.06</td>
</tr>
<tr>
<td>2T-38</td>
<td>0.52</td>
<td>0.05</td>
<td>0.96</td>
<td>0.61</td>
<td>0.04</td>
<td>0.77</td>
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<td>0.35</td>
<td>0.03</td>
<td>0.55</td>
<td>0.06</td>
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<tr>
<td>2T-39</td>
<td>0.48</td>
<td>0.05</td>
<td>0.99</td>
<td>0.96</td>
<td>0.06</td>
<td>1.37</td>
<td>0.02</td>
<td>0.35</td>
<td>0.03</td>
<td>0.51</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Note: Copper and Fe isotope data are expressed in per mil relative to NIST 976 and IRMM-014, respectively. n.d. = not detected.

Data from Zhao et al. (2017).
chalcopyrite (Fig. 4). The $\delta^{65}\text{Cu}$ values of disseminated sulfides (chalcopyrite) decrease with increasing S content and Pd/Ir ratio (Figs. 4, 6a and 7a), while an opposite trend is observed for $\delta^{56}\text{Fe}_{\text{chalcopyrite}}$ values (Figs. 4 and 6b). Experimental (e.g., Mikhlin et al., 2005; Pearce et al., 2006) and theoretical (e.g., Klekovkina et al., 2014) considerations indicate two probable ionic states of Cu and Fe in chalcopyrite. The stoichiometry of chalcopyrite is considered to be $\text{Cu}^{+}\text{Fe}^{3+}\text{S}_2^{2-}$ or $\text{Cu}^{2+}\text{Fe}^{2+}\text{S}_2^{2-}$, with $\text{Cu}^{+}\text{Fe}^{3+}\text{S}_2^{2-}$ as the dominant species (Klekovkina et al., 2014). High-valence Cu- and Fe-bearing minerals (containing $\text{Cu}^{2+}$ and $\text{Fe}^{3+}$) tend to be enriched in heavy isotopes ($^{65}\text{Cu}$ and $^{56}\text{Fe}$) due to their stronger bonds (Asael et al., 2007; Shahar et al., 2008; Mathur et al., 2005, 2009, 2012; Wall et al., 2011; Dauphas et al., 2014, 2017). Disseminated sulfides (chalcopyrite) segregated under high oxygen fugacity conditions (with low S contents and high Pd/Ir ratios) have higher $\delta^{65}\text{Cu}$ values (Zhao et al., 2017) and lower $\delta^{56}\text{Fe}$ values than those formed in low oxygen fugacity conditions (high S contents and low Pd/Ir ratios) (Figs. 4, 6a, b, 7c and d). Previous studies have indicated that incorporation of high valence elements into crystal structures causes enrichment in low valence elements to maintain charge balance (e.g., Schuessler et al., 2009). In the Tulaergen deposit, chalcopyrite formed in oxidizing conditions with high $\text{Cu}^{2+}$ contents would therefore incorporate more $\text{Fe}^{2+}$, while that

Fig. 3. Plots of Ir vs. Pt, Ni vs. Cu, and Pd vs. Ir, Ru, Rh and Cu for the Tulaergen deposit. Nickel, Cu and PGE contents are normalized to 100% sulfides.
Fig. 4. Variations of $\delta^{65}$Cu, $\delta^{56}$Fe$_{chalcopyrite}$ and $\delta^{56}$Fe$_{whole-rock}$ values as a function of whole-rock S contents (error bars are smaller than symbols). Host rocks and the oxygen fugacity trends are indicated. $\delta^{65}$Cu and $\delta^{56}$Fe values of bulk silicate Earth (BSE) and $\delta^{56}$Fe value of MORB are from Liu et al. (2015) and Dauphas et al. (2017), respectively.

Fig. 5. Modeling of PGE compositional variations resulting from segregation of sulfide melt from silicate melt with variable R factors (mass ratio of silicate- to sulfide-melts, Campbell and Naldrett, 1979) and internal fractionation within segregated sulfide melt for the Tulaergen Ni–Cu mineralization system. $F =$ the fraction of remaining sulfide liquid during fractional crystallization of monosulfide solid-solution (MSS). The partition coefficients used in our calculation are within the ranges of experimental results (Barnes and Lightfoot, 2005). It was assumed that partition coefficients remained constant during segregation of sulfide melt from silicate melt and internal fractionation within segregated sulfide melt. Better correlations of Ir against Pd for the Tulaergen deposit have been obtained by setting $D_{\text{sol/sul}}^\text{Ir} = 30,000$, $D_{\text{sol/sul}}^\text{Pd} = 40,000$, $D_{\text{MSS/sul}}^\text{Ir} = 3.5$, and $D_{\text{MSS/sul}}^\text{Pd} = 0.1$. 

Partition coefficients

(sulfide/silicate melt)

- $D_{\text{sul/sil}}^\text{Ir} = 30,000$
- $D_{\text{sul/sil}}^\text{Pd} = 40,000$
- $D_{\text{Cu}}^\text{sul/sil} = 15,000$
- $D_{\text{Cu}}^\text{sul/sil} = 10,000$
- $D_{\text{Fe}}^\text{sul/sil} = 60,000$
- $D_{\text{Fe}}^\text{sul/sil} = 40,000$

(MSS/sulfide melt)

- $D_{\text{Ir}}^\text{MSS/sul} = 3.5$
- $D_{\text{Pd}}^\text{MSS/sul} = 0.1$
- $D_{\text{Cu}}^\text{MSS/sul} = 2.0$
- $D_{\text{Cu}}^\text{MSS/sul} = 0.1$
- $D_{\text{Fe}}^\text{MSS/sul} = 2.0$
- $D_{\text{Fe}}^\text{MSS/sul} = 0.2$
formed under low oxygen fugacity, with higher Cu⁺ contents, would be enriched in Fe³⁺ (Figs. 4 and 6c). Such an effect has also been observed in other Fe-bearing minerals, including hematite, ilmenite, and titanomagnetite (Polyakov and Mineev, 2000; Polyakov et al., 2007; Schuessler et al., 2009).

The Fe isotopic composition of magmatic Ni–Cu mineralization systems is potentially affected by several mechanisms. Iron is found in both silicate (e.g., olivine and pyroxene) and sulfide minerals (e.g., pyrrhotite, pentlandite, and chalcopyrite), and whole-rock compositions appear to provide optimum estimates of its overall isotope signatures. Partial melting of mantle ($\delta^{56}$Fe = +0.03 ± 0.03‰) generates basaltic magmas with $\delta^{56}$Fe values of ~+0.1‰ (Dauphas et al., 2017). Magma fractionation results in heavier Fe isotopic compositions in evolved igneous rocks, with $\delta^{56}$Fe values of ~+0.25‰ in evolved rocks (Teng et al., 2008; Schuessler et al., 2011; Dauphas et al., 2014, 2017). Such variations are much smaller than those observed in the Tulaergen deposit (~0.4‰ for whole-rock samples and ~0.7‰ for chalcopyrite). Factors other than mantle melting and magma evolution must therefore govern the observed Fe isotope fractionation.

In a closed magmatic system, Fe³⁺ is more incompatible than Fe²⁺, so silicate melts become progressively more oxidized as crystallization proceeds (Dauphas et al., 2014, 2017; Foden et al., 2015). The crystallization of Fe²⁺-dominated olivine and pyroxene leads to Fe³⁺ enrichment in evolved silicate melts (Shahar et al., 2008; Sossi et al., 2012). Fe²⁺ is bonded to S in pyrrhotite, whereas oxygen-coordinated Fe is in a mixed Fe²⁺/Fe³⁺ state in silicate melts under magmatic conditions (Schuessler et al., 2007). Chalcopyrite is dominated by the Cu⁺Fe³⁺S²⁻ ionic state (Klekovkina et al., 2014) and is enriched in heavy Fe isotopes (Fig. 4).

The influence of the Fe isotopic composition of chalcopyrite (Fe³⁺-dominated phase) on whole-rock $\delta^{56}$Fe values needs to be evaluated first. The chalcopyrite contents of disseminated sulfides and Fe contents of different phases were estimated using the methods of Li et al. (2001). Calculations indicate that much less Fe is hosted by chalcopyrite (~0.07‰) than in Fe²⁺-dominated phases incorporating light Fe isotopes. Furthermore, quantitative estimations using mass-balance equation show that the Fe isotopic composition of chalcopyrite would not significantly ($<0.07‰$) change whole-rock $\delta^{56}$Fe values of disseminated sulfides in the Tulaergen deposit. As a consequence, crystallization of olivine and pyroxene with sulfide segregation (Fe³⁺-dominated phase) would incorporate light Fe isotopes, with $\delta^{56}$Fe values increasing in evolved silicate melts (Figs. 4 and 7d). Redox reactions are thus the
main factor governing Cu and Fe isotope fractionation during the formation of disseminated sulfides in high-temperature magmatic Ni–Cu mineralization systems.

5.3. Copper and Fe isotopes record the redox reactions during internal fractionation within segregated sulfide melt (massive sulfides)

As discussed in Section 5.1, accumulated sulfide liquid may fractionate into an Fe-rich MSS cumulate and a Cu-rich sulfide liquid, with Cu and Fe isotopes possibly being fractionated in this process. In the Tulaergen magmatic Ni–Cu mineralization system, chalcopyrite in Cu-rich massive sulfides has heavier Cu and lighter Fe isotopic compositions than those hosted by Fe-rich massive sulfides (Fig. 4). Possible factors contributing to the Cu and Fe isotope fractionation in massive sulfides are considered here.

Numerical modeling using mass-balance and Rayleigh equations indicates that Fe- and Cu-rich massive sulfides were generated by MSS–residual sulfide liquid fractionation (Figs. 5–7). The effects of crustal contamination and hydrothermal overprinting can be ignored, given that country rocks are extremely depleted in Cu and Fe compared with the massive sulfides and are unlikely to have influenced Cu and Fe isotopic compositions. In addition, hydrothermal veins are rarely observed in massive sulfides, precluding generation of different types of fluids with different Cu and Fe isotopic compositions. Copper and Fe isotopes can be strongly fractionated by diffusion-driven processes (Richter et al., 2009; Williams and Archer, 2011). If such processes governed Cu and Fe isotope fractionation, Cu-rich massive sulfides formed in later stages and at lower temperatures should have lower \( \delta^{65}\text{Cu} \) and \( \delta^{56}\text{Fe} \) values than those of Fe-rich sulfides. This hypothesis is inconsistent with the Cu and Fe isotopic variation observed in the Tulaergen magmatic Ni–Cu mineralization system (Fig. 4).
Crystallization of MSS could increase the oxygen fugacity of the residual sulfide liquid (e.g., Naldrett et al., 2000; Wohlgenmouth-Ueberwasser et al., 2013), and this is likely to drive Cu and Fe isotope fractionation due to their redox-sensitive affinities. In magmatic Fe–Ni–Cu–S systems, the increase in oxygen fugacity from MSS to evolved sulfide melt tends to transform ionic states from Cu$^{+}$Fe$^{3+}$S$_2$ to Cu$^{2+}$Fe$^{2+}$S$_2$ in chalcopyrite, and increase $\delta^{65}$Cu values. Accordingly, $\delta^{56}$Fe values of chalcopyrite should decrease from Fe- to Cu-rich massive sulfides due to the charge-balance effect. This is consistent with the Cu and Fe isotopic compositions of chalcopyrite in massive sulfides (Figs. 4 and 7c). Thus, the Cu and Fe isotope fractionation in chalcopyrite was mainly controlled by redox reactions during internal fractionation within segregated sulfide melt. Whole-rock $\delta^{56}$Fe values of Cu-rich massive sulfides are higher than those of Fe-rich massive sulfides (Figs. 4, 6 and 7). The Fe-rich massive sulfides comprise mainly Fe$^{2+}$-dominated pyrrhotite and pentlandite (e.g., Schuessler et al., 2007). The Cu-rich massive sulfides consist of abundant chalcopyrite and minor pentlandite and pyrrhotite, which can be regarded as an Fe$^{2+}$-dominated phase (e.g., Klekovich et al., 2014). Thus, redox reactions cause Cu and Fe isotope fractionation during internal fractionation within segregated sulfide melt in magmatic Fe–Ni–Cu–S systems.

Fractionation factors of Cu and Fe isotopes between fractionated melts and MSS can be estimated on the basis of the data acquired in this study. As discussed in Section 5.1, numerical modeling using mass-balance and Rayleigh equations indicates that disseminated sulfides with R factors of $\sim$500 underwent MSS–residual sulfide liquid fractionation to form Fe- and Cu-rich massive sulfides (Fig. 5). Thus, Cu and Fe isotopic variations during internal fractionation within segregated sulfide melt may also be simulated using the Rayleigh equation, with heavy Cu and Fe isotopes preferring evolved liquid to MSS. Fractionation factors are defined as follows (Fig. 8):

$$
\begin{align*}
\alpha^{65}_{\mathrm{Cu\text{residual sulfide melt--MSS}}} &= \left( \frac{6^{5} \text{Cu}_{\text{residual sulfide melt}}}{6^{5} \text{Cu}_{\text{MSS}}} \right) \times \left( \frac{6^{5} \text{Cu}_{\text{MSS}}}{6^{5} \text{Cu}_{\text{initial sulfide melt}}} \right) \\
\alpha^{56}_{\mathrm{Fe\text{residual sulfide melt--MSS}}} &= \left( \frac{56^{\text{Fe}_{\text{residual sulfide melt}}}}{56^{\text{Fe}_{\text{MSS}}}} \right) \times \left( \frac{56^{\text{Fe}_{\text{MSS}}}}{56^{\text{Fe}_{\text{initial sulfide melt}}} \right) 
\end{align*}
$$

The choice of Cu and Fe isotopic compositions of the initial sulfide melt is vital in these numerical calculations. On the basis of modeling by mass-balance and Rayleigh equations (Fig. 5), disseminated sulfides best matching the parental magma compositions seem to be the optimum choice. Mean $\delta^{65}$Cu ($-0.54 \pm 0.41\%$e) and $\delta^{56}$Fe ($-0.06 \pm 0.06\%e$) values for the disseminated samples were therefore selected to represent the initial Cu and Fe isotopic compositions of the segregated sulfides, respectively (Fig. 8). Numerical modeling using the Rayleigh equation indicates that the $\alpha^{65}_{\mathrm{Cu\text{residual sulfide melt--MSS}}}$ and $\alpha^{56}_{\mathrm{Fe\text{residual sulfide melt--MSS}}}$ values are $\sim1.0011$ and $\sim1.0005$, respectively (Fig. 8). It is notable that the fractionation factor between sulfide melt and MSS for Cu is higher than this value for Fe in the Fe–Ni–Cu–S system, which can be explained by the Cu contents being much lower than Fe in this system, and thus more easily influenced by redox reactions.

5.4. Implications

The formation of magmatic Ni–Cu mineralization involves a series of stages: (1) mantle melting; (2) magma ascent; (3) segregation of sulfide melt from silicate melt and sulfide enrichment; and (4) silicate mineral crystallization and possible internal fractionation within segregated sulfide melt (Barnes and Lightfoot, 2005; Naldrett, 2010). Copper and Fe isotope fractionation occurs as the

![Fig. 8. Modeling of changes in Cu and Fe isotope fractionation factors ($\alpha^{65}_{\mathrm{Cu\text{residual sulfide melt--MSS}}}$ and $\alpha^{56}_{\mathrm{Fe\text{residual sulfide melt--MSS}}}$) during internal fractionation within segregated sulfide melt. The star symbols represent $\delta^{65}$Cu ($-0.54\%e$) or $\delta^{56}$Fe ($-0.06\%e$) values of the initial sulfide melt. The Rayleigh equation is defined as follows: $\delta_\Lambda = (\delta_0 + 1000) \times (1 - f) - 1000$, where $\delta_0$ is the initial isotopic composition of an element in the sulfide melt, $\delta_\Lambda$ represents the isotopic composition of an element in the sulfide melt when a fraction $f$ of the original amount of the element is left, $\alpha$ refers to the fractional factor between fractionated melts and MSS, and $f$ is the fraction of Cu and Fe remaining. The fraction of remaining sulfide melt was set from $\sim0.6$ to $\sim0.8$, as calculated by the amount of Cu-rich massive sulfides that settled out from the Fe–Ni–Cu–S system from $\sim20\%$ to $\sim40\%$ (Fig. 5). The partition coefficients between MSS and sulfide liquid were set to 0.2 for Cu and 1 for Fe. Accordingly, the fractions of Cu and Fe left in the evolved sulfide melt ranged from $\sim92\%$ to $\sim96\%$ and $\sim60\%$ to $\sim80\%$, respectively.](image-url)
magma. Mantle melting generates negligible Cu isotope fractionation (Liu et al., 2015; Savage et al., 2015), and primary magma should have a Cu isotopic composition similar to that of the mantle ($\delta^{65}\text{Cu} = 0.06 \pm 0.20\%$; Fig. 9). However, partial melting of the mantle may cause measurable Fe isotope fractionation in basaltic magma, with $\delta^{56}\text{Fe}$ values from $-0.03 \pm 0.03\%$ (mantle) to $0.10 \pm 0.01\%$ (magma) (Fig. 9; Dauphas et al., 2017). Minor olivine crystallization and sulfide segregation may occur during magma ascent. However, this process only removed negligible Cu and Fe from the silicate melt, with a limited contribution to isotope fractionation.

Significant segregation of sulfide melt from silicate melt happened in a shallow magma chamber (Fig. 9). The crystallization of Fe$^{2+}$-dominated olivine and segregation of Fe$^{2+}$-dominated sulfides leads to the enrichment of Fe$^{3+}$ in the residual melts. The silicate melt evolved to progressively more oxidized conditions as crystallization proceeded (e.g., Dauphas et al., 2014, 2017; Zhao et al., 2017). Chalcopyrite segregated in early stages was enriched in light Cu and heavy Fe isotopes due to charge-balance effects (Fig. 9). In contrast, chalcopyrite formed in later stages preferentially incorporated heavy Cu and light Fe isotopes. The Fe isotopes of the whole system were progressively shifted towards heavier compositions (Fig. 9).

Sulfide droplets segregated in early stages accumulated at the base of the magma chamber and were fractionated into an Fe-rich MSS cumulate and a Cu-rich sulfide liquid as oxygen fugacity increased. The ionic state of chalcopyrite underwent slight transformation from Cu$^+\text{Fe}^{3+}\text{S}_2^2$ in MSS to Cu$^{2+}\text{Fe}^{2+}\text{S}_2^2$ in evolved sulfide melt, contributing to the increasing $\delta^{65}\text{Cu}$ and decreasing $\delta^{56}\text{Fe}$ values (Fig. 9). MSS crystallized mostly into Fe$^{2+}$-dominated pyrrhotite and pentlandite. In contrast, abundant chalcopyrite and minor pentlandite and pyrrhotite were exsolved from the evolved sulfide melt, with the sulfide assemblage being an Fe$^{3+}$-dominated phase. The Fe isotopic composition of the whole system became heavier from MSS cumulates to evolved sulfide melt, as the sulfide mineral assemblages changed (Fig. 9).

This study indicates that redox reactions drive Cu and Fe isotope fractionation in high-temperature magmatic Ni–Cu mineralization systems. Furthermore, Cu and Fe isotopes may thus be useful in tracing concealed orebodies. Elevated $\delta^{65}\text{Cu}$ and $\delta^{56}\text{Fe}_{\text{whole-rock}}$ values in mafic-ultramafic intrusions may indicate Cu-rich mineralization potential with enrichment in Cu, Ni, Pt, Pd, and Au (e.g., Li et al., 1996; Barnes and Lightfoot, 2005; Naldrett, 2010, 2011). In contrast, the mafic-ultramafic intrusions with light Cu and Fe isotopic compositions may be favorable hosts for disseminated and Fe-rich orebodies, which should be given more attention for Ni and PGE exploration.

6. CONCLUSIONS

The formation of the Tulaergen magmatic Ni–Cu mineralization system involved segregation of sulfide melt from silicate melt and internal fractionation within segregated sulfide melt, with significant changes of oxidation state occurring during these processes. During segregation of sulfide melt from silicate melt, crystallization of Fe$^{2+}$-dominated silicate minerals and segregation of Fe$^{3+}$-dominated sulfides led to the enrichment of residual

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Fig. 9. A schematic model for the Cu and Fe isotope fractionation in the Tulaergen magmatic Ni–Cu mineralization system (see text for explanation).
melts in Fe$^{2+}$. Chalcopyrite segregated in early stages was enriched in light Cu and heavy Fe isotopes due to charge-balance effects. Accordingly, chalcopyrite formed in late stages incorporated more $^{65}$Cu and $^{54}$Fe. Iron isotopes of the whole system were progressively shifted towards heavier compositions.

Accumulated sulfide melt fractionated into an Fe-rich MSS cumulate and a Cu-rich sulfide liquid. MSS crystallization caused an increase in oxygen fugacity of the evolved sulfide liquid, which would slightly transform chalcopyrite ionic states from Cu$^{+}$Fe$^{3+}$S$_2$ to Cu$^{2+}$Fe$^{2+}$S$_2$. The transformation resulted in increasing $\delta^{65}$Cu and decreasing $\delta^{56}$Fe values in chalcopyrite. Iron isotopes of the whole system were shifted towards heavier values from MSS cumulate to the evolved sulfide melt. Numerical modeling using the Rayleigh equation indicates that the fractionation factors $\alpha^{65}$Cu residual sulfide melt-MSS and $\alpha^{56}$Fe residual sulfide melt-MSS are $\sim$1.0011 and $\sim$1.0005, respectively, during internal fractionation within segregated sulfide melt.

This study demonstrates that redox reactions drive Cu and Fe isotope fractionation in high-temperature magmatic Ni–Cu mineralization systems. Furthermore, Cu and Fe isotopes can also be potentially used to trace concealed orebodies in magmatic Ni–Cu mineralization systems.

ACKNOWLEDGEMENTS

This study was financially supported by the National Key R&D Program of China (2017YFC0601202), National Natural Science Foundation of China (41473017 and 41803013), National Postdoctoral Program for Innovative Talents (BX201600136), Fundamental Research Funds for the Central Universities (53200759011) and China Geological Survey (121211220926 and 1212113089400). We thank Zhaoming Zhao and Huqiang Wang of the Hexin Mine for their assistance in field work. We also gratefully acknowledge Associate Editor Shichun Huang and three anonymous reviewers for thorough and constructive reviews of this manuscript, and Editor-in-Chief Marc Norman for efficient handling. The authors extend their gratitude to colleagues at the China University of Geosciences, Beijing for assistance in Cu and Fe isotope analyses and discussions on an earlier version of the manuscript. We would also like to thank Matthew Gonzalez for assistance on calibrating the Neptune MC–ICP–MS at Pennsylvania State University.

REFERENCES


Perspective Lett. 1, 52–64.


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**Associate editor:** Shichun Huang