Mineral composition control on inter-mineral iron isotopic fractionation in granitoids

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Abstract

This study reports elemental and iron isotopic compositions of feldspar and its coexisting minerals from four Dabie I-type granitoids to evaluate the factors that control inter-mineral Fe isotopic fractionation in granitoids. The order of heavy iron isotope enrichment is feldspar > pyrite > magnetite > biotite/hornblende. Feldspar has heavier iron isotopic compositions than its co-existing magnetite (Δ56Feplagioclase–magnetite = +0.376‰ to +1.084‰, Δ56Fealkali-feldspar–magnetite = +0.516‰ to +0.846‰), which can be attributed to its high Fe3+/Fe tot ratio and low coordination number (tetrahedrally-coordinated) of Fe3+. Δ56Femagnetite–biotite of coexisting magnetite and biotite ranges from 0.090‰ to 0.246‰. Based on homogeneous major and iron isotopic compositions of mineral replicates, the inter-mineral fractionation in this study should reflect equilibrium fractionation. The large variations of inter-mineral fractionation among feldspar, magnetite and biotite cannot be simply explained by temperature variation, but strongly depend on mineral compositions. The Δ56Feplagioclase–magnetite and Δ56Fealkali-feldspar–magnetite are positively correlated with albite mode in plagioclase and orthoclase mode in alkali-feldspar, respectively. This could be explained by different Fe–O bond strength in feldspar due to different Fe3+/ΣFe or different crystal parameters. The Δ56Femagnetite–biotite increases with decreasing Fe3+/ΣFe biotite and increasing mole (Na + K)/Mg biotite, indicating a decrease of β factor in low Fe3+/ΣFe and high (Na + K)/Mg biotite.

High-silica leucosomes from Dabie migmatites with a feldspar accumulation petrogenesis have higher δ56Fe values (δ56Fe = 0.42–0.567‰) than leucosome that represents pristine partial melt (δ56Fe = 0.117 ± 0.016‰), indicating that accumulation of feldspar could account for high δ56Fe values of these rocks. High δ56Fe values are also predicted for other igneous rocks that are mainly composed of cumulate feldspar crystals, e.g., anorthosites. Feldspar accumulation, however, cannot explain high δ56Fe values of most high-silica granitoids reported in the literature, based on their low Sr, Ba contents and negative Eu anomalies.

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Keywords: Fe isotopes; Inter-mineral fractionation; Compositional controls; Feldspar accumulation

1. INTRODUCTION

It is debated why high-silica granitic rocks (SiO2 > 71 wt.%, δ56Feaverage = 0.218 ± 0.154‰, 2SD, N = 84) have systematically heavier Fe isotopic compositions than dioritic-granodioritic rocks (53 wt.% < SiO2 < 71 wt.% , δ56Feaverage = 0.097 ± 0.126‰, 2SD, N = 103) (data from Poitrasson and Freydier, 2005; Heimann et al., 2008; Dauphas et al., 2009a; Schuessler et al., 2009; Sossi et al., 2012; Telus et al., 2012; Foden et al., 2015). This phenomenon was first observed by Poitrasson and Freydier (2005) and interpreted as a result of exsolution of late magmatic aqueous fluids that preferentially dissolved ferrous iron rich in lighter isotopes. This idea was examined further by Heimann et al. (2008), who proposed that the
chloride-rich Fe\(^{3+}\)-bearing fluids exchanged with magnetite before exsolution. Li and Zn are fluid-mobile elements and their isotopic compositions can be fractionated during fluid-rock interaction (Schuessler et al., 2009; Telus et al., 2012 and references therein). However, correlated Li-Fe and Zn-Fe isotope fractionations were not observed (Schuessler et al., 2009; Telus et al., 2012). Soret diffusion was proposed to account for this phenomenon (Lundstrom, 2009; Zambardi et al., 2014), but the expected correlated heavy Mg and U isotopic compositions were not detected in other plutons (Telus et al., 2012). Therefore, multi-isotopic studies do not support fluid exsolution or diffusion explanations for granitic rocks.

Fractional crystallization is a possible explanation for the heavy Fe isotopic compositions of high-silica granitic rocks (Schuessler et al., 2009; Sossi et al., 2012; Telus et al., 2012; Dauphas et al., 2014; Foden et al., 2015). Some modeling performed by Schuessler et al. (2009) indicated that the rhyolites can be produced by fractional crystallization of a dacitic melt with a bulk mineral-melt fractionation factor \(\Delta^{56}\text{Fe}_{\text{melt-mineral}}\) of about 0.1‰. However, some of the crystalline phases in granitic magma are Fe\(^{3+}\) rich oxides, such as magnetite. Crystallization of magnetite could reduce \(\delta^{56}\text{Fe}\) values of melt because magnetite has heavier isotopic compositions relative to silicate phases (Polyakov et al., 2007; Heimann et al., 2008; Telus et al., 2012). Foden et al. (2015) found that granites with high \(\delta^{56}\text{Fe}\) values are mainly A-type, corresponding to protracted fractional crystallization in which magnetite saturation is delayed. Dauphas et al. (2014) measured the mean force constants of iron bonds in silicate glasses and proposed that the \(\beta\) factor of iron is higher in rhyolitic glass than in basaltic-dacitic glass. In rhyolitic magma, the force constants of iron in melt may be even stronger than those of crystallizing magnetite. This will lead to a positive equilibrium isotopic fractionation between melt and crystals and drive the iron isotopic composition of the high-silica melts toward high \(\delta^{56}\text{Fe}\) values. However, it is still unclear how the \(\beta\) factors of minerals change with the variation of their compositions, which are determined by the co-existing melts.

Feldspar is generally ignored when considering Fe isotope fractionation during magma processes due to its low Fe content. However, mafic minerals are so rare while feldspar is abundant in high-silica granitoids that feldspar becomes an important iron carrier. For example, plagioclase from a Dabie high-silica granite T17 (SiO\(_2\): 72.37 wt. %, FeO: 1.80 wt.%), contains 0.26 wt.% FeO (Ma et al., 1998). Considering the proportion of feldspar in the granite (more than 70%), over 10% iron is estimated to be carried in feldspar. In addition, an extremely heavy Fe isotope composition is expected for feldspar, as Fe\(^{3+}\) is dominant and tetrahedrally coordinated in feldspar (Hofmeister and Rossman, 1984; Lundgaard and Tegner, 2004). An alkali-feldspar standard JF-2 from a pegmatite yields \(\delta^{56}\text{Fe}\) as high as +0.816 ± 0.025‰ (Millet et al., 2012). Therefore, feldspar may play a more important role in iron isotopic fractionation of high-silica magmas than previously thought. So far, iron isotopic fractionation factors between feldspar and its coexisting minerals are still lacking.

We carried out high-precision Fe isotopic analyses on four well-characterized I-type granitoids from the Dabie Orogen and minerals therein, including plagioclase, alkali-feldspar, biotite, hornblende, magnetite, pyrite and titanite. Our results show that feldspar has heavy \(\delta^{56}\text{Fe}: +0.557\pm 0.025 \)‰ to +1.326‰) iron isotopic compositions, with \(\Delta^{56}\text{Fe}_{\text{plagioclase-biotite}}\) ranging from +0.559‰ to +1.331‰ and \(\Delta^{56}\text{Fe}_{\text{alkali-feldspar-biotite}}\) from +0.698‰ to +1.092‰. Inter-mineral iron isotopic fractionations are most likely in equilibrium and controlled by chemical compositions of minerals. Based on feldspar data measured here, feldspar accumulation tends to produce high \(\delta^{56}\text{Fe}\) rocks, which is evidenced by Dabie leucosomes. Leucosomes from Dabie migmatites with feldspar accumulation petrogenesis yield \(\delta^{56}\text{Fe}\) up to 0.567‰, significantly higher than their pristine partial melt (~0.117‰).

### 2. SAMPLE DESCRIPTION

Four granites for this study (07ZB-6, 07XM-1, 07LD-2, and 06ZY-3) are Early Cretaceous post-collisional granitoids from the Dabie Orogen, East China. Their petrology and geochemistry have been previously studied and published (He et al., 2011, 2013). The four samples are typical I-type granites and have a wide range of SiO\(_2\) (64.6–76.6 wt. %, see Appendix 2 Table S1). These samples contain various amounts of quartz (20–35%), plagioclase (35–40%), alkali-feldspar (25–40%) and biotite (2–8%) with accessory titanite, magnetite, apatite, pyrite and zircon (see Table 1 and Appendix 1 Fig. S1). Hornblende was only found in 07LD-2 (6%) and 07ZB-6 (2–3%).

Five leucosomes from the Dabie Orogen were measured for whole rock iron isotopic composition to evaluate the effect of feldspar accumulation. Feldspar accumulation is evident for four of the five samples based on their extremely high Sr and Eu but low other REE concentrations (Wang et al., 2013). The other sample (0907MSH-8) may represent the pristine partial melt of dioritic to granodioritic gneisses (Wang et al., 2013). The five samples have SiO\(_2\) contents ranging from 72.10 to 76.14 wt.%. Four leucosomes with feldspar accumulation have low FeO concentrations (0.15–0.24 wt.%), while 0907MSH-8 has a FeO concentration of 1.90 wt.% (see Appendix 2 Table S1).

### 3. ANALYTICAL METHODS

#### 3.1. Electron analysis of minerals

Mineral compositions were measured at CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China. Major element concentrations of plagioclase, alkali-feldspar, biotite, titanite and hornblende were determined by a Shimadzu Electron Probe Micro analyzer (EMPA 1600) operating at 15 kV accelerating voltage with 20 nA beam current and <5 μm beam diameter. A series of natural minerals and synthetic oxides were used to calibrate the data based on a ZAF program. For major elements, the analytical precision is better than 2%. Iron content of feldspar was obtained...
with MC–ICP–MS by dissolution, since it’s too low to get an accurate FeO<sub>t</sub> content by EPMA.

3.2. Mineral separation

Pre-separation of minerals was conducted with the procedures of rough broken, fine crush, magnetic separation, manual extraction and density separation. After that, minerals were carefully handpicked under a binocular microscope twice to ensure purity and immunity of alteration. Special precautions were taken to guarantee feldspar separates are all colorless and without any magnetite or mafic mineral inclusions. In order to get enough iron for isotopic measurement, about 1000 small fragments (average total

Table 1
Iron isotopic compositions of granites, leucosomes, mineral separates and geostandards in this study.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Type Modal (%)</th>
<th>$\delta^{56}$Fe&lt;sup&gt;a&lt;/sup&gt;</th>
<th>2se</th>
<th>$\delta^{57}$Fe&lt;sup&gt;a&lt;/sup&gt;</th>
<th>2se</th>
<th>n&lt;sup&gt;b&lt;/sup&gt;</th>
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<td></td>
<td></td>
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<td>07LD-2</td>
<td>Plagioclase</td>
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<td>0.077</td>
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<td>0.052</td>
<td>0.170</td>
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<td>0.037</td>
<td>0.119</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>Whole-rock</td>
<td></td>
<td>0.092</td>
<td>0.037</td>
<td>0.119</td>
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<tr>
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<td>0.016</td>
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<td>0.567</td>
<td>0.016</td>
<td>0.848</td>
<td>0.036</td>
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<td>0.695</td>
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<td>0.016</td>
<td>0.685</td>
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<td>0.016</td>
<td>0.144</td>
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<td>0.052</td>
<td>1.053</td>
<td>0.066</td>
<td>4</td>
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<sup>a</sup> Reported relative to IRMM-014.

<sup>b</sup> n denotes the total number of analyses per newly purified sample solution by MC-ICPMS.

<sup>c</sup> Replicate: repeat sample dissolution, column chemistry and instrumental analysis.
weight: 23 mg) of feldspar were prepared for each sample. The biotite grains are laminar in shape, dark green to black in color and almost transparent. Hornblende grains are generally brown or black, columnar and translucent to transparent. One titanite sample was picked based on its sphenoid shape and reddish brown color.

3.3. Fe isotope analysis

Iron isotopic analyses were performed at Isotope Geochemistry Lab in China University of Geosciences, Beijing. Procedures for sample dissolution, column chemistry and instrument analysis are after Dauphas et al. (2009b) and He et al. (2015). A brief description is given below.

Variable amounts (0.35–39.55 mg) of samples were weighed into 6 ml Savillex PFA vials based on their Fe concentrations. Before dissolution, all minerals were leached by 1:1 mixture of BV-III grade ethanol and Milli-Q® water in an ultrasonic bath for 10 min and then carefully washed by Milli-Q® water three times. After the samples were totally dissolved by step-wise acid digestion, iron was purified with a polypropylene column filled with 1 ml AG1-X8 resin in a HCl medium. Whole procedural blanks processed along with Daibie samples yield iron concentrations less than 2 ng, and thus is considered negligible. Iron isotopic compositions were determined by the standard–sample bracketing method using a Thermo–Finningan Neptune Plus multiple collector–inductively coupled plasma–mass spectrometer (MC–ICP–MS) in HR mode. Typically, isotopic compositions reported here are the averages of nine times of repeat analyses. Iron isotopic variations are expressed in \( \delta \)-notation, \( \delta^{56}\text{Fe} = [(^{56}\text{Fe}^{2+}\text{Fe})_{\text{sample}}/(^{56}\text{Fe}^{2+}\text{Fe})_{\text{IRMM-014}} - 1] \times 10^3 \), where \( i \) refers to mass 56 or 57. All uncertainties in this study are reported as 2se (95% confidence intervals) and are calculated by \( (2\text{se})^2 = (2\text{se}\text{MS})^2 + (2\text{se}\text{chem})^2 \). Errors of bracketing calibrators measurement \( (2\text{se}\text{MS}) \) are calculated as \( 2\text{sd}_{\text{calibrator}}/\sqrt{n} \). Accidental error from the chemistry \( (2\text{se}\text{chem}) \) adopted here is 0.005‰ and 0.012‰ for \( \delta^{56}\text{Fe} \) and \( \delta^{57}\text{Fe} \), respectively (He et al., 2015). Analyses over a 2-year period of reference materials demonstrate a long-term reproducibility and accuracy of <0.03‰ for \( \delta^{56}\text{Fe} \) and \( \delta^{57}\text{Fe} \) values.

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4. RESULTS

Major elemental concentrations of minerals are reported in Appendix 2 Table S2. At least three analyses have been done for each mineral phase in each rock sample. Compositions of each mineral are uniform for every rock but vary sample by sample. Biotite has MgO and FeO contents ranging from 11.51 wt.% to 13.37 wt.% and from 16.84 wt.% to 19.94 wt.%, respectively. Fe\(^{3+}\)/Fe\(^{2+}\) ratio in biotite was calculated based on charge balance theory and ranges from 0.14 to 0.26. Based on albite–anorthite–orthoclase three end-member calculation, average albite mode (Ab%) of plagioclase and average orthoclase mode (Ol%) of alkali-feldspar in four granites varies from 68.6% to 86.9% and from 75.4% to 88.0%, respectively. FeO contents of feldspar are 0.07–0.15% for plagioclase and 0.03–0.10% for alkali-feldspar. The hornblende from sample 07LD-2 has FeO content of 19.64–19.87 wt.% and CaO contents of 10.85–11.46 wt.%. The titanite from sample 07ZB-6 has FeO content of 1.67–1.85 wt.%.

Iron isotopic data of granites and mineral separates, leucosomes, together with reference materials, are reported in Table 1. Four granites measured in this study have whole rock \( \delta^{56}\text{Fe} \) ranging from +0.092 ± 0.037‰ to +0.203 ± 0.029‰, typical of intermediate to felsic rocks (Fig. 2a). Plagioclase and alkali-feldspar from the Dabie granites yield rather high \( \delta^{56}\text{Fe} \) ranging from +0.557 ± 0.040‰ to +1.326 ± 0.040‰ and from +0.696 ± 0.040‰ to +1.087 ± 0.040‰, respectively, comparable to the K-feldspar reference sample from pegmatite (\( \delta^{56}\text{Fe} \): 0.816 ± 0.025‰) (Millet et al., 2012). Biotite yields \( \delta^{56}\text{Fe} \) ranging from −0.005 ± 0.040‰ to +0.108 ± 0.034‰, slightly below or comparable to their whole rocks (\( \Delta^{56}\text{Fe}_{\text{biotite-whole rock}} = −0.129% \) to −0.007‰) and consistent with the data previously reported (Fig. 2b) (Heimann et al., 2008; Telus et al., 2012). Magnetite was measured for only three granites, because no magnetite was separated from sample.

Fig. 1. Iron three-isotope plot of samples analyzed in this study. A-feldspar represents alkali-feldspar. Standard samples BHVO-2 and GSR-1 are also plotted. The gray line represents a linear regression of \( \delta^{56}\text{Fe} \) vs. \( \delta^{57}\text{Fe} \). The slope 1.466 is consistent with the values determined for mass-dependent fractionation (Young et al., 2002).

agree with published values (Craddock and Dauphas, 2011; He et al., 2015 and references therein) within quoted errors.
07LD-2. They tend to have higher 56Fe values than their whole rocks (56Fe = +0.181 ± 0.034 ‰ to +0.241 ± 0.034 ‰, D56Fe magnetite–whole rock = +0.006 ‰ to +0.118 ‰) (Fig. 2b). Hornblende from 07LD-2 has 56Fe of +0.106 ± 0.034 ‰. Titanite from 07ZB-6 yields a 56Fe value of +0.217 ± 0.033 ‰, slightly higher than its whole rock (56Fe titanite–whole rock ≈ +0.082) (Fig. 2b). Pyrite from 07XM-1 has a high 56Fe value of +0.433 ± 0.034 ‰. In summary, the observed order from highest to lowest 56Fe/54Fe is feldspar > pyrite > magnetite > titanite > biotite ≈ hornblende.

Four leucosomes from the Dabie Orogen with a plagioclase accumulation origin have rather heavy Fe isotopic compositions (+0.424 ± 0.016‰ to +0.567 ± 0.016‰, Table 1), their 56Fe values are even higher than published maximum 56Fe value of igneous rocks (Fig. 2a) (+0.400 ± 0.020‰; Heimann et al., 2008). By contrast, leucosome 0907MSH-8, which may represent the pristine partial melt of dioritic to granodioritic gneisses (Wang et al., 2013), yields relatively low 56Fe value of +0.117‰ ± 0.016‰ (Fig. 2a).

5. DISCUSSION

5.1. Equilibrium or disequilibrium isotope fractionation?

The iron isotopic fractionation among mineral pairs from the Dabie granites shows significant variations (e.g., D56Fe plagioclase–biotite = +0.559 ‰ to +1.331 ‰, D56Fe alkali-feldspar–biotite = +0.698 ‰ to +1.092 ‰). It is essential to evaluate whether these variations reflect disequilibrium isotope fractionation or represent equilibrium isotope fractionation controlled by varying parameters (e.g., mineral composition or temperature). Several lines of evidence indicate that chemical and isotopic equilibrium have been achieved within these granites.

Firstly, all four granites studied here have coarse-grained granular texture (see Appendix 1 Fig. S1), implying they had enough time to crystallize and equilibrate. Secondly, petrographic observations and compositional analyses do not show compositional zoning or heterogeneity in minerals of these granites (see electron probe results in Appendix 2 Table S2). Thirdly, oxygen isotope studies of the Dabie granitoids have demonstrated that oxygen isotope compositions of minerals are in equilibrium at crystallization temperature (Xie et al., 2001, 2006; Zhao et al., 2004; Chen et al., 2007). In feldspar, iron diffuses faster than oxygen (Behrens et al., 1990; Farver, 2010). Therefore, the inter-mineral iron isotopic equilibrium between feldspar and other minerals should also have been achieved within these granites. Finally, mineral replicates, for which different separates of minerals were dissolved independently, yield consistent 56Fe values. This suggests homogeneous iron isotopic composition for each kind of mineral from the individual sample. Hence, data of minerals from the Dabie granites may record equilibrium iron isotopic fractionation.
5.2. Mineral composition controls on inter-mineral iron isotopic fractionation

As revealed by theoretical studies (e.g., Urey, 1947), bonding environment of elements dominate equilibrium inter-mineral isotopic fractionation, with stronger bonds favoring heavier isotopes. Since Fe$^{3+}$ forms stronger bonds than Fe$^{2+}$, equilibrium isotope fractionation of iron is mainly controlled by redox status (Fe$^{3+}$/Fe$^{2+}$ ratio) (Fig. 4 in this study, Polyakov and Mineev, 2000; Blanchard et al., 2009; Dauphas et al., 2009a; Sossi et al., 2012; Dauphas et al., 2014). Fe-bearing silicates such as pyroxene, hornblende and biotite have relatively low iron force constants due to their comparably low Fe$^{3+}$/Fe$^{2+}$ ratios (Polyakov et al., 2007; Dauphas et al., 2014). Therefore, it is not surprising to observe comparable iron isotopic compositions between hornblende and co-existing biotite ($\Delta^{56}$Fe$_{\text{hornblende-biotite}} = -0.100\%e$ to 0.048\%e with an average of $-0.015\%e$) (this study, Heimann et al., 2008; Telus et al., 2012). Magnetite, in which two-thirds of iron occur as Fe$^{3+}$ [1/3 of the total Fe as VIFe$^{2+}$, 1/3 as IVFe$^{3+}$, and 1/3 as VIFe$^{3+}$], has higher $\Delta^{56}$Fe values than their co-existing biotite ($\Delta^{56}$Fe$_{\text{magnetite-biotite}} = 0.083$–0.560\%e with an average of 0.248\%e) (this study, Heimann et al., 2008; Sossi et al., 2012; Telus et al., 2012). Although pyrite is a Fe$^{2+}$-bearing mineral, it is calculated to have heavier iron isotopic compositions between coexisting magnetite and biotite due to its strong covalent Fe–S bond (Polyakov and Mineev, 2000; Blanchard et al., 2009). Pyrite from some hydrothermal deposits have very low $\delta^{56}$Fe values, which reflects non-equilibrium fractionation (e.g., Rouxel et al., 2004). The pyrite from 07XM-1 has heavier iron isotopic composition than its coexisting biotite and magnetite ($\Delta^{56}$Fe$_{\text{pyrite-biotite}} = 0.438\%e$; $\Delta^{56}$Fe$_{\text{pyrite-magnetite}} = 0.192\%e$). This supports the idea that inter-mineral fractionations here reflect the equilibrium conditions. Feldspar (especially orthoclase and albite-rich plagioclase) has high Fe$^{3+}$/Fe$^{2+}$ ratios and all Fe$^{3+}$ are tetrahedrally coordinated (Hofmeister and Rossman, 1984; Lundgaard and Tegner, 2004 and references therein). Therefore, strong Fe–O bond strength can explain why feldspar has higher $\Delta^{56}$Fe values than their coexisting magnetite and biotite ($\Delta^{56}$Fe$_{\text{feldspar-magnetite}} = +0.376\%e$ to $+1.084\%e$, $\Delta^{56}$Fe$_{\text{feldspar-biotite}} = +0.559\%e$ to $+1.331\%e$). In summary, the directions of inter-mineral fractionation among minerals (biotite, amphibole, and magnetite) are due to the different coordination environments of iron.

It is important to reveal the origin of the large variations of $\Delta^{56}$Fe among minerals. Equilibrium Fe isotopic fractionation between mineral pairs was theoretically controlled by temperature and can be approximated as an equation in which $\Delta^{56}$Fe between minerals is a linear function of 1/T$^2$ (Bigeleisen and Mayer, 1947; Urey, 1947). To evaluate the equilibrium temperature of minerals, the thermodynamic models for ternary feldspar of Elkins-Tanton and Grove (1990) and Fuhrman and Lindsley (1988) were applied to samples in this study (Appendix 2). The two models give similar results (the difference <7°C) and obtained temperature values vary from 458 to 694°C. This temperature represents the equilibrium temperature for coexisting feldspars, which would be a good estimate of the equilibrium temperature of coexisting feldspar, biotite, and magnetite. $\Delta^{56}$Fe values of every mineral pairs measured here do not follow the predicted, linear correlation with 10$^{6}$/T$^2$ with a certain slope (Fig. 3). Therefore, the inter-mineral fractionation observed in our study cannot be simply explained by variation in the equilibrium temperature. Instead, inter-mineral Fe isotopic fractionations correlate with the mineral compositions, reflecting a dominant role of mineral composition on the varying fractionation scale.

5.2.1. Fractionation between magnetite and biotite

In this study, $\Delta^{56}$Fe$_{\text{magnetite-biotite}}$ increases with increasing of (Na + K)/Mg (mole ratio) and decreasing Fe$^{3+}$/Fe in biotite ($\Delta^{56}$Fe$_{\text{magnetite-biotite}} = 1.16 \times (\text{Na} + \text{K})/\text{Mg}\text{(mole ratio)} - 0.56$, $\Delta^{56}$Fe$_{\text{magnetite-biotite}} = -0.054 \times (\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{biotite}}) + 1.29$, Fig. 4). Since magnetite has a simple structure and the coordination state of Fe in magnetite is stable (Wilke et al., 2001), the $\Delta^{56}$Fe$_{\text{magnetite-biotite}}$ may primarily depend on the composition of biotite. Given that Fe$^{3+}$ forms stronger bonds than Fe$^{2+}$ with oxygen, the negative correlation between $\Delta^{56}$Fe$_{\text{magnetite-biotite}}$ and Fe$^{3+}$/Fe ratio of biotite implies that less Fe$^{3+}$ in biotite would induce decreasing of biotite’s $\beta$ factor. The following substitution reaction could explain why increase of (Na + K)/Mg (mole ratio) will lead to decrease of Fe$^{3+}$/Fe in biotite:

$$\text{Fe}^{2+} + \text{Na}^+/\text{K}^+ \leftrightarrow 2\text{Mg}^{2+}$$

This reaction is based on the knowledge that Fe$^{3+}$ substitutes for Mg$^{2+}$ in biotite ($K(Mg,Fe)_{3}(AlSi_{3}O_{10})(OH)_{2}$).
and this substitution uses K⁺ or Na⁺ for charge balance. The equilibrium constant $\mathcal{X}$ of this reaction can be expressed by:

$$\mathcal{X} = \frac{[\text{Mg}^{2+}]^{1/2}}{[\text{Fe}^{2+}]} \times \frac{[\text{Na}^+]}{[\text{K}^+]}$$

This can be rewritten as $[\text{Fe}^{3+}] = ([\text{Mg}^{2+}]^{1/2}) / (\mathcal{X} \times [\text{Na}^+ \text{ or } \text{K}^+])$. At a given temperature and pressure, $\mathcal{X}$ is a constant. If (Na + K)/Mg ratio in biotite increases, the concentration of Fe³⁺ in biotite would decrease accordingly and resulting in lower $\beta$ factor of Fe and larger fractionation between magnetite and biotite.

5.2.2. Fractionation between feldspar and magnetite

The fractionation factors between feldspar and magnetite show even larger variations ($\Delta^{56}\text{Fe}_{\text{plagioclase-magnetite}} = +0.376\%$ to $+1.084\%$, $\Delta^{56}\text{Fe}_{\text{alkali-feldspar-magnetite}} = +0.516\%$ to $+0.846\%$). Mineral composition analyses show $\Delta^{56}\text{Fe}_{\text{plagioclase-magnetite}}$ and $\Delta^{56}\text{Fe}_{\text{alkali-feldspar-magnetite}}$ are positively correlated with albite mode of plagioclase and orthoclase mode of alkali-feldspar, respectively ($\Delta^{56}\text{Fe}_{\text{plagioclase-magnetite}} = 0.022 \times \text{Ab-1.15}$, $\Delta^{56}\text{Fe}_{\text{alkali-feldspar-magnetite}} = 0.026 \times \text{Or-1.46}$, Fig. 5a and b). This indicates that the iron isotopic fractionations between feldspar and magnetite depend on the composition of feldspar. Notably, the positive correlation between $\Delta^{56}\text{Fe}_{\text{plagioclase-magnetite}}$ and albite mode indicates iron isotopic composition is heavier in sodic plagioclase than in calcic plagioclase (Fig. 5a). A previous study revealed that the former has higher $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio than the latter (Hofmeister and Rossman, 1984). The $\Delta^{56}\text{Fe}_{\text{plagioclase-magnetite}}$ could depend on the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of plagioclase, because $\text{Fe}^{3+}$ has low coordination number and favors more heavy iron isotopes than $\text{Fe}^{2+}$. However, a similar explanation cannot be applied on alkali-feldspar, since its two end-members (potassic feldspar and sodic feldspar) both have high $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios (>95%, Hofmeister and Rossman, 1984). Variation of $\Delta^{56}\text{Fe}_{\text{alkali-feldspar-magnetite}}$ with orthoclase mode of alkali-feldspar can be attributed to the difference in $\text{Fe}–\text{O}$ bond strength between potassic feldspar and sodic feldspar. $\text{Fe}^{3+}$ occupies the $\text{T}$-site in feldspar. The $\text{T}$–$\text{O}$ interatomic distances in sanidine ($\text{T}_{1}\text{O}–\text{O}$: 1.651 Å, $\text{T}_{1}\text{m}–\text{O}$: 1.657 Å, $\text{T}_{2}\text{O}–\text{O}$: 1.638 Å, $\text{T}_{2}\text{m}–\text{O}$: 1.643 Å) are systematically shorter than those in albite ($\text{T}_{1}\text{O}–\text{O}$: 1.655 Å, $\text{T}_{1}\text{m}–\text{O}$: 1.657 Å, $\text{T}_{2}\text{O}–\text{O}$: 1.638 Å, $\text{T}_{2}\text{m}–\text{O}$: 1.643 Å) (e.g., Keefer and Brown, 1978). Accordingly, $\text{Fe}$–$\text{O}$ bonds are likely shorter and thus stronger in potassic feldspar than in sodic feldspar. Alkali-feldspar with higher Or % tends to have higher $\beta$ factor. Plagioclase in 07XM-1 is plotted off the trend defined by the other samples on Fig. 5a. This is explained here by the overprint of the temperature effect on isotopic fractionation, evidenced by the fact that 07XM-1 has the lowest two-feldspar equilibrium temperature (458 °C) among the four samples.

5.2.3. Fractionation between feldspar and biotite

To facilitate future applications of inter-mineral Fe isotopic data here, the fractionation factors between feldspar and biotite are also plotted, and their correlations with the compositions of feldspar are given ($\Delta^{56}\text{Fe}_{\text{plagioclase-biotite}} = 0.015 \times \text{Ab-0.48}$, $\Delta^{56}\text{Fe}_{\text{alkali-feldspar-biotite}} = 0.026 \times \text{Or-1.35}$, Fig. 5a and b). As noted in Section 5.2.1 and 5.2.2, variation of $\Delta^{56}\text{Fe}_{\text{feldspar-biotite}}$ reflects the combined compositional control from both biotite and feldspar.

5.3. Isotope effect of plagioclase accumulation

Rocks that experienced feldspar accumulation are common in nature, such as lunar and terrestrial anorthosite, some granites and some leucosomes from migmatites (e.g., Wiebe, 1980; Wu et al., 2005; Ohtake et al., 2009; Wang et al., 2013; Lee and Morton, 2015). Since feldspar has rather heavier iron isotopic composition than other rock-forming minerals, it is necessary to check whether feldspar accumulation can produce high $\delta^{56}\text{Fe}$ values of some igneous rocks. Leucosomes from Dabie migmatites with a feldspar accumulate origin yield high $\delta^{56}\text{Fe}$ values from $0.424 \pm 0.016\%e$ to $0.567 \pm 0.016\%e$. By contrast, the leucosome that represents pristine partial melt without substantial feldspar accumulation has a relatively normal $\delta^{56}\text{Fe}$ of $0.117\%e \pm 0.016\%e$, typical of granitic rocks. The four leucosomes with high $\delta^{56}\text{Fe}$ values have high SiO₂ contents (72.10–76.14 wt.%) and low FeO t concentrations (0.15–0.24 wt.%), indicating that a considerable amount of iron is present in feldspar. Combined with the iron isotopic composition results of feldspar in this study, feldspar accumulation can explain the high $\delta^{56}\text{Fe}$ values of these leucosomes. The iron isotopic data of leucosome-melanosome pairs could be used to assess iron isotopic fractionation during
partial melting of continental crust. However, the leucosomes may experience complex differentiation processes such as fractional crystallization, thus they may not represent pristine melts (Telus et al., 2012). Our results suggest feldspar accumulation can produce high $\delta^{56}$Fe leucosomes, and cautions should be taken when using migmatites to study iron isotope fractionation during crustal anatexis. Those intrusive rocks representing feldspar cumulates, e.g., anorthosites and some granites (e.g., Wiebe, 1980; Wu et al., 2005; Ohtake et al., 2009), are expected to have high $\delta^{56}$Fe values. Anorthosites from Paleoproterozoic Bushveld Complex in South Africa indeed have $\delta^{56}$Fe up to 0.27‰ (Stausberg et al., 2015), which can be explained by feldspar accumulation, considering the strong correlation between their bulk rock $\delta^{56}$Fe and modal mineralogy.

Lunar anorthosites have extremely high plagioclase proportions (>90%, Heiken et al., 1991), but they have an average $\delta^{56}$Fe value of 0.14‰ ($n = 3$, Poitrasson et al., 2004), which is only slightly higher than low-Ti basalts (average: 0.07‰, $n = 12$; Weyer et al., 2005; Liu et al., 2010). Unlike terrestrial feldspar, lunar anorthosite only contains Fe$^{3+}$ (Heiken et al., 1991), yielding $\Delta^{56}$Fe$_{plagioclase-pyroxene}$ smaller than 0.2‰ (Craddock et al., 2010). Therefore, plagioclase accumulation during lunar magmatism may only be able to produce minor iron isotopic fractionation.

The above observations demonstrate that heavy iron isotopic composition of feldspar could account for high $\delta^{56}$Fe values of some cumulates. Lee and Morton (2015) suggested that crystal accumulation may be more common in the origin of granites than what has been previously estimated. Therefore, it is important to examine whether feldspar-accumulation can account for high $\delta^{56}$Fe values of high-silica granite rocks. Theoretically, accumulation of plagioclase and alkali-feldspar would produce high $\delta^{56}$Fe values, high Sr, Ba content and high Eu/Eu$^*$ simultaneously. However, most high $\delta^{56}$Fe granitic rocks have low Sr, Ba contents and negative Eu anomalies, which doesn’t fit the predicted accumulation trend (Fig. 6a–c). This implies accumulation of feldspar cannot account for high $\delta^{56}$Fe values of most high-silica granitic rocks.

6. CONCLUSIONS

1. Feldspar has heavy iron isotopic compositions relative to the coexisting Fe–Mg minerals, with $\Delta^{56}$Fe$_{feldspar-biotite}$ = 0.56–1.33‰. The heavy iron isotopic signature of feldspar is due to their high Fe$^{3+}$/Fe$^{tot}$ ratio and low coordination number (tetrahedrally-coordinated) of Fe$^{3+}$.

2. Inter-mineral iron isotopic fractionations of magnetite–biotite, plagioclase–magnetite and alkali-feldspar–magnetite are correlated with the compositions of biotite, plagioclase and alkali-feldspar, respectively. This may reflect the compositional effect of mineral composition on the inter-mineral fractionation of Fe isotopes.

3. Leucosomes from Dabie migmatites with a feldspar accumulate origin have high $\delta^{56}$Fe values up to 0.567‰. High $\delta^{56}$Fe values are also predicted for other igneous rocks that are mainly composed of cumulate feldspar crystals, e.g., anorthosites. Feldspar accumulation, however, cannot explain high $\delta^{56}$Fe values of most high-silica granitic rocks reported in the literature, based on their low Sr, Ba contents and negative Eu anomalies.

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APPENDIX A. SUPPLEMENTARY DATA

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