Iron, zinc, magnesium and uranium isotopic fractionation during continental crust differentiation: The tale from migmatites, granitoids, and pegmatites

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Abstract

The causes of some stable isotopic variations in felsic rocks are not well understood. In particular, the origin of the heavy Fe isotopic compositions (i.e., high $\delta^{56}$Fe values, deviation in $\%$ of the $^{56}$Fe/$^{54}$Fe ratio relative to IRMM-014) of granites with $SiO_2 > 70$ wt.$\%$ compared with less silicic rocks is still debated. It has been interpreted to reflect isotopic fractionation during late stage aqueous fluid exsolution, magma differentiation, partial melting, or Soret (thermal) diffusion. The present study addresses this issue by comparing the Fe isotopic compositions of a large range of differentiated crustal rocks (whole rocks of migmatites, granitoids, and pegmatites; mineral separates) with the isotopic compositions of Zn, Mg and U. The samples include granites, migmatites and pegmatites from the Black Hills, South Dakota (USA), as well as I-, S-, and A-type granitoids from Lachlan Fold Belt (Australia). The nature of the protolith (i.e., I- or S-type) does not influence the Fe isotopic composition of granitoids. Leucosomes (partial melts in migmatites) tend to have higher $\delta^{56}$Fe values than melanosomes (melt residues) indicating that partial melting of continental crust material can possibly fractionate Fe isotopes. No clear positive correlation is found between the isotopic compositions of Mg, U and Fe, which rules out the process of Soret diffusion in the systems studied here. Zinc isotopes were measured to trace fluid exsolution because Zn can easily be mobilized by aqueous fluids as chloride complexes. Pegmatites and some granitic rocks with high $\delta^{56}$Fe values also have high $\delta^{66}$Zn values. In addition, high-SiO$_2$ granites show a large dispersion in the Zn/Fe ratio that cannot easily be explained by magma differentiation alone. These results suggest that fluid exsolution is responsible for some of the Fe isotopic fractionation documented in felsic rocks and in particular in pegmatites. However, some granites with high $\delta^{56}$Fe values have unFractionated $\delta^{66}$Zn values and were presumably poor in fluids (e.g., A-type). For these samples, iron isotopic fractionation during magma differentiation is a viable interpretation. Equilibrium Fe isotopic fractionation factors between silicic melts and minerals remain to be characterized to quantitatively assess the role of fractional crystallization on iron isotopes in granitoids.
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1. INTRODUCTION

With its complex redox chemistry, iron is a key element in biological and geochemical processes and its isotopic variations can be used to probe these interactions. Initial
studies found all terrestrial igneous rocks to have homogeneous Fe isotopic composition (Beard and Johnson, 1999, 2004; Beard et al., 2003), suggesting that Fe isotopes could be discriminative indicators of biological activity and low temperature aqueous processes, which can significantly fractionate Fe isotopes (Johnson et al., 2004; Dauphas and Rouxel, 2006; Anbar and Rouxel, 2007). However, growing evidence suggests that igneous processes such as partial melting, magmatic differentiation, and low temperature aqueous fluid exsolution can also impart measurable iron isotopic variations among bulk igneous rocks (Williams et al., 2004, 2005, 2009; Poitrasson and Freydiere, 2005; Weyer et al., 2005; Dauphas and Rouxel, 2006; Poitrasson, 2006; Schoenberg and von Blanckenburg, 2006; Schuessler et al., 2007, 2009; Weyer and Ionov, 2007; Heimann et al., 2008; Teng et al., 2008; Dauphas et al., 2009, 2010). This opens the prospect of using iron isotopes as petrogenetic tracers of mantle and crustal differentiation.

Poitrasson and Freydiere (2005) observed that several granites were isotopically heavier than the average $^{56}$Fe composition of igneous rocks and identified a positive correlation between $^{56}$Fe and SiO$_2$ wt.%. They suggested that fluids exsolved from the magma were responsible for removing isotopically light Fe from the crystallizing melt, resulting in a heavy granitic magma body. Heimann et al. (2008) found that magnetite from evolved granite rocks had high $^{56}$Fe values while Fe-silicates had $^{56}$Fe values close to the average $^{56}$Fe composition of igneous rocks, which they attributed to isotopic exchange between magnetite and fluid rich in ferrous chloride. Thus, these authors also concluded that fluid exsolution was responsible for high $^{56}$Fe values in evolved granites and rhyolites. Schuessler et al. (2009) found similar iron isotopic trends for Fe isotopes, but did not detect measurable variation in the isotopic composition of Li, which is easily mobilized by fluids. Based on the absence of a correlation between Li and Fe isotopic compositions, they ascribed these trends to fractional crystallization of a Fe-bearing phase that preferentially incorporated light Fe isotopes; thus, continually enriching the residual melt in the heavier isotopes of iron. Similar results were found for a basaltic system at Kilaeua Iki lava lake (Teng et al., 2008). In the latter study, the light Fe isotopic composition reflected diffusion-driven kinetic isotope fractionation during Fe-Mg exchange in olivine (Teng et al., 2011; Sio et al., 2011).

The present study addresses the range of hypotheses put forth to explain these iron isotopic variations by combining Fe, Zn, Mg and U isotopic data of migmatites, granitoids, and pegmatites to develop a more complete view of Fe isotopic fractionation during the formation and differentiation of felsic rocks. Particular attention is directed towards the following questions:

Does partial melting fractionate iron isotopes? This has been documented in mantle peridotites and arc lavas through correlations between $^{56}$Fe values and proxies of degree of partial melting (Weyer and Ionov, 2007; Dauphas et al., 2009). It is not known however whether iron isotopes are fractionated in the process of generating felsic melts. Migmatites may provide the opportunity to directly answer this question, as they represent highly metamorphosed rocks arrested in the process of generating granitic melts (Brown, 1994).

Does the nature of the protolith influence the iron isotopic composition of felsic rocks? It was suggested that during partial melting of the mantle, the iron isotopic composition of magmas was related to the degree of partial melting, the Fe$^{3+}$/Fe$^{2+}$ ratio, and oxygen buffering capacity (Dauphas et al., 2009). Is that true for felsic rocks? Do granites that were derived from sources with elevated Fe$^{3+}$/Fe$^{2+}$ ratios have higher $^{56}$Fe? To address this question, a comparison is made between S- and I-type granite rocks (Chappell and White, 2001) that are derived from sedimentary and igneous sources, which differ in their mineral assemblages and Fe$^{3+}$/Fe$^{2+}$ ratios (Flood and Shaw, 1975; Whalen and Chappell, 1988).

Is magmatic differentiation (fractional crystallization and restite unmixing), fluid exsolution or Soret (thermal) diffusion responsible for the correlation between iron isotopic composition and silica content? Magmatic differentiation should be supported by fractional crystallization models (Schoenberg and von Blanckenburg, 2006). The fluid exsolution hypothesis (Poitrasson and Freydiere, 2005; Heimann et al., 2008) requires that significant amounts of isotopically light iron be removed from the magma body. Pegmatites, which represent the latest stages of granitic magma evolution, should be particularly sensitive to such processes (Walker et al., 1989). Another means of testing the fluid exsolution hypothesis is to study the isotopic compositions of elements, such as Zn, that are mobile in such fluids (Nakano and Urabe, 1989; Shinozaki, 1994), and to search for correlations with iron isotopic variations. This is tested by comparing the Zn and Fe isotopic compositions of felsic rocks.

Finally, an alternative model to the standard view of granite formation was presented by Lundstrom (2009), who suggested that some granites form by a top-down thermal migration process. The model predicts that non-traditional stable isotope systems such as Fe, Mg and U should show signatures of thermal diffusion. To address this hypothesis, the isotopic compositions of Mg, U and Fe were measured in the same granite rocks. Magnesium, U and Fe isotopes show strong and correlated mass dependent fractionation during experiments of thermal diffusion in silicate melts (Richter et al., 2008, 2009; Huang et al., 2010; Lacks et al., 2012), thus providing a straightforward means of identifying Soret effect in geological processes (Dauphas et al., 2010).

2. SAMPLE SELECTION

2.1. I-, S- & A-type granites: bulk rocks and mineral separates

To determine whether the Fe isotopic compositions of granites depend on their source material, granitic rocks from the Silurian-Devonian Lachlan Fold Belt (LFB, Southeastern Australia) and Proterozoic Harney Peak Granite (Black Hills, South Dakota) were analyzed for their Fe isotopic compositions. These samples have been well characterized (Hine et al., 1978; Chappell, 1984; Nabelek...
and are divided into three groups according to their source rock (Chappell and White, 1974; Loiselle and Wones, 1979). I-type granites (nine samples; I1, I2, I3, I4, I5, I6, I7, I8, and I9) are derived from partial melting of infracrustal metagranitoid rocks. They are hornblende-bearing and have relatively high Ca and Na contents. S-type granites (11 samples; S1, S2, S3, S4, S5, S6, S7, S8, S9, HP49-A, and HP21-C) are derived from partial melting of supracrustal sedimentary source material that has been exposed to chemical weathering. They are generally more felsic than I-types and have low Ca and Na content relative to I-type granites due to aqueous removal of these elements during weathering of feldspars into clay minerals (Chappell and White, 2001). Another important difference between I- and S-type granites is that they tend to differ in their Fe$^{3+}$/Fe$^{2+}$ ratios. S-type granites generally have lower Fe$^{3+}$/Fe$^{2+}$ ratios (Whalen et al., 1992; Chappell and White, 1993; Sha and Chappell, 1998). The metasedimentary sources of S-type granites are generally rich in graphite (Flood and Shaw, 1975), which explains the more reducing conditions of their formation (French and Eugster, 1965). Classification of A-type granite (two samples; A1 and A2) is more complex as it also involves considerations of the tectonic setting (Loiselle and Wones, 1979). Whalen et al. (1987), Eby (1990) and Bonin (2007) provide detailed descriptions of the chemical and petrographic characteristics of A-type granites. They form in anorogenic environments, often in tensional regimes, are mildly alkaline, and their parental magmas are inferred to have been relatively anhydrous. There is considerable uncertainty regarding their origin and a unique petrogenetic model may not be appropriate. Some of the major models that have been proposed include melting of relatively anhydrous granulite meta-igneous residue left from a prior episode of melt extraction (Collins et al., 1982; Clemens et al., 1986; Whalen et al., 1987), melting of granulitic crust metamorphosed by mantle-derived alkaline fluids (Martin, 2006), derivation from basaltic magma by magmatic differentiation (Loiselle and Wones, 1979; Turner et al., 1992), and partial melting of crustal tonalitic-granodioritic rocks (Anderson, 1983; Creaser et al., 1991). The chemical compositions of most samples studied here are available in the literature (Hine et al., 1978; Chappell, 1984; Chappell and White, 1992, 1993; Nabelek et al., 1992; King et al., 1997; Sha and Chappell, 1999). However, when not available (four out of 22 samples studied; 14, 16, 17 and S7), the chemical compositions were measured at Service d’Analyse des Roches et des Minéraux, Nancy, France, using established protocols (Carignan et al., 2001). The SiO$_2$ concentrations of bulk samples range from 56 to 77 wt.%. In order to better understand the processes that control Fe isotopic fractionation in felsic rocks, mineral separates (magnetite, biotite and hornblende) from LFB granitoids (samples I1, I2, I3, I5 and A2) were also measured.

2.2. Migmatites and pegmatites

Migmatites are generally found in high-grade metamorphic terrains and are made up of leucosomes (L) that are dominated by large quartz crystals and are thought to represent partial melts, and melanosomes (M) that are dominated by biotite and sillimanite and are thought to represent the residues of partial melting. Although not sampled for this study, migmatites also consist of non-migmatised (non-separated) portions, called mesosomes, which consist of varying portions of quartz, biotite, sillimanite and plagioclase. Schists, which are compositionally very similar to mesosomes, were analyzed for this study. These schists are associated with both migmatites and granites of the Black Hills, South Dakota (Nabelek, 1999). Migmatites are important for studying melt segregation and processes governing granite genesis and differentiation. They represent rocks in which melt has segregated on a local scale but has not escaped from the system. Melting in migmatites begins at grain boundaries and as melting progresses, melt pockets combine to form a network of melt channels, which subsequently can migrate to produce granitic bodies (Sawyer, 1991, 1994; Brown, 1994, 2002).

A total of 11 migmatite components (five leucosome-melanosome pairs and one unpaired leucosome) and two schists from the Black Hills region of South Dakota were studied. Melanosomes are very similar in chemical composition, while leucosomes show more variations (e.g., 115-1-L and 131-1-L have very high concentrations of K$_2$O and Na$_2$O and 118-1-L has high concentrations of CaO and P$_2$O$_5$ compared to other leucosomes). The bulk SiO$_2$ content ranges from 72 to 79 wt.% for leucosomes, from 47 to 62 wt.% for melanosomes and from 63 to 69 wt.% for schists. The FeO concentrations range from 0.3 to 6.0 wt.% for leucosomes, and from 8 to 17 wt.% for melanosomes. Schists fall in between with ~5.5 wt.% FeO.

Pegmatites are coarse-grained rocks, typically associated spatially and compositionally with granites. Large quartz, feldspar and muscovite crystals make up the bulk of most pegmatites. They have been interpreted as the products of extreme crystal fractionation of granitic magmas (London, 1996, 2005). They provide insight to the final stages of granite differentiation, which is heavily influenced by fluid exsolution processes (Norton and Redden, 1990). Such processes have been suggested as the major mechanism for producing variations in the Fe isotopic composition of evolved felsic rocks (Poitrasson and Freydier, 2005; Heimann et al., 2008).

To address the influence of fluid exsolution on the Fe isotopic composition, we studied four samples from simple pegmatites (81BH 5-1, 81BH 6-3, 81BH 6-4, WC-9) and three wall zone samples from the more complex, zoned, Tin Mountain pegmatite (81BH9-2, 81BH10-3, 82BH43-1), which are closely associated (~12 km southwest) with the Proterozoic Harney Peak Granite and migmatites from the Black Hills (Walker, 1984; Teng et al., 2006). The Tin Mountain pegmatite consists of five zones (wall zone, first intermediate zone, second intermediate zone, third intermediate zone, and core), which are characterized by their distinct mineral assemblages, with the wall zone crystallizing first. Oxygen isotopic thermometry yields crystallization temperatures ranging from ~660 °C in the outer regions to 500 °C in the core (Walker et al., 1986), while some temperatures as low as 350 °C have been reported (Sirbescu et al., 1992; Chappell and White, 1993; Sha and Chappell, 1999).
and Nabelek, 2003). Trace-element data (Rb, Li, Sr, and Ba) suggest two possible origins for the Tin Mountain Pegmatite: low degree partial melting of metasedimentary rocks that experienced moderate fractional or equilibrium crystallization, or derivation from the Harney Peak Granite through multiple stages of crystal-liquid fractional crystallization (Walker et al., 1989).

Pegmatites from Little Nahanni, Logan Mountains, Northwest Territories, Canada (ca. 82 Ma) were also studied (six samples; P389704, P389910, P389913, P389726, P389739, and P389734). They have been characterized in detail by Groat et al. (2003). These samples are rare-element pegmatites, which generally have lower crystallization temperatures compared to simple and zoned pegmatites. The nearest granitic intrusion is 4.7 km, 84–87 Myr and ~15 km away. Rare-element granitic pegmatites typically contain high concentrations of H_2O, Li, B, F, and P. They solidify under chemical and physical conditions that differ from predictable paths of crystallization for normal felsic melts. The mechanism for the formation of these pegmatites is not well understood, but extreme fractional crystallization is the preferred interpretation (Černý, 1985, 1991). Chemical evolution of these pegmatites shows systematic trends of Mg and Fe decreasing, while Al, Mn, Rb and Cs increase from wall to core (Groat et al., 2003). Little Nahanni pegmatites are divided into spodumene-bearing and spodumene-free, but apart from this distinction, they are similar in their major element composition to each other and to pegmatites from the Black Hills. The SiO_2 concentrations of all pegmatites measured for this study range from 68 to 74 wt.% and FeO concentrations range from 0.3 to 2.2 wt.%.

The major element compositions for all samples analyzed in this study are compiled in Table 1. A total alkali vs. SiO_2 diagram (Fig. 1) provides an illustration of the compositional diversity of the samples studied.

### 3. ANALYTICAL METHODS

Samples were crushed to a fine powder in an agate mortar. Mafic minerals from samples 11, 12, 13, 15 and A2 were separated using a combination of magnetic separation, manual extraction and density separation for Fe isotopic analysis. Mineral mode compositions were estimated by analyzing thin sections of these rocks with an optical microscope. A chart was used as a visual aid to help determine the percentages of the Fe-bearing minerals in each thin section. The modal abundances range from 1–3% for magnetite, 6–20% for biotite and 10–18% for hornblende. These numbers are rough estimates. The samples were crushed, sieved under water, and fractions between 125 and 250 μm were collected. Magnetite was separated by covering a hand magnet with weighing paper and rastering it across the grains. A Frantz magnetic separator was used on each sample to separate mafic from non-mafic mineral fractions. Biotite was then separated from the mafic minerals by simply pouring out the sample on a sheet of paper and continuously tapping and rotating the paper at various angles until biotite was all that remained since its sheet silicate crystal structure allows it to stick to the sheet of paper. Pure hornblende was collected through heavy liquid separation and was then handpicked from the high-density fraction under an optical microscope.

### 3.1. Sample preparation and instrument analysis

The samples were prepared for iron isotope analyses according to the procedure described in Dauphas et al. (2004, 2009). Sizes of the sample powder aliquots ranged from 10 to 20 mg for geostandards, from 20 to 30 mg for plutonic rocks, from 21 to 35 mg for migmatites, from 18 to 70 mg for pegmatites, and from 2 to 9 mg for the mineral separates. Blanks and sets of geostandards were measured together with samples. The blank contribution (~40 ng) to iron isotope analyses was always negligible. After complete dissolution by step-wise acid digestion, the samples were loaded in HCl 6 M on columns filled with AG1-X8 anion exchange resin. After elution of matrix elements and direct isobars in 8 ml of HCl 6 M, iron was recovered from the resin in 9 ml total volume of HCl 0.4 M. This purification step was repeated a second time. All Fe isotope measurements were collected using the Neptune MC-ICPMS at the Origins Laboratory of the University of Chicago. The samples were introduced into the mass spectrometer using a 100 μl/min Teflon nebulizer inside a quartz cyclonic-scott spray chamber. The measurements were performed in medium resolution mode to resolve interferences of ArN, ArO, and ArOH on ^{54}Fe, ^{56}Fe, and ^{57}Fe. Instrumental mass fractionation was corrected for using standard-sample bracketing. Iron isotopic variations are expressed in δ-notation, δFe = [(Fe/^{54}Fe)sample/(Fe/^{54}Fe)_IRMM-014 − 1] × 10^3, where i refers to mass 56 or 57 and IRMM-014 is a reference material with near-chondritic iron isotopic composition (Dauphas and Rouxel, 2006; Craddock and Dauphas, 2010). Typical precisions on δ^{56}Fe and δ^{57}Fe are ±0.03 and ±0.05 (95% confidence interval), respectively. Dauphas et al. (2009) showed that the Fe isotopic measurements are accurate at this level. Several geostandards were also analyzed and these have iron isotopic compositions that are indistinguishable from recommended values (Craddock and Dauphas, 2010).

For zinc, the experimental procedures were adapted from those described by Moynier et al. (2006). Powdered samples weighing 200–300 mg were leached in water for 5 min in an ultrasonic bath. The leaching solution was removed and the residue was dissolved for 48 h in HNO_3/HF at 130 °C. The samples were loaded in 1.5 M HBr on AG-IX8 200–400 mesh and Zn was extracted in 0.5 M HNO_3. The same process was repeated to further purify Zn. Zinc isotopic compositions were measured on a Nu Plasma High Resolution MC-ICP-MS at the Ecole Normale Supérieure de Lyon (France), as described in Maréchal et al. (1999). The total blank is ~10 ng, which is negligible compared to the total amount of Zn in the samples (>10 μg). Isotope ratios are expressed as relative deviations, in δ-notation, from the Zn JMC-Lyon standard as:

$$\delta^{i}Zn = \left(\frac{(^{64}Zn/^{64}Zn)_{\text{sample}}}{(^{64}Zn/^{64}Zn)_{\text{JMC-Lyon}}} - 1\right) \times 10^3,$$
Table 1  
Iron isotope and major element compositions of geostandards, granitoids, pegmatites and migmatites.

<table>
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<th>Sample type</th>
<th>Name</th>
<th>$\delta^{56}\text{Fe}^{16}$</th>
<th>$\delta^{57}\text{Fe}^{16}$</th>
<th>Averages of replicate analyses*</th>
<th>Major element compositions (wt.%)</th>
<th>References</th>
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<tbody>
<tr>
<td>Granitoids</td>
<td>Tonalite, Tuross Head</td>
<td>0.123 ± 0.020 0.184 ± 0.026</td>
<td>60.13 16.42 2.04 3.73 0.11 3.27 5.91 3.94</td>
<td>1.41 0.99 0.28 1.03 0.18 0.28</td>
<td>Sha and Chappell (1999)</td>
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<tr>
<td>Granodiorite, Yurammie</td>
<td>0.081 ± 0.021 0.120 ± 0.038</td>
<td>65.27 15.22 1.76 2.83 0.09 2.01 4.40 2.74</td>
<td>3.43 0.58 0.19 1.26 0.09 0.20</td>
<td>Sha and Chappell (1999)</td>
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<td>Granodiorite, Glenbog</td>
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<td>67.39 14.48 1.58 3.02 0.09 1.72 4.32 2.63</td>
<td>2.99 0.53 0.11 0.95 0.13 0.08</td>
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<td>Adamellite, Wallagaraugh</td>
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<td>4.71 0.66 0.00</td>
<td>This study</td>
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<td>2.01 0.54 0.11 1.20 0.20 0.10</td>
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<td>2.99 0.53 0.11 0.95 0.13 0.08</td>
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Table 1 (Continued)

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<th>Sample type</th>
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<th>(\delta^{57}\text{Fe})</th>
<th>Averages of replicate analyzes*</th>
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<td>0.137 ± 0.027 0.206 ± 0.042</td>
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<td>(Spodumene-bearing)</td>
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<td>Migmatites</td>
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<td>Leucosomes, Black Hills, S. Dakota, USA</td>
<td>0.480 ± 0.029</td>
<td>0.738 ± 0.050</td>
<td>78.74</td>
<td>18.35</td>
<td>0.80</td>
</tr>
<tr>
<td>No melanosome pair</td>
<td>Schists, Black Hills, S. Dakota, USA</td>
<td>0.146 ± 0.031</td>
<td>0.253 ± 0.060</td>
<td>69.34</td>
<td>14.67</td>
</tr>
<tr>
<td>Schists, Black Hills, S. Dakota, USA</td>
<td>0.158 ± 0.028</td>
<td>0.213 ± 0.052</td>
<td>63.89</td>
<td>17.39</td>
<td>6.14</td>
</tr>
</tbody>
</table>

Notes: Error bars on \(\delta^{56}\text{Fe}\) and \(\delta^{57}\text{Fe}\) are 95% confidence intervals. * Replicates are for newly digested samples.
External reproducibilities (2SD) of δ$^{66}$Zn and δ$^{68}$Zn are estimated from 10 replicate measurements of one sample that had been split into 10 separate aliquots and measured independently by MC-ICP-MS (Herzog et al., 2009). Magnesium isotopic analyses were performed on a Nu Plasma MC-ICP-MC at the Isotope Laboratory of the University of Arkansas, Fayetteville, following established procedures (Yang et al., 2009; Li et al., 2010; Teng et al., 2010b). The digested samples were taken up in 1 M HNO$_3$ for column purification. Separation of Mg was achieved by cation exchange chromatography with Bio-Rad 200–400 mesh AG50 W-X8 resin in 1 M HNO$_3$. This step was repeated twice for each sample. The procedural blank was less than 10 ng (i.e., less than 0.1% of Mg loaded on the column). Geostandards were processed with samples to verify that the column purification does not introduce spurious effects (Teng et al., 2010a). Magnesium isotopic compositions were analyzed by the standard bracketing method and data are reported in standard δ-notations in permil relative to DSM3, a synthetic standard:

$$
\delta^{i}Mg = \left( \frac{^{i}Mg}{^{24}Mg} \right)_{sample} / \left( \frac{^{i}Mg}{^{24}Mg} \right)_{DSM3} - 1 \right) \times 1000,
$$

where $i$ refers to mass 25 or 26. The long-term precision, based on replicate analyses of synthetic solutions, minerals and rock standards, is ±0.07‰ (2SD). Two 234U notation relative to the U standard CRM-112a (also named SRM960, NBL112-a or CRM-145).

The typical precision on δ$^{238}$U is ±0.05‰ (2SD). Two granite geostandards were analyzed (G-2 and JG-1; Table 2) and show reasonable agreement with the data reported by Weyer et al. (2008). Comparison of a large record of geostandards analyzed at the Origins Laboratory shows no systematic bias when compared to literature data.

### 3.2. Replicates and geostandards

Samples that were especially difficult to dissolve were replicated to ensure reproducibility of δ$^{56}$Fe measurements. Replicates were done mostly for pegmatite samples. Out of five replicate analyses, only one (P389704) has a replicate value that does not agree within error (i.e., δ$^{56}$Fe = +0.202 ± 0.041‰ vs. +0.118 ± 0.036‰). The reason for this is unclear but could be due to incomplete digestion. The averages of the replicate analyses are used in the figures (Table 1).

Accuracy and precision of sample preparation and isotopic measurements were also evaluated by analyzing several international standards, such as AC-E, BE-N, BHVO-1, BHVO-2, DRC-1, DR-N, GA, and GSN. BHVO-1 was measured during each run and the replicate compositions agree within analytical uncertainty. The measured δ$^{56}$Fe values of the standards (Table 2) agree within error with previously published values (Craddock and Dauphus, 2010 and references therein).
Table 2
Iron, Zn, Mg and U isotopic compositions of geostandards.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Name</th>
<th>$\delta^{56}\text{Fe}$ ($%_{\text{PDB}}$)$^a$</th>
<th>$\delta^{57}\text{Fe}$ ($%_{\text{PDB}}$)</th>
<th>$\delta^{65}\text{Fe}$ ($%_{\text{PDB}}$)</th>
<th>$\delta^{66}\text{Zn}$ ($%_{\text{PDB}}$)$^b$</th>
<th>$\delta^{68}\text{Zn}$ ($%_{\text{PDB}}$)</th>
<th>$\delta^{25}\text{Mg}$ ($%_{\text{PDB}}$)$^c$</th>
<th>$\delta^{26}\text{Mg}$ ($%_{\text{PDB}}$)</th>
<th>$\text{U}$ (ppm)</th>
<th>$\delta^{238}\text{U}$ ($%_{\text{PDB}}$)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granite, Ailsa Craig, Scotland</td>
<td>AC-E</td>
<td>0.311 ± 0.027</td>
<td>0.471 ± 0.037</td>
<td>0.318 ± 0.025</td>
<td>0.479 ± 0.035</td>
<td>0.355 ± 0.065</td>
<td>0.556 ± 0.115</td>
<td>0.192 ± 0.045</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basalt, Essey-la-Cote, France</td>
<td>BE-N</td>
<td>0.162 ± 0.039</td>
<td>0.242 ± 0.060</td>
<td>0.146 ± 0.024</td>
<td>0.210 ± 0.036</td>
<td>0.466 ± 0.092</td>
<td>0.849 ± 0.302</td>
<td>0.192 ± 0.045</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basalt, Hawaii, USA</td>
<td>BHVO-1</td>
<td>0.091 ± 0.028</td>
<td>0.150 ± 0.040</td>
<td>0.118 ± 0.013</td>
<td>0.170 ± 0.019</td>
<td>0.135 ± 0.031</td>
<td>0.194 ± 0.045</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basalt, Hawaii, USA</td>
<td>BHVO-2</td>
<td>0.120 ± 0.052</td>
<td>0.173 ± 0.055</td>
<td></td>
<td></td>
<td>0.294 ± 0.092</td>
<td>0.601 ± 0.302</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolerite, North Carolina, USA</td>
<td>DNC-1</td>
<td>0.065 ± 0.039</td>
<td>0.106 ± 0.059</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diorite, Neuntelsein, France</td>
<td>DR-N</td>
<td>0.126 ± 0.039</td>
<td>0.202 ± 0.059</td>
<td></td>
<td></td>
<td>0.288 ± 0.092</td>
<td>0.502 ± 0.302</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc-alkaline granite, Voges Mountains, France</td>
<td>GA</td>
<td>0.137 ± 0.031</td>
<td>0.195 ± 0.045</td>
<td></td>
<td></td>
<td>0.267 ± 0.092</td>
<td>0.585 ± 0.302</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Granite, France</td>
<td>GSNN</td>
<td>0.152 ± 0.041</td>
<td>0.239 ± 0.047</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Trachyte, Mont Dore, France</td>
<td>MDO-G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.344 ± 0.092</td>
<td>0.773 ± 0.302</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Serpentinite, Scotland</td>
<td>UB-N</td>
<td>0.380 ± 0.092</td>
<td>0.726 ± 0.302</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ptitsurie Microgabbrro, Scotland</td>
<td>PM-S</td>
<td>0.444 ± 0.092</td>
<td>0.936 ± 0.302</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sill Dolerite, England synthetic standard</td>
<td>DSM-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.173 ± 0.092</td>
<td>0.372 ± 0.302</td>
<td></td>
<td></td>
<td>$-0.01 ± 0.07$ , $-0.01 ± 0.09$</td>
</tr>
<tr>
<td>Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:1:0.1</td>
<td>KH setp22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.18 ± 0.07</td>
<td>-0.33 ± 0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olivine, Kilbourne Hole, New Mexico, USA</td>
<td>G2</td>
<td>1.86 ± 0.01</td>
<td>-0.11 ± 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sori Granodiorite, Japan</td>
<td>JG-1</td>
<td>4.00 ± 0.02</td>
<td>-0.30 ± 0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Error bars on $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ are 95% confidence intervals.

$^b$ External reproducibilities (2SD) of ±0.09$^{\%}_{\text{PDB}}$ for $\delta^{66}\text{Zn}$ and ±0.3$^{\%}_{\text{PDB}}$ for $\delta^{68}\text{Zn}$ are estimated from 10 replicate measurements of one sample that had been split into 10 separate aliquots and measured independently by Herzog et al. (2009).

$^c$ External reproducibilities (2SD) of 0.06$^{\%}_{\text{PDB}}$ for $\delta^{25}\text{Mg}$ and 0.07$^{\%}_{\text{PDB}}$ for $\delta^{26}\text{Mg}$ is based on replicate analyses of synthetic solutions, mineral and rock standards reported in Yang et al. (2009) and Teng et al. (2010a). 2SD = 2 times the standard deviation of the population of 4 repeat measurements of a sample solution.

$^d$ External reproducibilities (2SD) of 0.05$^{\%}_{\text{PDB}}$ for $\delta^{238}\text{U}$ is based on numerous (>250) replicate measurements of the bracketing standard spiked at the same level as the samples.

* Replicates are for newly digested sample.
Fig. 2. $\delta^{56}\text{Fe}$ vs. SiO$_2$ wt.% of migmatites, granitoids and pegmatites measured in this study compared to results of previous studies for silicic plutonic and volcanic rocks (Poitrasson and Freyder, 2005; Heimann et al., 2008; Sossi et al., 2012). The shaded area represents the $\delta^{56}\text{Fe}$ value of terrestrial basalts (MORBs) of $+0.110 \pm 0.018$ (Dauphas et al., 2009). Granitic rocks become enriched in $\delta^{56}\text{Fe}$ with increasing SiO$_2$ wt.% (Fig. 2), which is in agreement with previous work. The $\delta^{56}\text{Fe}$ values of leucosomes are consistently heavier than average granites and MORBs, while the $\delta^{56}\text{Fe}$ values of melanosomes are scattered. Dashed lines connect leucosomes to their associated melanosomes. Schists are slightly heavier than MORBs, but similar in composition to average granitic rocks.

4. RESULTS

4.1. Iron isotopic compositions of felsic rocks

The Fe isotopic compositions of 22 granitic rocks (I-, S-, and A-type), 11 migmatite components (six leucosomes and five melanosomes), and 13 samples of pegmatites are reported in Table 1 and plotted in Fig. 2. The results for geostandards are reported in Table 2 and 14 mineral separates (five biotite, four amphibole, and five magnetite) are reported in Table 3. All samples follow mass-dependent fractionation, i.e., $\delta^{56}\text{Fe} = (+1.49 \pm 0.09) \times \delta^{56}\text{Fe}^\text{Mg}$. 

4.1.1. Granitoids

The $\delta^{56}\text{Fe}$ values of granitic rocks measured in this study range from $+0.064 \pm 0.021$ to $+0.305 \pm 0.022$ (95% confidence intervals). The range of $\delta^{56}\text{Fe}$ values for I-type granitoids is from $+0.064 \pm 0.021$ to $+0.193 \pm 0.021$. S-type granitoids have a similar range of $\delta^{56}\text{Fe}$ values (from $+0.072 \pm 0.021$ to $+0.240 \pm 0.041$). Poitrasson and Freyder (2005) and Heimann et al. (2008) found that plutonic and volcanic rocks with $>70$ wt.% SiO$_2$ had high $\delta^{56}\text{Fe}$ values. This study obtained similar results (Fig. 2) although some granitoids between 70 and 75 wt.% SiO$_2$ did not show the expected enrichment in heavy Fe isotopes. The $\delta^{56}\text{Fe}$ values of most of the granitic rocks measured in this study lie within the range of MORBs ($0.110 \pm 0.018$) (Dauphas et al., 2009) (Fig. 2).

4.1.2. Pegmatites

The iron isotopic compositions of pegmatites from the Black Hills are heavier than the average igneous rock composition with $\delta^{56}\text{Fe}$ values ranging from $+0.151 \pm 0.054$ to $+0.385 \pm 0.054$ (Fig. 2). The “rare-element” pegmatites from Little Nahanni have a range of $\delta^{56}\text{Fe}$ values between $-0.067 \pm 0.027$ and $+0.215 \pm 0.052$. It comprises the only pegmatite sample with a negative $\delta^{56}\text{Fe}$ value. They have been classified as spodumene-bearing and non-spodumene-bearing (Groat et al., 2003; see Table 1), but this classification does not seem to influence the $\delta^{56}\text{Fe}$ composition. Rare-element granitic pegmatites, like those from Little Nahanni, contain high concentrations of volatile elements, such as H$_2$O, Li, B, F, and P (Groat et al., 2003), which may explain the scatter in their $\delta^{56}\text{Fe}$ compositions (Fig. 2).

Pegmatites from both the Black Hills and Little Nahanni show no obvious correlation between $\delta^{56}\text{Fe}$ and SiO$_2$ wt.%, or any other major oxides or trace elements.

4.1.3. Migmatites

The Fe isotopic compositions of thirteen migmatite components from the Black Hills, South Dakota were measured (Fig. 2): six leucosomes, five melanosomes and two schists. The $\delta^{56}\text{Fe}$ values of the leucosomes range from $+0.246 \pm 0.031$ to $+0.480 \pm 0.029$. Melanosomes have $\delta^{56}\text{Fe}$ compositions ranging from $+0.077 \pm 0.029$ to $+0.302 \pm 0.028$. The two schists have an intermediate $\delta^{56}\text{Fe}$ composition of $+0.153 \pm 0.021$. Ten of the 13 migmatite components are leucosomes–melanosomes pairs (i.e., the leucosomes and melanosomes are spatially related to each other). The differences between $\delta^{56}\text{Fe}$ values for associated melanosomes and leucosomes range from $+0.038 \pm 0.056$ to $+0.196 \pm 0.058$. The Fe isotopic compositions of leucosomes are systematically heavier than melanosomes compositions. Three of the five pairs do not overlap in composition. Leucosome $\delta^{56}\text{Fe}$ values overlap with the heaviest granite and pegmatites. Unlike granitoids and pegmatites, none of the leucosome Fe isotopic compositions overlap with MORBs. Melanosome Fe isotopic compositions vary widely, some are indistinguishable from MORBs and others are comparable to the heaviest granites and pegmatites. Schists are slightly heavier than MORBs (Fig. 2).

4.1.4. Mineral separates

Magnetite was found to have the highest $\delta^{56}\text{Fe}$ composition with values that range from $+0.214 \pm 0.026$ to $+0.645 \pm 0.026$ (Fig. 3). Without considering A2, which has an anomalously high $\delta^{56}\text{Fe}$ value for biotite ($+0.249 \pm 0.029$), the range for biotite is from $-0.022 \pm 0.023$ to $+0.056 \pm 0.029$. The fractionation between magnetite and biotite ($\Delta^{56}\text{Fe}_{\text{mag-bt}}$) ranges between $+0.234 \pm 0.032$ and $+0.396 \pm 0.037$. Hornblende $\delta^{56}\text{Fe}$ values range from $-0.001 \pm 0.023$ to $+0.076 \pm 0.029$ and are very similar in compositions to biotite. Iron isotopic fractionation between biotite and amphibole ($\Delta^{56}\text{Fe}_{\text{bt-amph}}$) ranges between $-0.048 \pm 0.041$ and $+0.030 \pm 0.041$. The iron isotope measurements of mineral separates agree with previous results of Heimann et al. (2008).

To assess whether all of the major Fe-bearing minerals in each sample were accounted for, the bulk $\delta^{56}\text{Fe}$ value calculated from mineral mode analysis and the Fe isotopic
Table 3
Fe isotopic compositions of mineral separates from granitoids.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Name</th>
<th>$\delta^{56}$Fe ($^{%}$) (mineral)</th>
<th>$\delta^{57}$Fe ($^{%}$) (mineral)</th>
<th>$\delta^{56}$Fe ($^{%}$) bulk (measured)</th>
<th>Density ($\text{g/cm}^{3}$)</th>
<th>Fe Concentration (g/g)</th>
<th>Mineral mode (%)**</th>
<th>Fraction of Fe (mineral)</th>
<th>$\delta^{56}$Fe ($^{%}$) bulk (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amphibole, Tonalite</td>
<td>I1-Amph</td>
<td>0.053 ± 0.023</td>
<td>0.086 ± 0.036</td>
<td>0.123 ± 0.02</td>
<td>3.3</td>
<td>0.107</td>
<td>18</td>
<td>0.272</td>
<td>0.147 ± 0.040</td>
</tr>
<tr>
<td>Biotite, Tonalite</td>
<td>I1-Bt</td>
<td>0.045 ± 0.023</td>
<td>0.073 ± 0.036</td>
<td></td>
<td>3.0</td>
<td>0.129</td>
<td>18</td>
<td>0.301</td>
<td></td>
</tr>
<tr>
<td>Magnetite,</td>
<td>I1-Mgt</td>
<td>0.278 ± 0.023</td>
<td>0.423 ± 0.036</td>
<td></td>
<td>5.2</td>
<td>0.636</td>
<td>3</td>
<td>0.427</td>
<td></td>
</tr>
<tr>
<td>Amphibole,</td>
<td>I2-Amph</td>
<td>−0.001 ± 0.023</td>
<td>0.001 ± 0.036</td>
<td>0.081 ± 0.021</td>
<td>3.3</td>
<td>0.113</td>
<td>10</td>
<td>0.215</td>
<td>0.093 ± 0.042</td>
</tr>
<tr>
<td>Biotite, Granodiorite</td>
<td>I2-Bt</td>
<td>−0.022 ± 0.023</td>
<td>−0.038 ± 0.036</td>
<td></td>
<td>3.0</td>
<td>0.121</td>
<td>15</td>
<td>0.316</td>
<td></td>
</tr>
<tr>
<td>Magnetite,</td>
<td>I2-Mgt</td>
<td>0.214 ± 0.026</td>
<td>0.324 ± 0.041</td>
<td></td>
<td>5.2</td>
<td>0.520</td>
<td>3</td>
<td>0.469</td>
<td></td>
</tr>
<tr>
<td>Amphibole,</td>
<td>A2-Bt</td>
<td>0.249 ± 0.026</td>
<td>0.380 ± 0.041</td>
<td>0.305 ± 0.022</td>
<td>3.0</td>
<td>0.107</td>
<td>6</td>
<td>0.455</td>
<td>0.465 ± 0.037</td>
</tr>
<tr>
<td>Magnetite,</td>
<td>A2-Mgt</td>
<td>0.645 ± 0.026</td>
<td>0.945 ± 0.041</td>
<td></td>
<td>5.2</td>
<td>0.444</td>
<td>1</td>
<td>0.545</td>
<td></td>
</tr>
<tr>
<td>Amphibole,</td>
<td>I3-Amph</td>
<td>0.026 ± 0.029</td>
<td>0.051 ± 0.036</td>
<td>0.112 ± 0.021</td>
<td>3.3</td>
<td>0.124</td>
<td>16</td>
<td>0.338</td>
<td>0.163 ± 0.050</td>
</tr>
<tr>
<td>Biotite, Tonalite</td>
<td>I3-Bt</td>
<td>0.056 ± 0.029</td>
<td>0.071 ± 0.036</td>
<td></td>
<td>3.0</td>
<td>0.141</td>
<td>16</td>
<td>0.352</td>
<td></td>
</tr>
<tr>
<td>Magnetite,</td>
<td>I3-Mgt</td>
<td>0.433 ± 0.029</td>
<td>0.642 ± 0.036</td>
<td></td>
<td>5.2</td>
<td>0.573</td>
<td>2</td>
<td>0.310</td>
<td></td>
</tr>
<tr>
<td>Amphibole,</td>
<td>I5-Amph</td>
<td>0.076 ± 0.029</td>
<td>0.116 ± 0.036</td>
<td>0.067 ± 0.02</td>
<td>3.3</td>
<td>0.123</td>
<td>16</td>
<td>0.440</td>
<td>0.079 ± 0.050</td>
</tr>
<tr>
<td>Biotite, Tonalite</td>
<td>I5-Bt</td>
<td>0.028 ± 0.029</td>
<td>0.016 ± 0.036</td>
<td></td>
<td>3.0</td>
<td>0.108</td>
<td>20</td>
<td>0.443</td>
<td></td>
</tr>
<tr>
<td>Magnetite,</td>
<td>I5-Mgt</td>
<td>0.283 ± 0.029</td>
<td>0.409 ± 0.041</td>
<td></td>
<td>5.2</td>
<td>0.331</td>
<td>1</td>
<td>0.118</td>
<td></td>
</tr>
</tbody>
</table>

Notes: Bulk Fe isotopic data calculated using the fraction of Fe and the $\delta^{56}$Fe for each mineral. Error bars on $\delta^{56}$Fe and $\delta^{57}$Fe are 95% confidence intervals.

* Averages from Nesse (2000).

** Mineral modes were determined by examining thin sections under an optical microscope and estimating what percentages of the minerals occupy the thin sections.
compositions of mineral separates were compared with the measured bulk rock compositions. The mineral mode, the density of each mineral and the Fe concentration of each mineral give the fraction of Fe locked in each mineral, $(f_{Fe,x})$. A simple mass balance equation, $\delta^{56}\text{Fe}_{\text{bulk}} = \delta^{56}\text{Fe}_{\text{mgt}}/f_{\text{Fe,mgt}} + \delta^{56}\text{Fe}_{\text{amph}}/f_{\text{Fe,amph}} + \delta^{56}\text{Fe}_{\text{bt}}/f_{\text{Fe,bt}}$, was used to calculate the $\delta^{56}\text{Fe}$ bulk value from the compositions of the minerals separates (mgt refers to magnetite, amp to amphibole, and bt refers to biotite). Most of the calculated bulk $\delta^{56}\text{Fe}$ measurements are within the range of the measured $\delta^{56}\text{Fe}$ values (Table 3). Predicted values that are slightly inconsistent with measured values probably reflect inaccuracy in mineral mode estimation using visual charts (see “Methods” for the technique used to estimate the mineral modes).

### 4.2. Zinc isotopic compositions of felsic rocks

Zinc isotopic compositions were determined for 19 granitoids, three migmatite components, five pegmatites...
granites and migmatites by an average of lap with those of granitic rocks. Pegmatites are heavier than is no clear correlation between compositions of migmatites (average +0.23 ± 0.05 &d). M. Telus et al. / Geochimica et Cosmochimica Acta 97 (2012) 247–265

Fig. 5. δ66Zn vs. δ56Fe. Pegmatites and some granitic rocks have high δ66Zn and δ56Fe values. Since Zn is easily mobilized by aqueous fluids, this correlation suggests that fluid exsolution may be responsible for the iron isotope variations measured in some felsic rocks, as suggested by Poitrasson and Freydier (2005) and Heimann et al. (2008). However, some samples (e.g., A-type granites and migmatites) have high δ56Fe values, but unfracti-
ated δ66Zn values. For these samples, fractional crystallization is the most likely cause of iron isotopic fractionation.

Fig. 6. δ56Mg vs. SiO2 wt.% for granitic rocks compared to previous studies by Shen et al. (2009), Li et al. (2010) and Liu et al. (2010). The δ56Mg values for the I- and S-type granitoids from this study are indistinguishable from MORBs (−0.25 ± 0.07‰, Teng et al., 2010a,b). Sample A2 and many other A-type granites (Li et al., 2010) have significantly higher δ56Mg values than MORBS.

(Table 4, δ66Zn = (+1.80 ± 0.32) × δ56Zn), and eight geo-
standards (Table 2). The range in δ66Zn for granitic rocks is between +0.12‰ and +0.49‰ (2SD) and the range for pegmatites is from +0.53‰ to +0.88‰. The Zn isotopic compositions of migmatites (average +0.23 ± 0.05‰) overlap with those of granitic rocks. Pegmatites are heavier than granitoids and migmatites by an average of −0.4‰. There is no clear correlation between δ66Zn and SiO2 wt.% as observed for δ56Fe (Fig. 4). There is however a relationship between δ66Zn and δ56Fe for pegmatites (Fig. 5) in so much that samples with high δ56Fe values also have high δ66Zn values. For granites and migmatites, the systematics is less clear with some samples showing slightly heavy δ66Zn values, but for the most part, high δ56Fe values are not associated with high δ66Zn values.

Table 6

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Name</th>
<th>U(ppm)</th>
<th>δ238U/235U (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granitoids</td>
<td>I1</td>
<td>1.518 ± 0.010</td>
<td>−0.363 ± 0.033</td>
</tr>
<tr>
<td></td>
<td>I2</td>
<td>2.065 ± 0.015</td>
<td>−0.272 ± 0.033</td>
</tr>
<tr>
<td></td>
<td>I3</td>
<td>2.527 ± 0.017</td>
<td>−0.228 ± 0.033</td>
</tr>
<tr>
<td></td>
<td>I4</td>
<td>7.109 ± 0.064</td>
<td>−0.250 ± 0.049</td>
</tr>
<tr>
<td></td>
<td>I5</td>
<td>1.530 ± 0.007</td>
<td>−0.231 ± 0.030</td>
</tr>
<tr>
<td></td>
<td>I6</td>
<td>2.076 ± 0.014</td>
<td>−0.270 ± 0.037</td>
</tr>
<tr>
<td></td>
<td>I7</td>
<td>3.731 ± 0.026</td>
<td>−0.510 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>I8</td>
<td>7.595 ± 0.063</td>
<td>−0.385 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>I9</td>
<td>3.944 ± 0.027</td>
<td>−0.320 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>S1</td>
<td>3.455 ± 0.025</td>
<td>−0.234 ± 0.049</td>
</tr>
<tr>
<td></td>
<td>S1*</td>
<td>3.497 ± 0.025</td>
<td>−0.255 ± 0.033</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>2.911 ± 0.021</td>
<td>−0.306 ± 0.033</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>3.433 ± 0.025</td>
<td>−0.272 ± 0.049</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>3.343 ± 0.023</td>
<td>−0.300 ± 0.037</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>3.008 ± 0.021</td>
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</tr>
<tr>
<td></td>
<td>S6</td>
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<td>−0.401 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>S7</td>
<td>7.314 ± 0.070</td>
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</tr>
<tr>
<td></td>
<td>S8</td>
<td>7.533 ± 0.062</td>
<td>−0.285 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>S9</td>
<td>3.881 ± 0.028</td>
<td>−0.282 ± 0.039</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>5.913 ± 0.047</td>
<td>−0.328 ± 0.049</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>7.208 ± 0.055</td>
<td>−0.340 ± 0.049</td>
</tr>
</tbody>
</table>

Notes: External reproducibilities (2SD) of 0.05‰ for δ238U is based on numerous (>250) replicate measurements of the bracketing standard spiked at the same level as the samples. * Denotes replicates on a newly digested sample.

4.3. Magnesium isotopic data

The magnesium isotopic compositions of eight granitic rocks (two I-types, five S-types and two A-types) were ana-
yzed and are reported in Table 5. Results for the standards

Fig. 7. Solid/melt distribution coefficients of Fe and Zn in pyroxene, amphibole, biotite, olivine, magnetite, ilmenite, and plagioclase (Ewart and Griffin, 1994). Zinc is similar to Fe in radius and valence. In addition, fractionation of Fe and Zn in minerals common in granitic rocks such as biotite, amphibole, and oxides is small, so limited fractionation of the Zn/Fe ratio is expected during magmatic differentiation.
Table 2. Expectedly, the data follow mass-dependent fractionation, \( \delta^{25}\text{Mg} = (+0.530 \pm 0.146) / C_2 \delta^{26}\text{Mg} \). The average \( \delta^{26}\text{Mg} \) compositions for A-, S- and I-types are \(-0.094 \pm 0.065\%_\text{oo} \), \(-0.320 \pm 0.041\%_\text{oo} \), and \(-0.331 \pm 0.065\%_\text{oo} \), respectively (2SD). They are indistinguishable from MORBs \((-0.25 \pm 0.07\%_\text{oo}; \ \text{Teng et al., 2010a})\), except sample A2 \(+0.026 \pm 0.092\%_\text{oo} \), which is enriched in the heavier isotopes of Mg relative to MORBs by \(+0.2\%_\text{oo} \) (Fig. 6). These results agree with those reported by Shen et al. (2009), Liu et al. (2010) and Li et al. (2010).

4.4. Uranium isotopic data

The uranium isotopic compositions of 22 granitoids (I-, S-, and A-type) are reported in Table 6 and results for the standards are reported in Table 2. The typical uncertainty for measurements of granitic rocks is \( \pm 0.04 \) (95% confidence interval). For the most part granitoids show little isotopic variations with most of the samples between \(-0.2\%_\text{oo} \) and \(-0.2\%_\text{oo} \) in \( \delta^{238}\text{U} \). I-, S- and A-type granites have different protoliths and different modes of formation; however there is no significant difference in \( \delta^{238}\text{U} \) between these three granite types. Individual granitic rocks show variations in \( \delta^{238}\text{U} \). In particular, one I-type rock (I7) has a very low isotopic composition of \(-0.510 \pm 0.039\%_\text{oo} \). The average U isotopic composition of all the granitoids is \(-0.305 \pm 0.143\%_\text{oo} \) (2SD). These isotopic compositions agree well with previously documented U isotopic composition of igneous rocks, including basalts (Weyer et al., 2008; Tissot and Dauphas, 2012). There is no correlation between U isotope variations and proxies of felsic magma evolution, such as SiO2 content.

5. DISCUSSION

Previous work has suggested that Fe isotopes fractionate during partial melting (e.g., Weyer and Ionov, 2007; Dauphas et al., 2009), fractional crystallization (e.g., Schoenberg and von Blanckenburg, 2006; Teng et al., 2008; Schoenberg et al., 2009), fluid exsolution (Poitrasson and Freydierv, 2005; Heimann et al., 2008), and also as a result of Soret (thermal) diffusion in plutons (Lundstrom, 2009). Here we discuss the possible origins of Fe isotopic variations documented in felsic rocks and how our results can shed new light on this issue.

The fractional crystallization model has difficulties explaining why felsic rocks become heavy when a significant Fe-bearing phase crystallizing is an oxide (magnetite or...
Ilmenite). Indeed, magnetite and ilmenite are expected to have heavy rather than light Fe isotopic compositions relative to silicate phases (Poljakov et al., 2007; Shahar et al., 2008; Craddock et al., 2010), which should drive the system towards lower \( \delta^{56}\text{Fe} \) values, opposite to what is observed. However, in order to definitely rule out this model, the reduced partition function ratios for iron isotopes in silicate magmas remain to be determined. The Fe isotopic composition of most of the granitic rocks measured in this study did not show significant deviation from the igneous average (+0.09‰; Beard et al., 2003) (relative to IRMM-014), except for the most felsic granites (>70 wt.% SiO\(_2\)); Fig. 2). The \( \delta^{56}\text{Fe} \) values of I- and S-type granites overlap, so the redox state of the source rock cannot be the main control on iron isotopic variations in these samples.

5.1. Iron isotopic fractionation during partial melting

Migmatites are important samples for addressing the question of Fe isotopic fractionation during partial melting of granitic source material because they represent melts arrested in the process of migrating from their source. Although leucosomes form by partial melting, their Fe isotopic compositions can also be affected by fractional crystallization of the partial melts. Leucosomes measured in this study have \( \delta^{56}\text{Fe} \) values heavier by \( \sim +0.2\%_\text{oo} \) relative to schists, which are most representative of migmatic protoliths, and also relative to the average composition of bulk granitic rocks. In terms of mass-balance, most of the iron is expected to stay in melanosomes, which are the residues of partial melting and are rich in mafic minerals. Melanosomes are, therefore, expected to have an isotopic composition that is similar to that of the bulk protolith. All melanosomes have lighter Fe isotopic compositions than their leucosome complements (Fig. 2). Of the five leucosome-melansome pairs (Fig. 2) suggests that some of the melanosomes have equilibrated with isotopically evolved leucosomes. Re-equilibration has been shown to also affect the major and trace element compositions of leucosomes (Fourcade et al., 1992; Johannes et al., 1995). Despite this possible overprint, the Fe isotopic data preserve evidence that partial melting of crustal lithologies yields melts with fractionated Fe isotopic compositions, consistent with the interpretations of Weyer and Ionov (2007) and Dauphas et al. (2009). A remaining issue is the extent to which fractional crystallization and reequilibration of the leucosomes during cooling affected iron isotopes.

5.2. Iron isotopic fractionation during fluid exsolution and fractional crystallization

Pegmatites are evolved melts that may be particularly sensitive to fluid exsolution. For example, Shearer et al. (1986) documented extensive interaction between pegmatite-derived fluids and wallrock in the Black Hills, South Dakota. The \( \delta^{56}\text{Fe} \) values of pegmatites are similar or heavier than the igneous average (except for sample P389726), indicating that pegmatites are not the predominant reservoir for isotopically light Fe. Examining the fractionation between zinc and iron provides a method of further evaluating the effect of fluid exsolution on Fe isotopes. Zinc is a divalent element that is similar in ionic radius to Fe\(^{2+}\) (0.74 Å) and hence also similar in behavior. We measured the zinc isotopic compositions of many of our samples and found in pegmatites and some granites that high \( \delta^{56}\text{Fe} \) were accompanied by high \( \delta^{66}\text{Zn} \) values (Fig. 5), implying that fluid exsolution is indeed an important source of Fe isotopic variations in felsic rocks as suggested by Poirsson and Freydiere (2005) and Heimann et al. (2008). However, the \( \delta^{56}\text{Fe} \) values for most granitoids and in particular those of A-type, which formed under relatively dry conditions (Collins et al., 1982), do not correlate with their Zn isotopic compositions. For these samples that do not show fractionated \( \delta^{66}\text{Zn} \) values, the most likely cause of iron isotopic fractionation is fractional crystallization. A similar conclusion was reached by Sossi et al. (2012) based

Fig. 10. Expected isotopic fractionation of \( \delta^{56}\text{Fe} - \delta^{56}\text{Mg} \) (A), and \( \delta^{56}\text{Fe} - \delta^{238}\text{U} \) (B) produced by thermal (Soret) diffusion in a silicate melt (dashed lines; Richter et al., 2009 and Lacks et al., 2012). Soret diffusion has been proposed as a possible mechanism for fractionating iron isotopes in felsic rocks (Lundstrom, 2009). The data do not follow the correlations expected for Soret diffusion.
on the argument that A-type granites were unlikely to have experienced significant iron mobilization by fluid exsolution, yet these granites often have high $\delta^{56}$Fe values. Iron isotopic fractionation during magma differentiation is a process that could be tested by modeling. Unfortunately, most equilibrium iron isotopic fractionation factors between crystallizing minerals and melts are unknown, which should be the focus of future studies.

Mafic magmas show limited fractionation of Zn from Fe (Le Roux et al., 2010; Lee et al., 2010). Felsic magma differentiation is also not expected to induce large fractionation of Zn/Fe as the minerals involved have similar mineral/melt distribution coefficients (Fig. 7). The average $D_{Zn}/D_{Fe}$ ratios (where $D_i$ is the distribution coefficient between the solid and the liquid, $C_{solid}/C_{liquid}$) for the minerals involved are ~0.5 for pyroxene, ~0.3 for amphibole, ~0.6 for biotite, ~0.4 for olivine, ~0.5 for magnetite, ~0.2 for ilmenite, and ~1.0 for feldspar (Ewart and Griffin, 1994). All $D_{Zn}/D_{Fe}$ ratios (except for feldspar) are lower than one, meaning that the Zn/Fe ratio of the melt should increase during felsic magma differentiation. On the other hand, Zn and Fe can be significantly fractionated by complexation in chlorine-bearing magmatic fluids (Holland, 1972; Khitarov et al., 1982; Urabe, 1987; Simon et al., 2004; Zajacz et al., 2008). Fig. 8 shows a compilation of Zn/Fe ratios in granitoids from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/). As discussed, little fractionation of Zn/Fe ratios is expected during granitic magma evolution and only a small increase in Zn/Fe vs. SiO$_2$ is observed in the data. However, a notable feature is the large dispersion in Zn/Fe ratio of high-SiO$_2$ granites, which spans two orders of magnitude for the most silicic samples (>70 wt.-% SiO$_2$).

We modeled fractional crystallization of hydrous (1.36 wt.% H$_2$O) and anhydrous felsic melts to examine whether magmatic differentiation could explain the large dispersion in Zn/Fe ratios of granites. We used Rhyolite Melts, a program that enables calculations of fractional crystallization of hydrous silicic melts under a range of pressures and temperatures (Gualda et al., 2012; http://melts.ofm-research.org/). The initial composition of the melt is assumed to be dioritic (~66 wt.% SiO$_2$) with initial Zn and Fe contents of 50 ppm and 2.84 wt.%, respectively. The values for $D_{Fe}$ for orthopyroxene, clinopyroxene, magnetite and other oxides were determined by calculating the ratio of the concentration of Fe in the minerals to that in the melt and values for $D_{Zn}$ for each mineral were estimated by multiplying the $D_{Fe}$ values by published $D_{Zn}/D_{Fe}$ ratios (Ewart and Griffin, 1994). The concentration of Fe for the melt during fractional crystallization was computed by the Melts program, whereas changes in the concentration of Zn for the melt were determined by numerically modeling the incremental removal of Zn incorporated in the minerals that crystallized from the melt. Model results are plotted in Fig. 8 (green and purple circles) and indicate that fractional crystallization can explain the correlation between Zn/Fe and SiO$_2$ wt.%, but it cannot readily explain the large dispersion of Zn/Fe ratios observed for granites. This dispersion could potentially result from differences in the quality of Zn and Fe analyses reported in the GEOROC database. However, plots of Zn vs. SiO$_2$ content (Fig. 9A) and Zn/Fe vs. Zn (Fig. 9B) indicate that the Zn concentration data appear to be reliable. Thus, the dispersion in Zn/Fe ratios is likely produced by mobilization of Zn and possibly Fe in exsolved fluids.

During late stage crystallization of a granitic melt, Fe-chlorides can form and subsequently be lost in exsolved fluids (Simon et al., 2004; Zajacz et al., 2008), which could possibly leave the remaining silicate melt enriched in heavy iron isotopes. This mechanism has been proposed as a mechanism for enrichment of heavy Fe isotopes in evolved granitic rocks (Poitrasson and Freydiere, 2005; Heimann et al., 2008). Heimann et al. (2008) presented a quantitative assessment of this scenario based on solubility data and predicted equilibrium fractionation factors for iron in minerals and fluids. A significant result of the present study is that in pegmatites and some granitic rocks, Zn isotopes show a moderate correlation with Fe isotopes (Fig. 5). This observation, together with the observed scatter in Zn/Fe ratio for granitic rocks (Fig. 8), suggests that fluid exsolution is responsible in part for the isotopic fractionation of iron in felsic rocks. With the fluid exsolution model, a question is posed regarding the fate of the isotopically light exsolved reservoir. Significant amounts of iron must be removed to explain the heavy iron isotopic composition of pegmatites and some granitic rocks. Such a reservoir has not been conclusively identified but it is worth noting that the Little Nahanni pegmatites, which are from volatile-rich sources, have $\delta^{56}$Fe compositions that are highly variable, including light Fe isotopic compositions ($-0.07^{+10}_{-7}$; Fig. 2). Further work on fluid inclusions is needed to ascertain the nature of the putative complementary reservoir to isotopically heavy iron in pegmatites and some granites.

5.3. Demonstration that Soret effect is absent in the studied granitoids from Mg, U and Fe isotope systematics

Magnesium isotope compositions of granitic rocks are important to compare with Fe isotopic data because Mg isotopes do not fractionate during partial melting or magmatic differentiation, but are fractionated significantly during diffusion and weathering (Teng et al., 2007, 2010b; Richter et al., 2008; Shen et al., 2009; Lundstrom, 2009; Liu et al., 2010). The Lachlan Fold Belt granitoids measured in this study are fresh samples and their Mg isotopic compositions were not affected by weathering. We measured Mg isotopic data for granitic rocks with the highest $\delta^{56}$Fe values to determine whether Soret diffusion and/or derivation from sedimentary protoliths are influencing the $\delta^{56}$Fe composition of these felsic rocks. Little variation in $\delta^{26}$Mg among the different types of granitic rocks was found. The one exception is sample A2, which has a $\delta^{26}$Mg composition of +0.025 ± 0.092‰, significantly heavier than MORB. Sample A2 also has the highest $\delta^{56}$Fe of +0.305 ± 0.022‰. Heterogeneous $\delta^{26}$Mg values for A-type granites have also been reported by Li et al. (2010). The Mg isotopic variations of A-type granites possibly reflect chemical heterogeneities inherited from the source (Shen et al., 2009; Li et al., 2010; Liu et al., 2010). The reason for hea-
vier Mg and Fe isotopic compositions in this sample is unclear. Soret (thermal) diffusion has been proposed as a mechanism for producing heavy $\delta^{56}\text{Fe}$ and $\delta^{56}\text{Fe}$ compositions in plutons (Lundstrom, 2009). Based on the experimental results from Richter et al. (2009) and Lacks et al. (2012), Fe and Mg isotopes from a source that has experienced Soret diffusion in a thermal gradient should follow the trend illustrated in Fig. 10A; however, the granitic rocks that were measured for both $\delta^{56}\text{Fe}$ and $\delta^{54}\text{Mg}$ do not clearly follow the expected correlation.

Further evidence that Soret diffusion played no role in the isotopic fractionation documented here comes from U and Fe isotope measurements. One of our motivations to investigate the U isotopic composition of granitic rocks was to assess whether the U isotopic compositions of zircons could be related to the nature of the protolith (i.e., sedimentary vs. igneous) with potential application to Hadean zircons, which provide the only record of Earth’s evolution during that eon. We did not find any evidence for that; U isotope variations in granites are not related to the nature of their protoliths. Another reason for measuring U isotopes is that Soret diffusion could fractionate U isotopes in silicate melts (Lacks et al., 2012). Such fractionation would produce correlated Fe–U isotopic variations (the slope between $\delta^{56}\text{Fe}$ and $\delta^{26}\text{U}$ in laboratory experiments is 3.18). As shown in Fig. 10B, we do not see any correlation in the sample set studied that would suggest that Soret diffusion was present. If anything, the variations would define a trend that is orthogonal to the trend predicted for Soret diffusion. We conclude, based on the absence of correlation between Mg, U and Fe isotopic compositions, that the granitoids investigated here (I-, S-, and A-type granitoids from Lachlan Fold Belt) were not influenced by Soret effect.

**6. CONCLUSIONS**

The $\delta^{56}\text{Fe}$ values of granitoids are positively correlated with SiO$_2$ wt.%, consistent with previous studies (Poitrasson and Freydier, 2005; Heimann et al., 2008). Several mechanisms for enriching the melt in heavy Fe isotopes have been proposed including: partial melting, fractional crystallization, fluid exsolution and thermal migration (Soret diffusion). This work sheds new light on the mechanisms governing the isotopic fractionation of iron and other non-traditional stable isotope systems in the crust:

1. The enriched Fe isotopic compositions of leucosomes provide evidence that partial melting of the crust can fractionate the isotopes of Fe by at least 0.2‰ in $\delta^{56}\text{Fe}$ (Fig. 2). However, the extent to which the measured leucosomes were affected by fractional crystallization and reequilibration is unknown.

2. The nature and redox state of the protolith do not appear to influence the $\delta^{56}\text{Fe}$ and $\delta^{38}\text{U}$ compositions of granitic rocks.

3. Poitrasson and Freydier (2005) and Heimann et al. (2008) suggested that exsolved fluids could have removed isotopically light iron and hence explain the heavy iron isotopic composition of some felsic rocks. This idea was tested by measuring the isotopic variations of an element sensitive to fluid exsolution, Zn, in the same samples that were analyzed for iron. Pegmatites and some granitoids show high $\delta^{56}\text{Fe}$ values that are accompanied by high $\delta^{68}\text{Zn}$ values (Fig. 5), so fluid exsolution is most likely responsible for the iron isotope variations measured in these samples. This is supported by the observation that the Zn/Fe ratio shows increasing scatter in more silicic granites, which cannot easily be explained by magma differentiation and could be due to fluid exsolution instead (Fig. 8).

4. Fluid exsolution alone cannot explain the high $\delta^{56}\text{Fe}$ values measured in all granitoids, as many of these samples show no variations in $\delta^{56}\text{Zn}$. Fractional crystallization is the most likely cause of iron isotope variations in these samples. This is particularly relevant to A-type granites, which presumably formed in relatively dry conditions and are not expected to have experienced significant fluid exsolution.

5. Finally, $\delta^{26}\text{Mg}$ and $\delta^{38}\text{U}$ results for granitic rocks suggest that thermal migration (Soret diffusion), which has been proposed as a mechanism of granitic magma differentiation (Lundstrom, 2009), can be ruled out in our sample set because the $\delta^{26}\text{Mg}$, $\delta^{38}\text{U}$ and $\delta^{56}\text{Fe}$ do not follow the correlations expected for Soret diffusion (Richter et al., 2009; Lacks et al., 2012) (Fig. 10).

Our results on a limited, albeit representative, sample set support fluid exsolution and fractional crystallization as the primary mechanisms for the $\delta^{56}\text{Fe}$ variations of felsic rocks. Equilibrium fractionation factors between silicate melts and minerals have to be characterized to quantitatively assess the role of fractional crystallization on iron isotopes in granitoids.

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