Comment on “Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS”, by F. Poitrasson and R. Freydier [Chem. Geol. 222 132–147]

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Abstract

Scrutiny of published Fe isotope data for igneous rocks that have >71 wt.% SiO₂ reveals that most samples have the same Fe isotope composition as mafic igneous rocks, contrary to the conclusions of Poitrasson and Freydier [Poitrasson, F. and Freydier, R., 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. Chem. Geol. 222, 132–147]. The only silicic igneous rocks that have Fe isotope compositions that are significantly different than mafic igneous rocks are 4 granitic samples that have SiO₂ >75 wt.% analyzed by Poitrasson and Freydier [Poitrasson, F. and Freydier, R., 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. Chem. Geol. 222, 132–147]; three silicic igneous rocks analyzed by Beard et al. [Beard, B.L., Johnson, C.M., Skulan, J.L., Nealson, K.H., Cox, L., Sun, H., 2003a. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. Chem. Geol. 195 87–117] (SiO₂ >75 wt.%) have Fe isotope compositions that are identical to mafic igneous rocks, but these samples were ignored. Moreover, the Fe isotope composition of upper continental crust as deduced from the 58 sedimentary clastic rocks (shales, loess, modern marine sediments, and suspended load of rivers), reported by Beard et al. [Beard, B.L., Johnson, C.M., von Damm, K.L. and Poulson, R.L, 2003b. Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans. Geology 31 629–632], is the same as the average of igneous rocks. These data suggest that granitic rocks which deviate from the igneous average may be rare.

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Keywords: Fe isotopes; Igneous rocks; Continental crust composition; Granitic rocks; Clastic sedimentary rocks
expulsion of late-stage magmatic fluids that had relatively low $\delta^{56}$Fe values. Poitrasson and Freydier (2005) imply that these results are generally reflective of silicic igneous rocks, stating “Our data indicate that granites with MgO<0.6 wt.% and SiO$_2$>71 wt.% have $\delta^{57}$Fe/$^{54}$Fe values that are significantly heavier than the bulk mafic Earth.” They further state that these results provide arguments against using the average of terrestrial igneous rocks as a reference in defining $\delta$ values.

In support of the proposal that granitic rocks have high $\delta^{57}$Fe and $\delta^{56}$Fe values, Poitrasson and Freydier (2005) plot three evolved igneous rocks from the study of Beard et al. (2003a) in their Fig. 6, but, remarkably, they ignore whole-rocks or minerals from the data sets of Beard et al. (2003a) and Beard and Johnson (2004) that do not lie on their proposed trend. Poitrasson and Freydier (2005) note that they only plotted data from our studies “for which SiO$_2$ contents were available”, and yet bulk-rock SiO$_2$ contents and Fe isotope compositions for these, and 37 additional samples, were shown in Fig. 1 of Beard and Johnson (2004), a paper that appears in the reference list of Poitrasson and Freydier (2005) but whose implications are ignored. Fig. 1 in Beard and Johnson (2004) showed no correlation between SiO$_2$ contents and Fe isotope compositions. This observation, which is in direct opposition to Poitrasson and Freydier’s (2005) thesis, was omitted in their discussion.

The complete set of Fe isotope data for evolved igneous rocks that have a bulk-rock SiO$_2$ content >65 wt.% are plotted in Fig. 1, which comes from the studies Beard et al. (2003a), Beard and Johnson (2004), and Poitrasson and Freydier (2005). All data in Fig. 1 have been cast in terms of $^{56}$Fe/$^{54}$Fe values relative to the average of igneous rocks, which may be related to $^{56}$Fe/$^{54}$Fe ratios reported relative to IRMM-014 by subtraction of 0.09 or to $^{57}$Fe/$^{54}$Fe ratios reported relative to the IRMM-014 standard through:

$$\delta^{56}$Fe$^{\text{Igneous Rocks}} = 0.667*\delta^{57}$Fe$^{\text{IRMM-014}} - 0.09$$

using the data in Beard et al. (2003a). Consideration of all data available indicates that all published Fe isotope analyses of silicic rocks that have SiO$_2$<75 wt.% have Fe isotope compositions that overlap the isotopic composition of mafic- to intermediate-composition igneous rocks (Fig. 1). In contrast, of the 7 samples that have SiO$_2$>75 wt.%, the four samples analyzed by Poitrasson and Freydier (2005) have $\delta^{56}$Fe values between +0.14‰ and +0.30‰, which are outside the range defined for more mafic compositions, whereas the three high-SiO$_2$ samples analyzed by Beard et al. (2003a) have $\delta^{56}$Fe values between −0.04‰ and −0.08‰, overlapping the average of more mafic igneous rocks within analytical uncertainty.

The origin of the differences in the Fe isotope compositions of the silicic igneous rocks analyzed by Poitrasson...
and Freydier (2005) relative to previously published results is uncertain. As pointed out by Poitrasson and Freydier (2005), inter-laboratory bias in measurement techniques is not a likely origin for these differences. Using the conversion between IRMM-014 and the average of igneous rocks noted above, three USGS rock standards analyzed by Poitrasson et al. (2004) agree within 0.04% relative to the δ⁵⁶Fe values reported in Beard et al. (2003a). Moreover, agreement on suites of mafic- to intermediate-composition volcanic and plutonic rocks analyzed by various groups is excellent, where the average δ⁵⁶Fe value of thirty four rocks reported by Beard et al. (2003a) is +0.01±0.04‰ (1–S.D.), which is the same within error of ten samples of similar composition rocks reported by Poitrasson et al. (2004), which have an average δ⁵⁶Fe value of −0.02±0.03‰ (1–S.D.) (3 peridotite/dunite samples omitted, given the heterogeneity of mantle rocks, as shown by Beard and Johnson, 2004). In addition, Weyer et al. (2005) recently reported data for five mafic lavas, and obtained an average δ⁵⁶Fe value of −0.01±0.03‰ (1–S.D.). The reproducibility in δ⁵⁶Fe values for two USGS rock standards (BCR-1 and PCC-1) that are common to the work of Beard et al. (2003a) and Weyer et al. (2005) is better than 0.02‰.

There are no systematic differences in precision of the analyses between the Beard et al. (2003a) and Beard and Johnson (2004) studies and the study of Poitrasson and Freydier (2005) that can explain the different results. The error bars for the isotopic compositions plotted in Fig. 1 reflect the reported 1–S.D. external precision in these studies, except for two samples analyzed by Beard et al. (2003a) that were only analyzed one time; for these two samples, which have SiO₂ contents of 65.6 and 73.4 wt.% the internal 2 standard error was used. We note that Poitrasson and Freydier (2005) obtained their precision through 9 or more duplicate analyses of each sample, using ~1 μg of Fe for each analysis, whereas the precision reported by Beard et al. (2003a) generally reflects 2 or 3 duplicate analyses of each sample (occasionally more) and much smaller sample sizes of 5–10 times less Fe per analysis, highlighting the great sensitivity of low-mass resolution, collision-cell based Fe isotope analysis.

One of the most significant differences between these two data sets is that all of the samples analyzed by Poitrasson and Freydier (2005) are plutonic rocks and all Fe isotope compositions were determined on bulk-rock analyses. In contrast, the silicic samples analyzed by Beard et al. (2003a) and Beard and Johnson (2004) include volcanic lava flows, as well as plutonic rocks. Additionally, in 6 of the 11 samples analyzed by Beard et al. (2003a) and Beard and Johnson (2004), Fe isotope compositions were determined on ferromagnesian minerals including biotite, magnetite, and amphibole. Of the three samples that have SiO₂ > 75 wt.%, two samples are plotted in Fig. 1 using the composition of biotite (one sample is a rhyolite, the other a granite), and the third sample is a bulk-rock analysis of an aphyric rhyolitic lava flow. In light of the evidence that crystal fractionation is an unlikely mechanism for producing significant changes in δ⁵⁶Fe values for igneous rocks (Beard and Johnson, 2004), the proposal by Poitrasson and Freydier (2005) that exsolution of late-stage magmatic fluids may produced changes in bulk-rock compositions.

Fig. 2. δ⁵⁶Fe–Fe₂O₃ (total Fe) variations for evolved igneous rocks (same samples as in Fig. 1), as well as sedimentary rocks reported in Beard et al. (2003b) that provide estimates for the bulk Fe isotope composition of the continental crust. The grey line and field are the average and 1–S.D., respectively, of the 58 sedimentary rocks analyzed by Beard et al. (2003b). The greatest variability in sedimentary rocks occurs in shales, which may contain a diagenetic component. It is important to note that the relatively low-Fe loess samples do not record evidence for a high ⁵⁶Fe/⁵⁴Fe source that is significantly different than the average of igneous rocks.
$\delta^{56}\text{Fe}$ values is an intriguing one that certainly merits further exploration.

The results of Poitrasson and Freydier (2005) bear on Fe isotope compositions of the silicate Earth, specifically the continental crust, which has been a topic of recent discussion in the literature. Poitrasson and Freydier (2005) recognize that high-$\delta^{56}\text{Fe}$, low-Fe content igneous rocks would have minimal impact on a calculated average Fe isotope composition for the continental crust, but consideration of Fe isotope compositions of sedimentary rocks suggests that high-$\delta^{56}\text{Fe}$ igneous rocks may, in fact, be quite rare. Beard et al. (2003b) reported Fe isotope compositions for 58 clastic sedimentary rocks that included bulk-rock analyses of 21 Proterozoic to Phanerozoic shales, 10 samples of loess, 14 modern marine sediments, and 13 samples of the suspended load from rivers, and these are compared with the isotopic compositions of evolved igneous rocks in Fig. 2. Nineteen of these shale samples were used to evaluate the chemical composition of post-Archean sediments (Nance and Taylor, 1976), and the 10 loess samples were used by Taylor et al. (1983) to characterize the chemical composition of the upper continental crust. Most of the modern marine sediments were analyzed by McLennan et al. (1990) to evaluate chemical differences between turbidites that were deposited in different tectonic settings. The turbidite samples analyzed by Beard et al. (2003b) include sands and muds from different tectonic settings, including trailing-edge margins, forearc and back-arc basins, continental arcs, and continent–continent collision zones. The suspended river load sediments were collected by Canfield (1997) to evaluate chemical weathering by comparison of riverine solute chemistry to particulate chemistry. Complete chemical analyses of the samples in these suites may be found in the papers cited above or in the references cited in the supplemental information from Beard et al. (2003b).

The average $\delta^{56}\text{Fe}$ of the 58 sedimentary rocks plotted in Fig. 2 is $+0.02 \pm 0.10\%\text{o}$ (1–S.D.); if the modern Asian and North American aerosol samples, as well as soil samples that were sieved to approximate an aerosol, are included, the average $\delta^{56}\text{Fe}$ for the 82 “sediment” samples is identical at $+0.02 \pm 0.10\%\text{o}$ (1–S.D.). The greatest range in $\delta^{56}\text{Fe}$ values occurs in bulk shale samples, which may contain diagenetic Fe components, increasing the spread in isotopic compositions (Yamaguchi et al., 2005). It is particularly noteworthy that the loess samples in Fig. 2 do not record evidence for high-$\delta^{56}\text{Fe}$ sources, given the fact that the sources of these samples had relatively low Fe contents. We conclude that consideration of the entire data set of igneous and clastic sedimentary rocks that have not been subjected to significant diagenesis provides very strong evidence that a diverse range of rock types in the continental crust has the same Fe isotope composition, identical to either the average of all igneous rocks as defined by Beard et al. (2003a), or a more restrictive reference frame of mafic- to intermediate-composition igneous rocks.

References


On the iron isotope homogeneity level of the continental crust

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Abstract

Assessing the level of homogeneity of different planetary reservoirs is an essential step to establish a new isotopic tracer. In recent studies, we concluded that most igneous rocks from the continental crust were homogeneous to $\pm 0.05$‰ in $\delta^{57}$Fe [Poitrasson, F., Halliday, A.N., Lee, D.C., Levassuer, S., Teutsch, N., 2004. Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. Earth Planet. Sci. Lett., 223, 253-266.; Poitrasson, F., Freydier, R., 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. Chem. Geol., 222, 132-147.]. This conclusion was previously reached by Beard et al. [Beard, B.L., Johnson, C.M., Skulan, J.L., Nealson, K.H., Cox, L., Sun, H., 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. Chem. Geol., 195, 87-117.]. The main purpose of the Beard and Johnson [Beard, B.L., Johnson, C.M., 2006. Comment on "Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS" by F. Poitrasson and R. Freydier, Chemical Geology, volume 222, pages 132-147. Chem. Geol., this issue.] comment is to emphasize again this conclusion reached by the two groups: the degree of the iron isotope variability observed in most bulk rocks from the continental crust is small. However, controversy lies with high silica magmatic rocks ($N \sim 71$ wt.% SiO$_2$) that we concluded were significantly heavier than less silicic rocks from the crust on the basis of Fe isotopic analyses of seven bulk rock samples from different geological settings. Beard and Johnson [Beard, B.L., Johnson, C.M., 2006. Comment on “Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS” by F. Poitrasson and R. Freydier, Chemical Geology, volume 222, pages 132-147. Chem. Geol., this issue.] comment is to emphasize again this conclusion reached by the two groups: the degree of the iron isotope variability observed in most bulk rocks from the continental crust is small. However, controversy lies with high silica magmatic rocks ($> \sim 71$ wt.% SiO$_2$) that we concluded were significantly heavier than less silicic rocks from the crust on the basis of Fe isotopic analyses of seven bulk rock samples from different geological settings. Beard and Johnson [Beard, B.L., Johnson, C.M., 2006. Comment on “Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS” by F. Poitrasson and R. Freydier, Chemical Geology, volume 222, pages 132-147. Chem. Geol., this issue.] challenge this finding on the basis of previously “published” data. It is shown here that this controversy stems from the confusion between whole-rock and mineral iron isotope analyses, since this isotopic tracer, like many others, is more heterogeneous at the mineral scale than the bulk rock scale. Thus, minerals cannot be used in place of bulk rock Fe isotope compositions. The controversy also arises from different levels of analytical uncertainties. If only the best Fe isotope probes of planetary reservoirs — bulk rocks — are considered, then the conclusion that igneous rocks with SiO$_2$ $>$ 71 wt.% are significantly heavier than the mean $\delta^{57}$Fe of the continental crust [Poitrasson, F., Freydier, R., 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. Chem. Geol., 222, 132-147.] remains valid. Nonetheless, given that granites represent only a minor fraction of the continental crust, this finding does not change the bulk igneous Fe isotope composition estimate previously defined for the Earth.

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Keywords: Fe isotopes; Igneous rocks; Continental crust composition; Granites
1. Introduction

It is only since the beginning of the present decade that analytical developments in plasma-source mass spectrometry led to the levels of precision (Belshaw et al., 2000) required to study the tenth of permil variations shown by iron isotopes in high temperature geological environments (Zhu et al., 2002). An important initial step in the use of this new geochemical tracer is the characterization of the isotopic composition of the main planetary reservoirs (Beard et al., 2003; Poitrasson et al., 2004). These first studies concluded that most rocks from the continental crust display a very small level of iron isotope heterogeneity (Beard et al., 2003; Dauphas et al., 2004b; Poitrasson et al., 2004; Beard and Johnson, 2006-this issue), well below 0.1‰ in $\delta^{57}$Fe.

However, in a study of the iron isotope signature of granitoids from various geological settings, we found that the most silicic samples appear to be an exception to this isotopic homogeneity rule (Poitrasson et al., 2002; Poitrasson and Freydier, 2005). As discussed below, although most igneous rocks display a tiny iron isotope range, a few show such large deviations that using a random igneous sample for normalization purposes (e.g., Khem et al., 2003) may lead to inaccurate comparisons with other studies.

Iron isotope results reported in the literature are frequently expressed in the delta notation, in permil, mostly as $\delta^{57}$Fe or $\delta^{56}$Fe. As detailed previously (Poitrasson and Freydier, 2005), this convention is essentially due to analytical constraints, the data produced in a given laboratory being discussed in terms of the most precisely determined ratio. Although high resolution MC-ICP-MS allow measurement of both $\delta^{57}$Fe and $\delta^{56}$Fe with a similar level of precision per atomic mass unit (Poitrasson and Freydier, 2005), the $\delta^{57}$Fe ratio is quoted here, since this is the most precisely determined quantity in our previous studies (Poitrasson et al., 2004, 2005). It also has the advantage to show larger variations since 3 amu are involved instead of 2 for $\delta^{56}$Fe, although what really matters is the difference between the variations observed relative to the analytical uncertainties.

3. The matter of debate

On the basis of new analyses, and the inclusion of previously published data from Beard et al. (2003), for which SiO$_2$ content were available (because they are international geostandards), we found 7 samples having an Fe isotope composition significantly above the “mean mafic Earth” baseline previously defined (0.103±0.032‰ $\delta^{57}$Fe; Poitrasson et al., 2004). These seven rocks are all highly evolved (rhyolite or granite) with SiO$_2$>71 wt.% and MgO<0.6 wt.%. In fact, no samples from this category have an isotopic composition that overlaps that of the “mean mafic earth” (Poitrasson and Freydier, 2005).

Beard and Johnson (2006-this issue) plot these results again, recast in terms of $\delta^{56}$Fe and referenced to their igneous rocks baseline. They find that only the 4 most silica-rich granites have an iron isotope composition above the mafic igneous rock composition. They also report analyses of rocks with SiO$_2$>75 wt.% that have iron isotope compositions that do not deviate from the terrestrial igneous rock baseline.

How might such a discrepancy arise? This is in large part due to the difference in the definition of the isotopic range of igneous rocks. Although the mean value used in Beard et al. (2003) and Poitrasson et al. (2004) agree to <0.02‰ in $\delta^{57}$Fe, when the Beard et al. (2003) mean value is translated through IRMM-14 (i.e., 0.12‰ $\delta^{57}$Fe), the range in $\delta^{57}$Fe used by Beard and Johnson (2006-this issue) is approximately four times larger than that used by Poitrasson et al. (2004). In using such a large range, recognizing significant high temperature Fe isotopic variation becomes more difficult. A precise definition of the mean iron isotope composition of igneous rocks from the continental crust is therefore required for magmatic studies. The problem with the Madison group range is that it varies from publication to publication without clear geological justification: it is defined as ±0.05‰ $\delta^{57}$Fe in Beard et al. (2003), then as ±0.1‰ $\delta^{56}$Fe in Beard and Johnson (2004) and finally as ±0.08‰ $\delta^{56}$Fe in Beard and Johnson (2006-this issue). This illustrates the difficulty in defining an uncertainty for the mean value of a geological reservoir, which necessarily comprises some subjective interpretation. I nevertheless prefer to stick to our original definition of the “mean mafic earth” $\delta^{57}$Fe value because it is only made from bulk rock analyses since minerals may induce an extra scatter, as discussed in Poitrasson et al. (2004). Nor does this mean value (and associated range) include highly evolved
granites, that even Beard and Johnson (2006-this issue) recognize to be isotopically heavy in some cases. Furthermore, from Figs. 5 and 6 of Poitrasson and Freydier (2005), it is apparent that the 12 analyses presented define a smooth trend, with a conspicuous increase in \( \delta^{57}\text{Fe} \) from above 71 wt.% SiO\(_2\) and below 0.6 wt.% MgO. This trend suggests that this is not a random effect, but rather must delineate some global geological process, given that the rocks come from various geological settings. I have since analyzed two new granitoid rocks from the Ntem Archean complex in Cameroon (Table 1), located near Sangmelima (see details in Braun et al., 2005). These new analyses on very old rocks confirm our previous \( \delta^{57}\text{Fe} \) vs. SiO\(_2\) (Fig. 1) and \( \delta^{57}\text{Fe} \) vs. MgO (not shown) trends on Palaeozoic granitoids (Poitrasson and Freydier, 2005).

Another reason for the difference of opinion between Poitrasson and Freydier (2005) and Beard and Johnson (2006-this issue) on the number of silica-rich igneous rocks having an Fe isotope signature significantly heavier than other igneous rocks lies in the better precision of the \( \delta^{57}\text{Fe} \) value reported by Beard et al. (2003) for the rhyolite RGM-1 that was used by Poitrasson and Freydier (2005) in their Figs. 5 and 6 (0.30±0.05‰, relative to IRMM-14), than the less precisely defined \( \delta^{56}\text{Fe} \) value for this sample (0.18±0.11‰) considered in the Fig. 1 of Beard and Johnson (2006-this issue). Incidentally, this is the only sample analyzed by Beard et al. (2003) out of the three we could use to make our compilation that was significantly above the terrestrial mafic mean.

Contrary to what Beard and Johnson (2006-this issue) write, there is a significant difference between the level of precision in the Fe isotope analyses of Beard et al. (2003) and Beard and Johnson (2004), compared to those reported in Poitrasson and Freydier (2005). We concluded that the 2SD reproducibility of our measurements is \( \sim 0.013\%\text{amu} \) on both \( \delta^{57}\text{Fe} \) and \( \delta^{56}\text{Fe} \) ratio, whereas Beard et al. (2003) show that they have a 1SD reproducibility of \( \sim 0.025\%\text{amu} \) on their determinations: a difference of nearly a factor of four. Further, we demonstrated on the basis of measurements that computing the 2SE uncertainties of 6 replicate analyses yielded a good proxy of the long term 2SD reproducibility of a standard (Poitrasson and Freydier, 2005). Beard and Johnson (2006-this issue) cannot ignore this conclusion and recast our uncertainties as 1SD, since they incorrectly degrade our actual precision. Another recent high resolution MC-ICP-MS study on Fe isotope measurements found a similar level of reproducibility (Schoenberg and von Blanckenburg, 2005). In plotting the Beard et al. (2003) data in our Figs. 5 and 6, we used the analytical uncertainty reported in their paper (their Table 2).

Of the three samples with SiO\(_2\) > 75 wt.% plotted in the Fig. 1 of Beard and Johnson (2006-this issue) and in Fig. 1A of Beard and Johnson (2004), two are biotite analyses (thus in contradiction to the caption of Fig. 1A of Beard and Johnson (2004) which only mentions amphibole and magnetite isotopic analyses), the third being an aphyric rhyolitic lava flow. The problem is that, despite the practice used by the Madison group since the TIMS days (e.g., Beard and Johnson, 1999), mineral separates cannot be taken as a proxy of bulk rock composition for high precision iron isotope measurements. As shown by Poitrasson et al. (2004) on the basis of olivine and pyroxene separates from a lunar basalt, the 0.2‰ \( \delta^{57}\text{Fe} \) difference between these two phases in a single igneous rock was equivalent to the estimated bulk planetary differences observed between the Moon and Mars or Vesta. If in that study we would have used

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Table 1
New iron isotope results from bulk granitoids obtained by high resolution MC-ICP-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Location</th>
<th>[SiO(_2)] (wt.%(^a))</th>
<th>( \delta^{57}\text{Fe} ) (%)</th>
<th>Uncertainty (2SE)(^b)</th>
<th>( \delta^{56}\text{Fe} ) (%)</th>
<th>Uncertainty (2SE)(^b)</th>
<th>Number of analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRA</td>
<td>Granodiorite</td>
<td>Nsimi, Cameroon</td>
<td>62.80</td>
<td>0.080</td>
<td>0.080</td>
<td>0.048</td>
<td>0.049</td>
<td>6</td>
</tr>
<tr>
<td>MONZ</td>
<td>Granite</td>
<td>Nsimi, Cameroon</td>
<td>74.46</td>
<td>0.323</td>
<td>0.117</td>
<td>0.219</td>
<td>0.069</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^{a}\)See Braun et al. (2005) for complete major element analyses and mineral modes. \(^{b}\)The iron isotope composition and two standard error uncertainties quoted are calculated from the number of analyses indicated and using the Student’s \( t \)-correcting factors (Platzner, 1997).
Table 2

Input parameters used in the computation of the mean continental crust Fe isotopic composition

<table>
<thead>
<tr>
<th></th>
<th>Bulk continental crust</th>
<th>Upper continental crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abundance of granites with SiO$_2$ $&gt;$ 71 wt.%$^a$</td>
<td>13%</td>
<td>25%</td>
</tr>
<tr>
<td>[Fe]$^b$</td>
<td>43200 ppm</td>
<td>30890 ppm</td>
</tr>
<tr>
<td>[Fe] of granites with SiO$_2$ $&gt;$ 71 wt.%$^a$</td>
<td>14000 ppm</td>
<td>14000 ppm</td>
</tr>
<tr>
<td>$^{57}$Fe of granites with SiO$_2$ $&gt;$ 71 wt.%$^b$</td>
<td>0.25‰</td>
<td>0.25‰</td>
</tr>
<tr>
<td>Calculated bulk crustal $^{57}$Fe</td>
<td>0.107‰</td>
<td>0.120‰</td>
</tr>
<tr>
<td>“Mean mafic earth” reference $^{57}$Fe$^c$</td>
<td>0.103 ± 0.032‰</td>
<td>0.103 ± 0.032‰</td>
</tr>
</tbody>
</table>

$^{57}$Fe are reported relative to IRMM-14.

$a$Estimates from Wedepohl (1995); $^b$Value derived from the trend on Fig. 6 of Poitrasson and Freydier (2005), using a mean value of 73.4 wt.% SiO$_2$ for granites taken by Wedepohl (1995). $^c$Value from Poitrasson et al. (2004).

mineral separates instead of powders made from the largest possible aliquots of rocks to minimize the effect of the variable Fe isotopic composition of minerals, it would have been impossible to define these planetary differences. A larger spread of mineral $^{57}$Fe than corresponding whole-rock analyses was also demonstrated by Williams et al. (2005) for ultramafic samples. The inclusion of mineral analyses in the igneous rock compilation of the Madison group is one likely reason for the larger uncertainty given by these authors in their definition of the mean igneous rocks values discussed above. A larger isotopic heterogeneity at the mineral scale than the bulk rock scale is a common feature in isotope geochemistry, and this is evident in the Beard and Johnson (2004) data. Inspection of the “mass spec average” analyses of mineral separates from basalt to rhyolite (Table 5 of Beard and Johnson, 2004) reveal the large isotopic scatter of minerals, even within a given rock. The difference in $^{57}$Fe values between various minerals of a given rock ranges from 0.13‰ to 0.36‰, in all cases well beyond the reported analytical uncertainties. It is also interesting to learn that even two different aliquots from the same mineral dissolution from a given rock can differ by up to 0.29‰ (i.e., two amphibole aliquots from a basaltic andesite), thus probably revealing some analytical difficulties. Although the authors attempted to partially minimize these isotopic heterogeneity problems in computing “aliquot averages” in their tables, they will certainly not replace bulk rock analyses. These isotopic variations observed at the mineral scale are not trivial because most granites heavier than the “mean mafic rocks” reported in Poitrasson and Freydier (2005) differ from this baseline by less than 0.4‰ $^{57}$Fe.

Hence, Fig. 1A of Beard and Johnson (2004) that we “ignored”, according to Beard and Johnson (2006-this issue), does not add much in terms of bulk rock isotopic analyses relative to the Beard et al. (2003) data since the new data were not bulk rock analyses but averages of mineral Fe isotopic analyses. Furthermore, the SiO$_2$ contents of the bulk rocks analyzed for Fe isotopes in Beard et al. (2003) are still not tabulated in Beard and Johnson (2004). It was therefore difficult, on the basis of Fig. 1A of Beard and Johnson (2004), to relate the Fe isotope bulk rock analyses of Beard et al. (2003) to SiO$_2$ concentrations.

However, armed with the only tool that can be used to examine these high precision Fe isotopic analyses reported in figures—a ruler—, a close inspection of the Fig. 1A of Beard and Johnson (2004) and the Fig. 1 of Beard and Johnson (2006-this issue) reveal some differences, besides those associated with the uncertainties assigned to the mean of igneous rocks discussed above. Of the three samples with SiO$_2$ between 69 and 72 wt.% reported in the Fig. 1A of Beard and Johnson (2004), only two remain in the Fig. 1 of Beard and Johnson (2006-this issue). One has disappeared for some unknown reason despite the comprehensiveness of this figure according to Beard and Johnson (2006-this issue). As mysterious is the shift towards higher SiO$_2$ values for the two remaining samples, by approximately 2 wt.%, well outside analytical uncertainties for SiO$_2$ determinations. We also learn from the caption of Fig. 1A of Beard and Johnson (2004) that “bulk-rock SiO$_2$ contents [were] measured for the sample or inferred based on similar rock type”. Apparently, they did not tabulate their whole-rock SiO$_2$ contents simply because many of them were not measured, but merely guessed, with a likely level of uncertainty of 2 wt.%, as discussed above, and possibly more. So challenging our previous conclusions that granites above 71 wt.% SiO$_2$ may be isotopically heavier than most other crustal igneous rocks, and stating that this should apply more to rocks with SiO$_2$ contents above 75 wt.% (Beard and Johnson, 2006-this issue) is difficult to maintain in the absence of measured SiO$_2$ contents, not to mention the uncertainty associated with the mean Fe isotope composition of mafic and intermediate igneous rocks defined by these authors.

Since mineral Fe isotope analyses cannot be equated with bulk rock signatures, there remains only one bulk rock—an aphyric rhyolitic lava flow—from Beard and
Johnson (2004) that does not follow the trend depicted in Poitrasson and Freydier (2005). It is difficult to find a possible explanation for this given the scarcity of information on this sample (we just know its petrographic name, an estimate of its silica content but its very precise Fe isotope composition), but if it is an obsidian, these rocks may show a strong modification of their isotopic signatures by aqueous fluid-rock interaction. This was illustrated for the normally robust Nd isotope signatures (Poitrasson et al., 1995) and it is hypothesized that this may also affect Fe isotopes in this type of volcanic rock.

4. The iron isotope composition of the continental crust

It appears that all but one of the analyses presented by Beard and Johnson (2006-this issue) are consistent with the observations of Poitrasson and Freydier (2005) that granites with SiO₂ > 71 wt.% have δ⁵⁷Fe significantly above the mean mafic earth Fe isotopic composition. Inclusion of mineral separate analyses and bulk rocks with SiO₂ > 71 wt.% can explain the larger range attached to the igneous baseline of Beard and Johnson (2006-this issue). Using only bulk igneous rock analyses with SiO₂ < 71 wt.% leads to a much tighter definition of this igneous baseline (0.10 ± 0.03‰ δ⁵⁷Fe relative to IRMM-14; Poitrasson et al., 2004). Since that study, a new component of uncertainty has arisen from the demonstration of a significant level of heterogeneity in the Earth’s mantle, as shown by Williams et al. (2005) on bulk rock δ⁵⁷Fe and inferred by Beard and Johnson (2004) from mineral separate values. Only three mantle-derived bulk peridotites were analysed in Poitrasson et al. (2004) and they did not define a specific signature relative to crustal rocks. The bulk mantle rock analyses of Williams et al. (2005) make a tight definition of a “mean mafic earth” iron isotope value more difficult, given the scatter found. However, what fraction of the mantle do the bulk rocks with the most extreme δ⁵⁷Fe represent? If we take the argument of Beard and Johnson (2004), according to which the isotopic homogeneity of mantle-derived basalts in fact favours an overall rather homogeneous bulk isotopic composition of the mantle, then it follows that the extreme bulk rock δ⁵⁷Fe found by Williams et al. (2005) do not represent a large proportion of the mantle. There are therefore no compelling reasons to consider that the mantle is isotopically different from the crust. The “mean mafic earth” Fe isotope signature of Poitrasson et al. (2004) therefore applies to the earth’s crust and mantle in this view. This aspect is discussed in further detail elsewhere (Poitrasson, submitted for publication).

Given that most igneous rocks with SiO₂ > 71 wt.% (with one possible exception, so far, presented by Beard and Johnson, 2004, 2006-this issue) are isotopically heavier than other igneous rocks from the crust (Fig. 1), what influence will these rocks have on the mean δ⁵⁷Fe of the continental crust? This mass balance calculation was outlined in Poitrasson and Freydier (2005) and it is presented in somewhat more detail here (Table 2). The input data consist of Wedepohl’s (1995) compilation of the petrological and geochemical composition of the continental crust. They are combined with an estimated mean δ⁵⁷Fe composition of granites of 0.25‰, obtained from their mean SiO₂ content taken by Wedepohl (1995) and the trend shown in Fig. 6 of Poitrasson and Freydier (2005), or Fig. 1 here. Using these input data, the bulk continental crust composition is virtually unaffected by these heavier Fe isotopic composition of granites (Table 2). The upper crust shows an increase to 0.12‰ δ⁵⁷Fe, which remains indistinguishable from the mean mafic earth isotopic baseline (0.103 ± 0.032‰). Varying the parameters shown in Table 2 within reasonable limits will not significantly affect these conclusions. For example, if the less well constrained parameter, the mean granite δ⁵⁷Fe value, rises from 0.25‰ to 0.35‰, the bulk upper continental crust (δ⁵⁷Fe = 0.133‰) will remain indistinguishable from the mean mafic earth reference value. A δ⁵⁷Fe of 0.35‰ is only observed in granites with SiO₂ > 75 wt.%, so the computed bulk upper crust value of 0.133‰ is in fact an overestimate, since much less than 25% of the upper continental crust corresponds to such silica-rich granites (Wedepohl, 1995).

Combined with the Beard and Johnson (2006-this issue) compilation of sedimentary rock analyses which show minimal Fe isotopic variations (except for samples affected by diageneis), these observations militate in favour of a constant isotopic composition of the continental crust, at around 0.10 ± 0.03‰ δ⁵⁷Fe relative to IRMM-14.

Despite this global homogeneity, reporting Fe isotope data by reference to igneous rocks should be abandoned, because no igneous rock standard that is widely available to the community has been identified. As a result, a laboratory can use any igneous rock to normalise its Fe isotopic data (see, e.g., Khem et al., 2003), and if it happens to be a granite, then the δ⁵⁷Fe values produced will not be comparable to those from other laboratories. Although granites are an extreme case, there are also slight variations between less felsic magmatic rocks, while remaining within the brackets used to define the igneous rocks mean. Comparison of the high precision Fe isotope data now achievable by modern MC-ICP-MS instruments will thus unnecessarily suffer from this lack
of accuracy. It is therefore much simpler and straightforward to report Fe isotope data relative to the widely available European iron isotope reference material IRMM-14. Furthermore, this sample happens to have an isotopic composition close to that of bulk chondrites (Poitrasson et al., 2005) and it therefore has a geochemical significance.

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