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Invited review article

Fe isotopes and the contrasting petrogenesis of A-, I- and S-type granite

John Foden [a,*], Paolo A. Sossi [a,b], Christine M. Wawryk [a]

[a] *Department of Geology and Geophysics, School of Physical Science, University of Adelaide, 5000 Adelaide, SA, Australia*
[b] *Research School of Earth Sciences, Australian National University, 0200 Acton, ACT, Australia*

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ABSTRACT

We present new Fe isotope data of 42 S-, I- and A-type (ferroan) granites from the Cambrian Delamerian orogen in South Australia, the Palaeozoic Lachlan Fold Belt and Western USA. Interpretation of these data, together with modelling suggests that magmatic processes do result in quite complex Fe-isotopic differentiation trends and can lead to granites with isotopically heavy iron with δ^{57}Fe > 0.35‰. By comparison Mid-Ocean Ridge Basalts (MORBs) have δ^{57}Fe = 0.15‰ (Teng et al., 2013). These variations are similar to those previously reported (Poitrasson and Freydier, 2005; Heimann et al., 2008; Telus et al., 2012), but, contrary to some interpretations (Beard and Johnson, 2006; Heimann et al., 2008), heavy values are not necessarily the product of late-stage hydrothermal fluid loss, though this process is undoubtedly also an important factor in some circumstances. A-type (ferroan) granites reach very heavy δ^{57}Fe values (0.4–0.5‰) whereas I-types are systematically lighter (δ^{57}Fe = 0.2‰). S-type granites show a range of intermediate values, but also tend to be isotopically heavy (δ^{57}Fe ≈ 0.2–0.4‰). Our results show that the iron isotopic values and trends are signatures that reflect granite generation *processes*. A modelling using the Rhyolite-MELTS software suggests that contrasting trajectories and endpoints in Fe isotope evolution towards granite depend on: oxidation state of the evolving magma and, whether or not the system is oxygen-buffered. Iron isotopic evolution supports an origin of ferroan A-type granite from protracted, closed magma chamber fractionation of moderately reduced mafic magmas. In these systems magnetite saturation is delayed and the ferric iron budget is finite. I-type systems originate with the supply of relatively oxidised, hydrous, subduction-related magmas from the mantle wedge to the upper plate crust. These then experience oxygen-buffered open-system AFC processes in lower crustal hot-zones. S-type magmas are crustal melts that crystallise under reduced conditions initially imposed at source by sulphidic or graphitic sedimentary protoliths. The composition of the resulting melts reflects the domination of partial melting where conditions are hence buffered (open system) followed by subsequent late-stage, closed system fractionation of these extracted, reduced magmas.

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* Corresponding author.
E-mail address: john.foden@adelaide.edu.au (J. Foden).

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1. Introduction

The igneous spectrum of granites (sensu lato) is derived from a diversity of source rock compositions and petrogenetic processes (Chappell and White, 1974, 2001; Frost and Frost, 2011; Frost et al., 2001; Tuttle and Bowen, 1958). In order to simplify and characterise the extant types of granites, the A-, I- and S-type classification scheme (Frost et al., 2001) is often used. In broad terms, I-types have an 'igneous' protolith, whereas S-types are derived from sedimentary sources. A-types, by contrast, are more difficult to categorise, where the 'A' may stand for anorogenic or alkaline (Bonin, 2007). It has been shown that these petrologic subdivisions reflect the tectonic environment in which they were formed (Pearce et al., 1984).

Iron isotopes are a powerful tool for tracking magmatic processes, and, in particular, for equilibria in high temperature systems (e.g. Dauphas et al., 2009). Variations arise because Fe^{3+} enters smaller tetrahedral sites, while the larger Fe^{2+} ion prefers octahedral coordination. As $^{IV}Fe-O$ bonds are shorter and stiffer, they tend to concentrate on the heavy isotopes (e.g. Schauble, 2004). Expected iron isotope compositions of mineral phases calculated by Mössbauer spectroscopy and NRIXS (Dauphas et al., 2012; Polyakov and Mineev, 2000; Polyakov et al., 2007) reveal β-factors which increase with $Fe^{3+}/\sum Fe$ in the sequence $\beta_{Hem} > \beta_{Mtn} > \beta_{Ol,Px}$. Iron isotope partitioning in the quartz–fayalite–magnetite system, typical phases found in granitic rocks, confirmed enrichment in ^{57}Fe in magnetite over fayalite, expressed as: $\Delta^{57}Fe_{Mtn-Fay} = +0.30‰ \pm 0.024‰ \times 10^6/T^2$ (Shahar et al., 2008). In the closed system differentiation of mafic tholeiite to granophyre, Sossi et al. (2012) made precise determinations of melt–pyroxene and melt–magnetite fractionation factors yielding; $\Delta^{57}Fe_{Px-Melt} = -0.25‰ \times 10^6/T^2$ and $\Delta^{57}Fe_{Mtn-Melt} = +0.20‰ \times 10^6/T^2$. This vector of fractionation is also evidenced by analyses of co-existing magnetite and ferromagnesian minerals (amphibole and biotite), where the oxide phase is invariably ^{57}Fe-enriched compared with the silicates, which have a composition similar to the bulk rock (Heimann et al., 2008; Telus et al., 2012).

Based on these established fractionation factors and typical analytical precisions for $\delta^{57}Fe$ of $\approx \pm 0.03$ (2SE) (Sossi et al., 2014) it is clearly feasible to expect significant variation in the Fe isotopic composition of differentiating magmatic systems. Indeed, Poitrasson and Freydier (2005) were the first to highlight the departure toward ^{57}Fe-enriched values of granites ($\delta^{57}Fe$ up to $+0.58‰$) compared with terrestrial basalts ($\delta^{57}Fe \approx 0.1‰$; Weyer and Ionov, 2007; Teng et al., 2013), a tendency attributed to the exsolution of a hydrothermal fluid phase. Such a contention was supported in a more extensive study of differentiated magmas by Heimann et al., 2008, who found similarly heavy iron isotope values. Studies focusing on the iron isotope composition of evolving magmatic suites (Schoenberg and von Blanckenburg, 2006; Schuessler et al., 2009) also identified a kick towards higher values, particularly above 70% SiO_2, though a fluid exsolution cause for this change was not favoured. Telus et al. (2012) asserted that fluid loss could explain the heavy $\delta^{57}Fe$ composition of pegmatites, but granitic rocks, owing to their unfractionated zinc isotope composition relative to basaltic rocks, had not experienced exsolution. Such behaviour was pointed to by Sossi et al., 2012, who suggested that mineral–melt equilibria had a role to play in determining the final iron isotopic composition of granites.

In this study we address two fundamental questions. First, how do magmatic processes that lead to the production of granite yield systematic and measurable iron isotopic variations, in some cases producing quite heavy $\delta^{57}Fe$ values? Second, do the differences in petrogenetic processes and in critical intensive and extensive variables such as T, P, fO_2 and water content, that produce different types of granites (I-, S-, A-type), lead to contrasting and potentially diagnostic iron isotopic variations? Here, we present data for 42 granitic (>60% SiO_2) rocks from South-East Australia (Black et al., 2010; Foden et al., 2002; Wawryk and Foden, 2014) and the western United States (Bonnichsen et al., 2008; Savov et al., 2009) that serve to answer these questions. The data is evaluated in the light of the existing classification schemes for granitic rocks and their petrogenetic history and tectonic environment.

2. The samples

In order to investigate the potential role of petrogenetic processes that might have on the fractionation of iron isotopes during granite formation, we have assembled a set of granite samples that represent clear representatives of the A-, I- and S-type suites. These have been culled from well characterised suites from the Cambrian Delamerian orogen in SE Australia (Foden et al, 2002) or from Devonian–Carboniferous suites from the Australian Lachlan Fold Belt, in this case sampled in Tasmania (Black et al., 2010; Wawryk and Foden, 2014). Both of these Australian Cambrian and Devonian–Carboniferous orogenic systems are part of the Pacific margin evolution of SE Gondwanaland (Foden et al., 2006), and are products of "Andean" marginal style subduction of the Pacific plate under the Gondwanan margin.

3. Analytical techniques

3.1. MC-ICP-MS

Samples were dissolved in a concentrated $HF-HNO_3-HCl$ solution before being passed through anion exchange columns (AG1-X4, 200–400 mesh) in chloride form to ensure quantitative separation of iron from matrix elements (Poitrasson and Freydier, 2005). 4 ppm Fe solutions spiked with 8 ppm Ni were run on a ThermoFinnigan Neptune Multicollector ICP-MS (CSIRO/University of Adelaide, Waite Campus) in solution mode and H-cones with a glass spray chamber and Scott double-pass assembly coupled to a low-flow PFA Nebuliser sample introduction mechanism. The resulting sensitivity was 0.2 V ^{57}Fe/ppm and 0.1 V ^{61}Ni/ppm. Data are corrected using the Ni-spiking method of Poitrasson and Freydier (2005), resulting in external precision of $\pm 0.02‰$ for $\delta^{56}Fe$ and $\pm 0.03‰$ for $\delta^{57}Fe$, provided $^{61}Ni \approx 1$ V (Sossi et al., 2014). Sample solutions were repeatedly run up to six times. All data are reported relative to the international isotopic reference standard IRMM-014 (Taylor et al., 1992).

3.2. FeO determinations

The ferrous iron content of the whole rocks was determined by the volumetric wet chemical analysis as developed by Wilson (1960). The procedure relies upon the quantitative oxidation of Fe^{2+} in the sample by V^{5+}, as the V^{4+} produced is more resistant to accidental oxidation during hot acid dissolution (48% HF-9M H_2SO_4) than is ferrous iron. Ferrous iron is regenerated by back-titration with ammonium ferrous sulfate, from which the original Fe^{2+} content may be calculated.