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Earth and Planetary Science Letters 268 (2008) 330–338

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Equilibrium high-temperature Fe isotope fractionation between fayalite and magnetite: An experimental calibration

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Received 20 October 2007; received in revised form 14 January 2008; accepted 17 January 2008
Available online 6 February 2008
Editor: R.W. Carlson

Abstract

The iron isotopic fractionation factor between magnetite and fayalite was measured at high temperature in a piston–cylinder apparatus. For the first time, the three-isotope method [Matsuhisa, J., Goldsmith, J. R., and Clayton, R. N., 1978. Mechanisms of hydrothermal crystallisation of quartz at 250 °C and 15 kbar. Geochim. Cosmochim. Acta 42, 173–182.] has been used to determine equilibrium fractionation between two minerals directly. The experimentally-determined temperature-dependent iron isotope fractionation between fayalite and magnetite is described by $10^3\ln\alpha^{57}_{\mathrm{Mag-Fa}} \cong \Delta^{57}\mathrm{Fe}_{\mathrm{Mag-Fa}} = 0.30\ (+/-0.024)\times 10^6/T^2$. The equation predicts measurable fractionation at magmatic temperatures. Our work bears on the magnitude of Fe isotope fractionation attending differentiation in magmatic systems and provides a new isotope thermometer for co-existing fayalite and magnetite.

Keywords: iron isotope; thermometer; igneous rocks; high-temperature; three-isotope exchange; magnetite

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1. Introduction

Iron isotope ratios have proven to be especially useful tracers in a variety of geochemical settings due to the ubiquitous nature of Fe and to its variable oxidation states. Differences in iron isotope ratios have been used to address a myriad of questions including, but not limited to, those relating to: biosignatures (Beard and Johnson, 1999), early solar system processes (Zhu et al., 2001), and planet formation processes (Poitrasson et al., 2004). Each of these applications depends critically on understanding factors that fractionate Fe isotopes.

Most work involving Fe isotopes has focused on low-temperature processes because differences between minerals equilibrated at high temperature are expected to be small due to decreasing fractionation with increasing temperature (T). But, with the advent of the multiple-collector inductively coupled plasma-source mass spectrometer (MC-ICPMS), these smaller differences in δ^{56}Fe and δ^{57}Fe(1) can now be measured more precisely.

Differences between $\delta^{56(57)}$Fe values of mantle minerals have been measured, but no consensus has been reached as to whether there are consistent iron isotopic fractionations amongst them. Zhu et al. (2002) found that olivine separates from lherzolites are isotopically lighter (by >0.2‰ in ^{57}Fe/^{54}Fe) than co-existing orthopyroxene and clinopyroxene. Beard and Johnson (2004) found that olivine and orthopyroxene separates from spinel peridotites have indistinguishable ^{57}Fe/^{54}Fe, whereas co-existing clinopyroxene and olivine were found to show some measurable differences in δ^{57}Fe. A compilation of $\Delta^{56}\mathrm{Fe}_{\text{mineral-olivine}}$ ($\Delta^{56}\mathrm{Fe}_{i-j} = \delta^{56}\mathrm{Fe}_i - \delta^{56}\mathrm{Fe}_j$) representing separates of co-existing minerals in igneous rocks (Williams et al.,

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doi:10.1016/j.epsl.2008.01.026

[1] $\delta^{56(57)}\mathrm{Fe} = (^{56(57)}\mathrm{R}_{\mathrm{smp}}/^{56(57)}\mathrm{R}_{\mathrm{IRMM\text{-}014}} - 1)*1000$ where $^{56(57)}\mathrm{R} = ^{56(57)}\mathrm{Fe}/^{54}\mathrm{Fe}$ and IRMM-014 is an international Fe standard. In what follows reference will be made to both δ^{56}Fe and δ^{57}Fe since both values are reported by various authors. In all cases considered here Fe isotope fractionation is mass dependent and so there is no significance to choosing one ratio over the other.

2005; Beard and Johnson, 2004; Zhu et al., 2002) is shown in Fig. 1. The plot underscores the fact that there are no clear systematic inter-mineral relationships emerging from the studies thus far. The peaks for the fractionations between olivine (Ol) and clinopyroxene (Cpx), orthopyroxene (Opx), spinel (Spl), and magnetite (Mag) all overlap, with no mineral defining a population that is clearly resolvable from olivine. Calculations of bond strength predict that magnetite and spinel should concentrate ^{56}Fe and ^{57}Fe relative to ^{54}Fe more than co-existing silicate minerals because of the lower Fe coordination in the spinel-group minerals (Polyakov and Mineev, 2000). Of the minerals presented in Fig. 1, magnetite should show the largest difference from olivine due to its crystal chemistry and yet the magnetite data are centered on $\Delta^{56}\mathrm{Fe}_{\mathrm{Mag-Ol}}=0$.

One explanation for a lack of a clear trend in Fig. 1 may be that differentiation processes are accompanied by Fe isotope fractionation, resulting in variable mineral ^{56}Fe/^{54}Fe values that reflect not only equilibrium mineral fractionation, but differences in bulk rock Fe isotope ratios from open-system processes. In the absence of direct experimental determination of Fe isotope fractionation factors it is not possible to determine what causes the lack of systematics among mantle igneous minerals shown in Fig. 1.

Understanding the equilibrium inter-mineral ^{57}Fe/^{54}Fe (and ^{56}Fe/^{54}Fe) differences amongst high-temperature minerals should be valuable for interpretations of the significance of iron isotope ratios in igneous rocks, especially at the sub-‰ level currently being investigated. *Ab initio* predictions for Fe isotope fractionation among high-*T* minerals exist, but experiments will ultimately be required to verify predictions, and in some cases to supplant them. To date there have been just two published high-temperature iron isotope experimental studies. Roskosz et al. (2006) investigated the kinetic fractionation of iron isotopes between a silicate melt and metal alloys at high temperature and room pressure. Schuessler et al. (2007) reported the iron isotopic fractionation factor between pyrrhotite and silicate melt at high pressure and temperature.

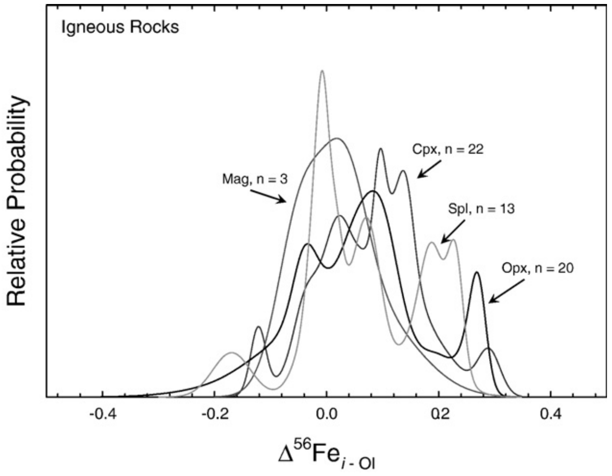

Fig. 1. Relative probability plot showing $\Delta^{56}\mathrm{Fe}_{\mathrm{mineral\text{-}olivine}}$ in natural igneous rocks. Data compiled from Williams et al. (2005), Beard and Johnson (2004), and Zhu et al. (2002).

In this study we use the three-isotope exchange method (originally used for oxygen by Matsuhisa et al., 1978) to experimentally determine the equilibrium iron isotope fractionation factor between fayalite and magnetite as a function of temperature in the assemblage magnetite + quartz + fayalite (Fa) comprising the "QFM" oxygen fugacity buffer. This study is a first step in experimentally quantifying inter-mineral Fe isotope fractionation in natural samples at high temperatures and known oxygen fugacity. Our results demonstrate that igneous differentiation involving magnetite, and by extension other spinel phases with tetrahedrally coordinated Fe, can result in shifts in igneous rock Fe isotope ratios. They also provide a well-calibrated Fe isotope thermometer for magnetite-fayalite-bearing rocks in equilibrium.

2. Methods

2.1. Piston–cylinder experiments

Starting materials were finely ground powders of synthetic, high-purity fayalite, quartz, and hematite. The fayalite and quartz were synthesized hydrothermally. Hematite was prepared by mixing α-Fe_2O_3 powder (Alfa Aesar) with high-purity α-$^{54}Fe_2O_3$ (Oak Ridge National Laboratory Batch 154891, ^{54}Fe 98.37%, ^{56}Fe 1.55%, ^{57}Fe 0.07%, ^{58}Fe 0.008%) in a 99:1 ratio. The mixture was twice ground under acetone in a mortar and pestle for 30 min. The starting mineral assemblage which consisted of ~50 mg of synthetic fayalite and quartz and ~10 mg of hematite, was ground for 20 min under acetone to produce a homogeneous mixture.

For each experiment the starting assemblage was loaded with ~15 mg nanopure H_2O into segments of Au tubing of 3.5 mm outer-diameter and 0.18 mm wall thickness. The capsule was then welded shut and checked for leaks by heating at 100 °C for 30 min and checking for weight loss. Any capsule that lost weight was incompletely sealed and discarded.

All experiments were performed in a 1-inch diameter piston–cylinder apparatus with NaCl pressure medium and graphite heater sleeve. A thin piece of Au was placed on top of the capsule to prevent puncture by the thermocouple. Temperature was monitored with $Pt/Pt_{90}Rh_{10}$ thermocouples in contact with the capsule, with no correction for the effect of pressure on emf. The accuracy of the reported temperature is estimated to be ±3 °C. All experiments were brought to a pressure of 7 kbar and then heated to the desired run temperature, where thermal expansion of the assembly brought the pressure to 10 kbar. Pressure was monitored with a Heise gauge and maintained to within 200 bar gauge pressure. Experiments were quenched by cutting power to the apparatus, which resulted in cooling of the experiment to <50 °C in <1 min (Manning and Boettcher, 1994).

Following each run, the capsules were retrieved, cleaned, and pierced with a needle, releasing water through the hole. The presence of water indicated that the capsule did not leak during the experiment. The run products were then carefully removed and placed in a glass container. After optical inspection using a binocular microscope, magnetite and fayalite were separated