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Isotope fractionation in silicate melts by thermal diffusion

It was recently shown that relatively large (compared to analytical precision) steady state thermal isotope fractionations are produced in silicate melts whenever temperature differences are maintained for a sufficiently long time[1,2]. Huang *et al.*[3] reported new data on thermal isotopic fractionation of magnesium, calcium, and iron in silicate liquids, and claimed (1) that thermal isotopic fractionations in silicate liquids are independent of composition and temperature, and (2) that their "results lead to a simple and robust framework for characterizing isotope fractionations by thermal diffusion in natural and synthetic systems". Here I consider whether the data and arguments presented by Huang *et al.*[3] support their claims. In summary, I caution against assuming (on the basis of the data presented by Huang *et al.*[3]) that the thermal isotopic fractionations are independent of temperature and composition, or that a framework of the type claimed has been found.

Huang *et al.*[3] reported new data on thermal isotopic fractionation of magnesium, calcium and iron in silicate liquids that extend the earlier results[1,2] to a larger temperature range and to compositions other than basalt. The magnesium isotopic composition versus temperature reported by Huang *et al.*[3] for molten andesite and basalt are shown in Fig. 1. The local slope in such a plot determines the thermal-diffusion isotopic sensitivity Ω, defined as the magnitude of isotopic fractionation per temperature offset, and expressed in units of ‰ $°C^{-1}$ AMU^{-1} (here AMU indicates atomic mass unit). If Ω is independent of temperature, the data would fall on straight lines, which is clearly not the case for the andesite experiments (squares in Fig. 1), where the slope of the isotopic fractionations versus temperature shows
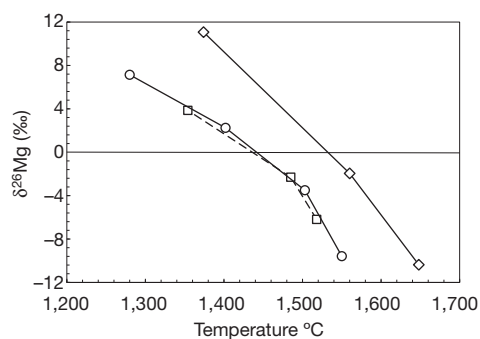

Figure 1 | Isotopic fractionation of magnesium as a function of temperature. Data are taken from table 1 in Huang *et al.*[3]. Shown are values for molten Mount Hood andesite (squares for data from a 46-h experiment, circles for data from a 168-h experiment), and for molten mid-ocean-ridge basalt (diamonds for data from a 264-h experiment). The isotopic fractionations are given as $\delta^{26}Mg(‰) = \left(\dfrac{(^{26}Mg/^{24}Mg)_{sample}}{(^{26}Mg/^{24}Mg)_{starting\ material}} - 1 \right) \times 1,000$. The figure shows that in the case of andesite, Ω_{Mg} is not constant, but rather decreases by a factor of more than two between $T > 1,500\ °C$ and $T < 1,500°C$. The data for basalt are too few to support a conclusion to the effect that Ω_{Mg} is independent of composition.

that Ω_{Mg} varies from about 0.05‰ $°C^{-1}$ AMU^{-1} for $T > 1,450\ °C$ to about 0.02‰ $°C^{-1}$ AMU^{-1} for $T < 1,450\ °C$. Despite this, Huang *et al.*[3] imply in their figure 1 that $\Omega_{Mg} = 0.03$ ‰ $°C^{-1}$ AMU^{-1} with an uncertainty of only ±10%. The iron isotope data reported by Huang *et al.*[3] also show large variations of Ω_{Fe} with temperature.

Huang *et al.*[3] claim to have cast their experimental observations in a theoretical framework. This 'theoretical framework' is simply a parameterization of an assumed, not theoretically derived, functional form for the mass dependence of a quantity they call ΔS_T, which, like Ω, is proportional to the slope of the thermal isotope fractionations versus temperature. The assumed expression for ΔS_T is $\Delta S_T = c \left(\dfrac{Z^2}{a} \right)^{\beta} (X^{\alpha} - Y^{\alpha})$, where X and Y are the mass of two isotopes of an element of valence Z and ionic radius a. The three quantities c, α and β were adjusted such that the calculated ΔS_T reproduces three values of ΔS_T taken from their experiments. Leaving aside the issues of what specific value of ΔS_T to choose, given its variation with temperature, which is proportional to the slope of $\delta^{26}Mg$ versus temperature shown in Fig. 1, or that all the elements considered have the same Z, using a parameterization with three free parameters to fit three data does not constrain and validate the functional form of the parameterization. One can, however, test the proposed parameterization by calculating ΔS_T for all the major elements of basalt (magnesium, calcium, iron, silicon and oxygen) and comparing these to the experimental data reported by Richter *et al.*[2]. As might be expected, the parameterization works reasonably well in reproducing the measured ΔS_T for magnesium, calcium and iron; however, when applied to oxygen and silicon, the calculated values and the measured values differ by more than a factor two for oxygen and more than a factor of ten for silicon.

I caution against assuming (on the basis of the data presented by Huang *et al.*[3]) that thermal isotope fractionations in silicate liquids are independent of temperature and composition or that they have found "a simple and robust framework for characterizing isotope fractionations by thermal diffusion in natural and synthetic systems".

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3. Huang, F. *et al.* Isotope fractionation in silicate melts by thermal diffusion. *Nature* **464**, 396–400 (2010).

Huang *et al.* reply

In our Letter[1], we showed that the phenomenon of isotope fractionation in silicate melts by thermal diffusion, first reported in 1998 (ref. 2), can be characterised by a parameter ΔS_T that is independent of temperature and composition. (Here ΔS_T is the difference in the Soret coefficient, S_T, between isotopes of a diffusing element.) Richter[3] questioned this finding by plotting Mg isotope ratio versus temperature data (figure 1 in ref. 3) for a subset of experiments from figure 3f of ref. 1.

Using the same coordinate system as Richter (figure 1 of ref. 3), here in Fig. 1a we plot the Mg data for all of the experiments (figure 3f of ref. 1), and in Fig. 1b we plot the Fe data for all of the experiments (figure 3d of ref. 1). Focussing on individual experiments, we find that isotope fractionation, as measured by the local slope of the data, may increase (as emphasised by Richter[3]) or decrease, but commonly follow a near-linear distribution. Further, when the same data are plotted as isotope ratios versus relative temperature (ΔT), as was done in ref. 1,
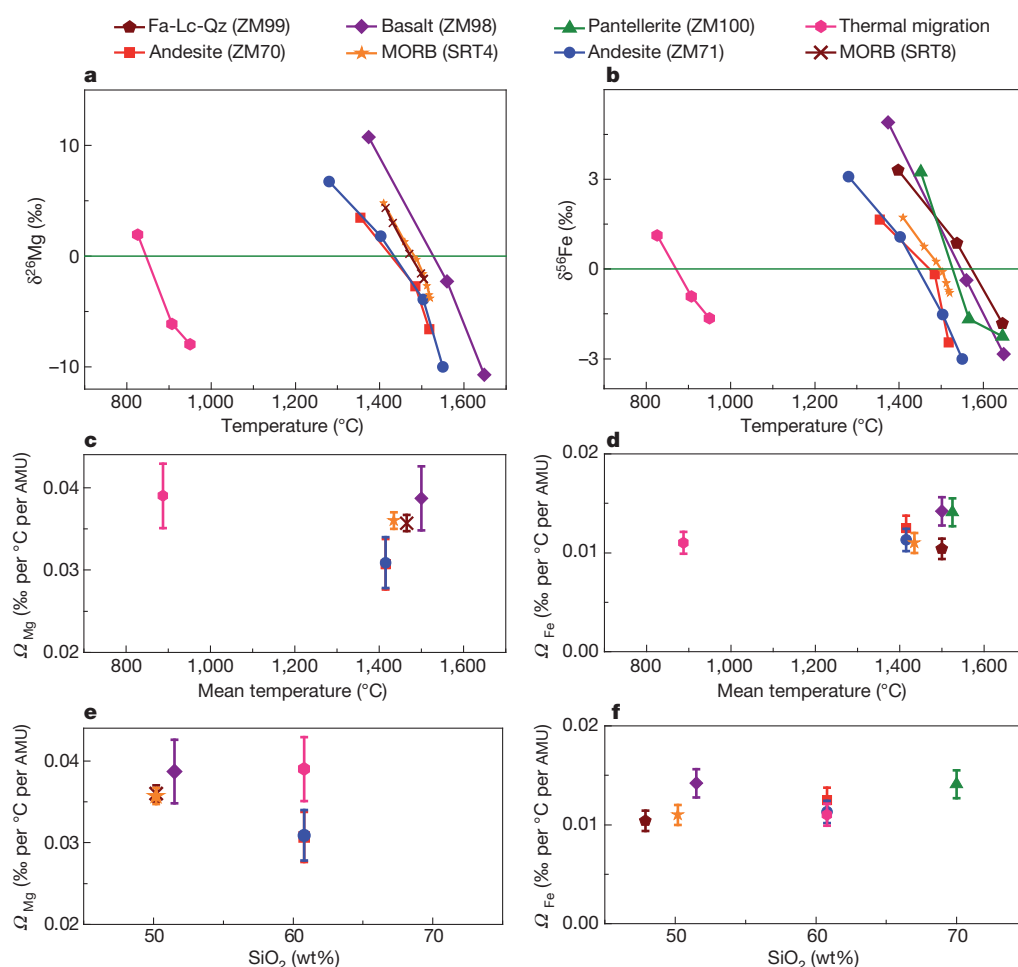

Figure 1 | Variation of Mg and Fe isotope data with composition and temperature. a, b, Mg (**a**) and Fe (**b**) isotope ratio versus temperature. The same data are presented as isotope ratio versus relative temperature (ΔT) in figure 3d, f of ref. 1. The isotope ratios are expressed as
$\delta^{26}Mg = 1{,}000 \times [(^{26}Mg/^{24}Mg)_{sample}/(^{26}Mg/^{24}Mg)_{DSM\text{-}3} - 1]$ (‰) and
$\delta^{56}Fe = 1{,}000 \times [(^{56}Fe/^{54}Fe)_{sample}/(^{56}Fe/^{54}Fe)_{IRMM\text{-}14} - 1]$ (‰). **c, d,** Mg (**c**) and Fe (**d**) thermal-diffusion isotopic sensitivity (Ω, expressed in units of ‰ $°C^{-1}$ AMU^{-1}) versus mean temperature; **e, f,** Ω_{Mg} (**e**) and Ω_{Fe} (**f**) versus SiO_2 content of the experimental starting materials. The slope of isotope ratio versus temperature data for Mg and Fe (in **a** and **b**) is proportional to Ω_{Mg} and Ω_{Fe} (in **c–f**), respectively. Here (and in figure 1 of ref. 1) we compute the Ω (and the corresponding error bar, ± 1 s.d., calculated on the basis of errors in isotope analyses and temperature measurements) for each experiment using the data from the cold and hot ends. Note that despite wide variations in experimental

conditions, the isotope ratio versus temperature profiles are approximately linear, and the Ω values are approximately independent of temperature and composition. The same conclusion, albeit based on a limited range of experimental conditions, also applies for Ca (ref. 1). The data sources for the experiments are: ref. 1 for Fe_2SiO_4-$KAlSi_2O_6$-SiO_2 (Fa-Lc-Qz), pantellerite, andesite and basalt; ref. 4 for thermal migration; and refs 9 and 10 for MORB. The thermal migration experiment was conducted using USGS andesite standard AGV-1 (plus 4% H_2O) as starting material at 5 kbar and in a temperature gradient from 950 to 350 °C (ref. 4). Thermal diffusion experiments of ref. 1 were carried out at 10 kbar using starting materials with SiO_2 content ranging from 47.9 to 70 wt% (refs 11, 12). (As an aside, we note a labelling error in figure 3b of ref. 1: the red curve corresponds to ZM70 and the blue curve corresponds to ZM71.)

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all experiments to first order collapse onto a linear distribution (with the coefficient of determination, R^2, being 0.94 for Mg data and 0.93 for Fe data; see figure 3d and f in ref. 1); this is despite wide variations in starting composition (48–70 wt% SiO_2), mean temperature (850–1,525 °C), and in one case, the presence of co-existing mineral phases[4]. These findings cannot be reconciled if there are significant temperature and compositional dependences on isotope fractionation arising from thermal diffusion.

Moreover, it is ill-advised to attach much significance to incremental changes in slope along a thermal diffusion profile composed of relatively few, widely spaced analyses, and with non-trivial temperature uncertainties for the intermediate positions as compared to the cold and hot ends of the temperature gradient. If, instead, one considers the thermal-diffusion isotopic sensitivity (Ω), which reflects the overall fractionation between the hot and cold ends, the differences for Mg and Fe (Fig. 1c–f), as well as for Ca, are small and unsystematic with temperature or composition—observations that reinforce our original claim.

Richter[3] also maintains that our theoretical treatment is little more than data fitting. This view seems to miss the significance of the linear relationships shown in figure 3d–f of ref. 1, which demonstrate no significant variation in ΔS_T with temperature or composition. These observations enabled the additive decomposition of S_T (equation (5) in ref. 1), which provides a strong constraint for a general theory of thermal diffusion in silicate melts. It further permits links to thermal diffusion in other systems[5–8]. The fit that we presented in the Supplementary Information of ref. 1 was simply an example of using equation (5)[1] to seek empirical formulae for ΔS_T using the available data for network modifiers.

Last, we agree with Richter[3] that our treatment is not suitable for silicon and oxygen, but we find his criticism misplaced, as we explicitly stated in our letter[1] that "We limit our attention to the steady state of thermal diffusion and, furthermore, to the isotopic fractionation of iron, calcium and magnesium (which break up the polymerization of the silicate melt and are thus termed network modifiers), and do not consider network formers (for example silicon and oxygen, which form tetrahedron networks in silicate melts)."

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