

## Experimental determination of the Si isotope fractionation factor between metal and silicate liquids

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The conditions of core formation on Earth are still debated and stable isotope fractionation is explored as a new tool to further constrain metal-silicate segregation conditions. It has been shown that chondrites and (ultra)mafic terrestrial silicates have different Si isotope compositions<sup>1-3</sup>, although there is no consensus yet<sup>4</sup>. Recent experimental work has found  $-1.77 \pm 0.32\%$  fractionation between liquid metal and olivine at  $1800^\circ\text{C}$ <sup>5</sup>, which implies that Si isotope fractionation may occur during core formation in planetesimals and on Earth.

To better constrain the conditions of core formation, Si isotope fractionation between metal and silicate must be well calibrated. We therefore performed liquid metal, liquid silicate equilibration experiments at  $1450^\circ\text{C}$  and  $1750^\circ\text{C}$  at 1 GPa in a centrifuging piston cylinder at ETH Zurich. The physically segregated liquids were mechanically separated prior to dissolution by alkali fusion. After ion exchange chromatography, isotopic analyses were carried out on a Nu Instruments 1700 MC-ICPMS at ETH Zurich.

The silicate liquids had consistently heavier Si isotopes than the equilibrated metal liquids. The average fractionation factor between metal and silicate liquids ( $\Delta^{30}\text{Si}_{\text{Metal-Silicate}}$ ) was  $-1.48 \pm 0.08\%$  at  $1450^\circ\text{C}$  and  $-1.11 \pm 0.14\%$  at  $1750^\circ\text{C}$ . Given a  $1/T^2$  functional form, the temperature dependence of Si isotope fractionation between metal and silicate liquids can be described as  $\Delta^{30}\text{Si}_{\text{Metal-Silicate}} (\%) = -4.47 (\pm 0.31) \times 10^6 / T^2$ .

Our equilibrium data yield a smaller fractionation than previously deduced<sup>5</sup>. Calculations at 2500-3500 K for metal-silicate equilibration during core segregation on Earth imply a bulk Earth  $\delta^{30}\text{Si}$  of  $-0.38$  to  $-0.33$  ( $\pm 0.02\%$  propagated error), respectively, for a bulk silicate Earth  $\delta^{30}\text{Si}$  of  $-0.29 \pm 0.01\%$  and 6 wt% Si in the Earth's core. Although the calculated values fall in the range of observed chondrite Si isotope compositions, they do not match all observations for the Si isotope composition of chondrites.

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## Combining radiogenic and stable Ca isotopes to explore sub-glacial weathering reactions

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The interpretation of weathering processes based on the stable isotopes of calcium (Ca) is complicated by the difficulty of distinguishing between source and process fractionation effects. The combination of radiogenic Ca isotopes ( $\epsilon^{40}\text{Ca}$ ) with stable Ca isotopes ( $\delta^{44/42}\text{Ca}$ ) would provide the ability to separate source and process fractionation effects. The aim of this study was to combine both the stable and radiogenic Ca isotope systems to investigate the sources of Ca and Ca isotope fractionation processes in glaciated environments, providing great potential to increase understanding of the behaviour of Ca during weathering.

This study is based on a one month sampling campaign to Leverett Glacier, West Greenland in July 2009. The bedrock (granite/gneiss) is of Archean age (ca 1850 Ma), theoretically old enough to have acquired radiogenic  $^{40}\text{Ca}$  anomalies. Water samples were collected twice daily for a period of 28 days together with spot samples of water end-members (ice, supra-glacial water) and four representative rock samples from which the main Ca bearing minerals were separated.

The bulk rock samples exhibit a range in both stable ( $\delta^{44/42}\text{Ca} = +0.20$  to  $+0.50\%$ ) and radiogenic ( $\epsilon^{40}\text{Ca} = -1.0$  to  $+6.9$ ) Ca isotopic compositions. Two of the analysed mineral separates had significant radiogenic Ca anomalies: sanidine ( $\epsilon^{40}\text{Ca} = +15.3$ ) and biotite ( $\epsilon^{40}\text{Ca} = +7.7$ ). Radiogenic anomalies up to  $\epsilon^{40}\text{Ca} = +5.3$  were detected in river water samples, coincident with an outburst event. The change in  $\epsilon^{40}\text{Ca}$  measured in the river water samples during the outburst event indicates a change in the relative contribution from different mineral sources to the dissolved load of Ca. In contrast, the stable Ca isotopic composition of river water showed no discernable temporal variation and had an average  $\delta^{44/42}\text{Ca}$  of  $+0.60\%$ , which was significantly higher than the source rocks. The combination of  $\epsilon^{40}\text{Ca}$  and  $\delta^{44/42}\text{Ca}$  data clearly indicates that  $\delta^{44/42}\text{Ca}$  values cannot be reconciled with mixing processes and have been fractionated.