

Calibrating Mg Isotope Signatures for Magma Ocean Evolution: A Combined Experimental and Computational Approach

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Understanding the high-temperature equilibrium fractionation of Mg isotopes between mineral and melt phases is crucial for elucidating large-scale magmatic processes, particularly the crystallization dynamics of Earth's primordial magma ocean. A challenge in understanding the isotope fractionation measured in natural sample arises from the significant influence of kinetic fractionation and various complicating factors inherent in natural systems.

In order to isolate the effect of equilibrium isotope fractionation we employed a combination of experimental and theoretical methodologies targeting forsterite, diopside and a model basaltic melt, as well as a range of other mantle phases. The experimental approach enables measurement of isotope fractionation of Mg and Si between crystals and a co-existing melt phase. Our findings yielded $\delta^{26}\text{Mg}_{\text{di/ol}} = 0.118 \pm 0.045 \text{ ‰}$ at 1300 °C (1573 K), which fall with error analytical error ranges with our density functional theory (DFT) calculations of 0.146 ‰. This provides strong support for the conclusion that equilibrium isotope fractionation could leave a measurable signature in solids or melts extracted from crystallising magmas.

Additionally, we evaluated the impact of various exchange-correlation functionals on the calculated Mg isotope fractionation in crystalline phases using our DFT approach. Our results revealed that the choice of functional significantly affects the outcomes; notably, the PBESOL functional demonstrated the best fit to our experimental data, thus proving to be particularly useful for investigating Mg and Si equilibrium isotope fractionation under temperature and pressure conditions that are inaccessible to experiment.

We took advantage of this finding and conducted DFT calculations focusing on silicate melts using the snapshot methodology of Rabin et al. (2023). The chemical compositions of our silicate melts correspond closely with those used in our experimental setup and our results are consistent with experimental findings, indicating an experimental $\delta^{26}\text{Mg}_o / \text{‰}$ value of $-0.058 \pm 0.032 \text{ ‰}$ and computational value of -0.07 ‰ . Our findings lay the groundwork predictive calculations of isotope fractionation at the higher pressures and temperatures relevant to the evolution of Earth's magma ocean.

[1] Rabin, Blanchard, Pinilla, Poitrasson, & Grégoire, M. (2023). *Geochimica et Cosmochimica Acta*, 343, 212–233.