The Ca isotope composition of bulk Earth: Revisited

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The Ca isotope composition of Bulk Earth is an important parameter for many models of global Ca cycling. The $\delta^{44/40}$Ca value for Bulk Earth has previously been inferred from analyses of various meteorites and terrestrial silicate rocks yielding -0.9±0.2‰ relative to seawater [1;2]. Estimating Bulk Earth using meteorites is hampered by potential Ca isotope heterogeneity in the solar nebula [3], and terrestrial silicates have recently been shown to vary much more widely than previously believed, particularly, mantle peridotites, whose $\delta^{44/40}$Ca values may range as low as -0.7‰ [4].

In this study, we reevaluate the $\delta^{44/40}$Ca of Bulk Earth with new analyses of (1) Primitive and differentiated meteorites that cover various regions of the solar nebula and degrees of planetary differentiation, including carbonaceous chondrites, eucrites and SNCs, and (2) Mantle xenoliths that are 'fertile' with respect to their refractory, lithophile, major element compositions (spinel peridotites previously used to constrain the composition of the Earth's primitive mantle [5]). $\delta^{44/40}$Ca analyses were performed by TIMS using a 43/42-double spike, and are reported in delta notation relative to modern seawater with an analytical uncertainty of <0.1 ‰ (2sd). The $\delta^{44/40}$Ca value for BHVO-2 measured in our laboratory is -0.99±0.04‰.

Five different mantle xenoliths cluster around an average $\delta^{44/40}$Ca value of -0.93±0.04‰ suggesting a homogeneous Ca isotope composition for the upper mantle. The eucrite Camel Donga is identical to this within the quoted uncertainties (-0.92‰). The carbonaceaous chondrites Orgeuil and Allende are shifted to lower $\delta^{44/40}$Ca values by up to 0.3‰. SNC meteorites range from -0.66‰ to -0.99‰. The range of Ca isotope variation in these Martian meteorites is consistent with the range of $\delta^{44/40}$Ca values in terrestrial silicate rocks reported in [4], suggesting that Ca isotope fractionation is associated with igneous differentiation processes on Earth and Mars. Although the fractionation mechanism is not understood, the primitive compositions and uniform $\delta^{44/40}$Ca values of the xenoliths point to a Bulk Earth value of -0.9‰.

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Absolute diffusion rates in $MgSiO_3$ perovskite and post-perovskite

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Diffusion controls most physical and chemical processes in the solid Earth. While experiments are limited to conditions of the shallow lower mantle, ab initio calculations allow us to probe conditions at any pressure and temperature. By applying harmonic transition state theory (Vineyard-theory [1]), we have calculated self-diffusion coefficients of MgO and $MgSiO_3$ perovskite and post-perovskite at conditions of Earth's lower mantle from first principles. This is, to best of our knowledge, the first time that diffusion coefficients of complex materials such as $MgSiO_3$ perovskite and post-perovskite have been calculated from first principles. Our approach relies on determining exact migration pathways using the climbing-image nudged elastic band method [2].

Our analysis shows that magnesium and oxygen in $MgSiO_3$ perovskite migrate via simple single jumps to nearest neighbour sites. For silicon we propose diffusion via a six-jump cycle on the silicon-magnesium-B2 sublattice. In this mechanism, silicon diffuses by making use of vacated magnesium sites and magnesium uses vacated silicon sites. We investigated the rate of this mechanism using mean first passage theory [3] and the kinetic Monte-Carlo method [4].

We compared our absolute diffusion rates with experimental data of magnesium and oxygen diffusion in MgO at temperatures between 1873 K and 2273 K and at pressures ranging from 7 GPa to 35 GPa. Our calculated diffusion rates of magnesium, silicon and oxygen in $MgSiO_3$ perovskite have also been compared with experiments at 25 GPa with temperatures ranging from 1259 K to 2273K. All our diffusion rates are in perfect agreement with all the available experimental data.

The six-jump cycle mechanism works also in MgSiO3 post-perovskite allowing both cations to cross the octahedra-layers. However, diffusion in $MgSiO_3$ post-perovskite remains very anisotropic.

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