

Calcium isotopes in Martian meteorites

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Mass-dependent fractionation of Ca isotopes at high temperatures has long been considered minor; consequently, Ca isotopes have mostly been used to study low-temperature processes [1,2]. Here we report high-precision Ca isotope data for a suite of Martian meteorites revealing a $\delta^{44/40}\text{Ca}$ variation of $\sim 0.4\%$ among shergottites, nakhlites, chassignites and orthopyroxenite. Calcium isotope ratios of Martian crust generally fall into the range of terrestrial basalts but tend to be slightly heavier than Earth's crust. $\delta^{44/40}\text{Ca}$ exhibits no clear relationship with modal contents of olivine, plagioclase and/or pyroxene although pyroxene is the main Ca carrier in the mantle [3]. No systematic behavior is observed between individual groups of shergottites, despite the range in element depletion/enrichment, suggesting a lack of Ca isotope fractionation imparted by different degrees of melting. $\delta^{44/40}\text{Ca}$ of 1.06 in orthopyroxenite ALH 84001 is in the mantle range whereas low $\delta^{44/40}\text{Ca}$ in NWA 2737 may reflect the presence of carbonate minerals. Nakhlites mostly have distinctive $\delta^{44/40}\text{Ca}$ similar to terrestrial plume basalts [4], supporting the derivation of nakhlites from a Martian mantle plume. Whether this difference is directly linked to the dominance of clinopyroxene (with generally lower $\delta^{44/40}\text{Ca}$) in nakhlite lavas or is an intrinsic feature of nakhlite mantle source remains to be solved. Nevertheless, Ca appears to evolve distinctively different isotope ratios in plumes and mantle rocks, providing evidence for resolved Ca isotope fractionation at magmatic temperatures.

Collectively, the new data suggest $\delta^{44/40}\text{Ca} \sim 1.0\text{--}1.1$ for the bulk silicate Mars. This is identical to an estimate of the Earth's upper mantle [3] and suggests broadly similar processes for mantle melting in the interiors of Mars and Earth, independent of time constraints on the activity of mantle dynamics. Unlike other stable isotope systems, the bulk Ca isotope composition of Earth and Mars differs from enstatite chondrites [5,6]. Thus, they are probably not the major building material for Earth and possibly also not for Mars.

[1] Gussone *et al.* (2006) *Geology* **34**, 625-628; [2] Heuser *et al.* (2005) *Paleoceanography* **20**, PA2013; [3] Huang *et al.* (2010) *EPSL* **292**, 337-344; [4] Amini *et al.* (2009) *GGR* **33**, 231-247; [5] Simon & DePaolo (2010) *EPSL* **289**, 457-466; [6] Simon *et al.* (2009) *ApJ* **702**, 707-715

Lead(II) sorption to soil materials – Binding heterogeneity and influence of phosphate

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Lead (Pb) is a common pollutant, but still the environmental behaviour of lead is incompletely known. Attempts to simulate the binding of lead(II) to soils by use of geochemical models have usually underestimated lead binding with about one order of magnitude.

Here, new evidence will be presented about some key mechanisms that can explain the failure of most previous modeling attempts. First, the adsorption of Pb^{2+} to ferrihydrite, an important Pb^{2+} sorbent in soils, is shown to be very strong, particularly at low Pb^{2+} / ferrihydrite ratios. Second, the sorption of Pb^{2+} to ferrihydrite is greatly enhanced in the presence of phosphate. The effect is stronger than that predicted by electrostatic interactions only. The mechanisms involved are being studied with spectroscopic methods.

Third, data will be presented that show that the sorption of Pb^{2+} to solid-phase organic matter, especially mor layer material, is much stronger than that of fulvic or humic acid, which are often used as model compounds for solid-phase organic matter. Apparently, Pb^{2+} is strongly bound to a non-humic organic fraction of the solid-phase organic matter, but the mechanism by which this occurs remains obscure. Taken together, these observations may explain the often observed deviation between model and reality concerning lead(II) binding.