

Lithium isotopes as a tracer for diagenetic processes in deep subsurface sediments

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Submarine mud volcanoes and cold seeps represent important geochemical pathways along which volatiles and solute elements are recycled from deeply buried sediments into the global ocean.

Pore fluids from various cold vent sites, in different geological settings, were analysed for their chemical and Li isotopic composition. A pronounced negative correlation between Li concentration and $\delta^7\text{Li}$ reflects the temperature-dependent isotope fractionation during early diagenetic Li uptake and burial diagenetic Li release from sediments. Deviations from this general trend are observed for pore fluids with elevated salinity derived from dissolution of evaporites or admixing of evaporated seawater. Attempts to constrain fluid formation temperatures are particularly complicated by retrograde isotope fractionation during upward migration; especially in settings where intense authigenic mineral formation takes place (e.g. fresh volcanogenic sediments). Some of the investigated pore fluids, however, reveal very high Li concentrations (up to 3 mM) and exceptionally low $\delta^7\text{Li}$ values (as low as 7.5 ‰), which has to date only been observed in hydrothermal environments. This geochemical analogy indicates a close coupling of low and high temperature (i.e. hydrothermal) processes in deep-rooted cold seep environments.

The cadmium isotope composition of the Earth

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It is well established that volatile elements, such as Cd, are significantly depleted in most planetary bodies relative to the sun and CI chondrites. The origin of this depletion, however, is not well understood. Previous studies have shown that Cd isotopes can be fractionated by evaporation or condensation [1]. Impact related rocks such as tektites and lunar breccias show large Cd fractionations of up to 0.8 percent/amu [1, 2]. Cadmium isotopes therefore offer the opportunity to investigate if such impacts represent a process by which the terrestrial planets lost a significant part of their volatiles.

The goal of this study was to perform a survey of terrestrial Cd in order to obtain an estimate for the Cd isotope composition of bulk silicate Earth (BSE). This composition can then be compared to that of volatile-rich asteroids, i.e. carbonaceous chondrites to obtain information about volatile depletion. Schmidt *et al.* [4] deduced an epsilon $^{114}\text{Cd}/^{110}\text{Cd} = 0.32 \pm 0.24$ for BSE from four mantle derived basalts and three loess samples ($^{114}\text{Cd}/^{110}\text{Cd}$ recalculated relative to the Alfa Cd Zurich standard). However, the data set is limited and to date only a few high precision Cd isotope data are available for basalts and none for peridotites or komatiites. To this end, we developed a ^{111}Cd - ^{113}Cd double spike method using MC-ICPMS. All data were measured relative to the Alfa Cd Zurich standard, which was also employed by [3]. We report Cd isotope data for a comprehensive suite of terrestrial rocks including peridotites, komatiites, MORB, OIB and loess. MORB and OIB yield an average Cd isotope composition of epsilon $^{114}\text{Cd}/^{110}\text{Cd} = 1.9 \pm 0.4$. This is identical within uncertainty with deep ocean seawater (3.2 ± 1.0 [3]). However, the basalts appear to be enriched in heavy Cd isotopes compared to komatiites and peridotites (-0.6 ± 0.6), indicating that Cd isotopes may fractionate during magmatic/degassing processes as found for Fe [5].

[1] Wombacher *et al.* (2003) *GCA* **67**, 4639-4654. [2] Schediwy *et al.* (2006) *EPSL* **243**, 326-335. [3] Ripperger & Rehkämper (2007) *GCA* **71**, 631-642. [4] Schmitt *et al.* (2009) *EPSL* **277**, 262-272. [5] Teng *et al.* (2008) *Science* **320**, 1620-1622.