Origin of the calcium isotopic composition of rocky planets

JUSTIN I. SIMON* AND DONALD J. DEPAOLO

Center for Isotope Geochemistry, University of California, Berkeley (*correspondence: simon@eps.berkeley.edu)

Calcium isotopic effects in bulk planetary materials were measured by double-spiked TIMS analysis to establish the degree of heterogenity in the early solar system. The Ca isotope record is complementary to those of Fe, Si, and Mg. Both Fe and Si could be affected by core formation. Mass dependent isotope effects in Mg and Si, moderately volatile elements, are common among refractory inclusions (CAIs) and known to originate during evaporation at low pressure. Ca presumably is not incorporated into planetary cores, and is not affected by evaporation except under extreme conditions because of its low vapor pressure.

Measured meteorites, lunar and terrestrial rocks show that Earth, Moon, Mars, Vesta, an angrite, and an aubrite match the ordinary chondrites (OC), and all have $\delta^{44}Ca$ = -0.30±0.10‰. Carbonaceous chondrites (CC) are enriched in light Ca isotopes, $\delta^{44}Ca$ = -0.66 to -0.63‰ and enstatite chondrites (EC) are distinctly heavy, $\delta^{44}Ca$ = -0.10 to +0.24‰. These data suggest that OC are representative of the evolutionary pathway and/or materials that formed the planets. EC and CC, however, are unlikely to have constituted a large fraction of the material that formed the rocky planets.

A majority of measured refractory inclusions (CAIs) exhibit low $\delta^{44}Ca$ values [1], mostly in the range $\delta^{44}Ca$ = 0 to -4‰. The low $\delta^{44}Ca$ of bulk CC suggest that their effects have a similar origin. These mass-dependent Ca isotope effects favoring the light isotopes could originate by non-equilibrium condensation. Condensates of, for example, hibonite formed under conditions of 0 to 15 K undercooling, at total pressure less than 10^{-3} bar, could have $\delta^{44}Ca$ in the range of the CAIs if only a small fraction of the available Ca condensed. Later growth from light Ca isotope-depleted gas might explain the EC data. This hypothesis is consistent with observed HREE enrichment patterns in ultrarefractory hibonite and group II (LREE enrichment) patterns of later condensing hibonite, respectively. The low values of $\delta^{44}Ca$ in bulk CC imply that they contain material that formed prior to complete condensation of Ca and therefore do not represent a bulk sample of the solar nebula.

[1] Niederer and Papanastassiou, *GCA* **48**, 1279, 1984.

Experimental determination of water diffusion in porous basaltic rocks of the oceanic crust

A.V. SIMONYAN[1], H. BEHRENS[1] AND S. DULTZ[2]

[1]Institute of Mineralogy, Leibniz Universitaet Hannover, Callinstr. 3, 30167 Hannover, Germany (simonian@mineralogie.uni-hannover.de)
[2]Institute of Soil Science, Leibniz University of Hannover, Herrenhäuser Str. 2, D-30419 Hannover, Germany

Studying diffusion transport in porous rocks is of fundamental importance in understanding a variety of geochemical processes including mineral dissolution and precipitation kinetics and cementation of pores by secondary minerals. The rate of seawater/rock interaction and alteration of the oceanic crust depends on the rock permeability and on the accessible specific surfaces. This, in turn, is mainly controlled by the fraction of total pore space that forms a connected network in rock matrices. Here we present the results of systematic study of the role of pores and rock permeability on element turnover in oceanic rocks. Samples from ODP leg 169 at Middle Valley, Juan de Fuca Ridge and dredged basalts from the East Pacific Rise are used to investigate the effect of rock alteration on diffusion transport.

Diffusion processes of solutions within the porous basalts were studied *in situ*, using a novel experimental cell attached to a *FTIR*-microscope. $H_2O \rightarrow D_2O$ exchange at T from 5 to 50°C at ambient pressure was performed with strongly and partially altered basalt from ODP drilling and fresh dredged basalt from Juan de Fuca Ridge. The calculated effective diffusion coefficients D_{eff} for water diffusion in the oceanic basaltic rocks vary in the range from 10^{-9} to 10^{-11} m^2/s. These values are one-two orders of magnitude smaller than the diffusion coefficients D_{H2O} for H_2O in liquid water (Mills, 1973). The calculated activation energies for water diffusion in strongly altered rock is slightly higher than that in fresh and partly altered basalts (14.5 kJ/mole vs. 13.1 kJ/mole). The tortuosity factors X (D_{H2O}/D_{eff}) for basaltic samples vary from 25 to 80, indicating that the morphology and structure of pore network may have a strong influence on the diffusivity of aqueous solutions. The presence of precipitated minerals inside the pore system affects the transport ways for water molecules by bound H_2O layers and an increased tortuosity.

[1] Mills R. (1973) Self-diffusion in normal and heavy water in the range 1-45°C. *J. Phys. Chem.* **77**, 685-689.