

## Low-temperature reactive transport of Fe-Mg-Si-bearing solutions in sedimentary carbonate host-rock

S. GADISH<sup>1</sup>, A. MATTHEWS<sup>1</sup>, S. ILANI<sup>2</sup>

<sup>1</sup> Institute of Earth Sciences, Hebrew University of Jerusalem, 91904 Israel (sharongadish@hotmail.com; alan@vms.huji.ac.il)

<sup>2</sup> Geological Survey of Israel, Jerusalem, 95501 Israel (ilani@mail.gsi.gov.il)

The sub-surface reactive transport of solute species through carbonate (limestone/chalk) host rock is a major process of geochemical mobilization. This work studies iron and silica mineralization and dolomitization in Cretaceous limestones cut by a major tectonic fault zone (Paran tectonic line in the Negev desert of southern Israel). The aims are to understand the spatial extent, mechanism and physical conditions (temperature, fluid source) of the reactive transport process. Two groups of rocks were studied: 1) iron oxide-silica lenses located in the sub-vertical fault zone and 2) layer-parallel dolomitic bands in the carbonate rocks adjacent to the fault zone.

Laser fluorination oxygen isotope measurements on sample chips give  $\delta^{18}\text{O}$  values of *ca* -5 ‰ for iron oxide (hematite/goethite) minerals in the fault-zone lenses and *ca* 25 ‰ for silica minerals (amorphous and microcrystalline quartz). A temperature of 30-40 °C is estimated from the silica-iron oxide fractionation using quartz-water and hematite-water geothermometers. The calculated  $\delta^{18}\text{O}$  value of the water from which the minerals precipitated is *ca* -5 ‰, thus pointing to a meteoric groundwater source for the mineralizing fluid.

The dolomitization immediately adjacent to the fault zone is massive, but laterally spreads away from the fault zone and gradually resolves into horizontal dolomitic bands varying in thickness from less than a metre to several tens of metres and with transport distances up to 1 km from the fault zone. Impermeable clay-rich marl horizons strongly controlled layer-parallel direction of fluid movement. Field, XRD, optical and SEM microscopic studies show that almost all the dolomites are ferroan, but they are also partially coated by small iron oxide crystals and cut by iron oxide veins. These observations indicate that the lens formation and dolomitization are genetically linked processes, but that transport of Mg, Fe and Si was to some extent decoupled. The dolomitization reaction possibly created a porosity that allowed Fe-bearing solutions to continue moving through the altered rock.

The present study shows that the reactive transport is related to upward movement of fluid along the fault line and its subsequent chemical interaction with the limestone host rock. Gravitationally over-pressured meteoric water brines in the underlying sandstone aquifer were the most probable fluid source. C, O, and Fe stable isotopic studies currently in progress will shed further light on the reactive transport processes.

## Diffusive Reequilibration of CaO in Olivine-Hosted Melt Inclusions

GLENN A GAETANI<sup>1</sup>, DANIELE J. CHERNIAK<sup>2</sup>, AND E. BRUCE WATSON<sup>3</sup>

<sup>1</sup>Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole MA 02543

<sup>2</sup>Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy NY 12180

Silicate melts included in olivine phenocrysts exhibit compositional variability not found in erupted lavas. Recently, there has been increased recognition of unusually CaO-rich (ultracalcic) melt inclusions, typically hosted in olivine (e.g., Kamenetsky et al., 1998, EPSL, 164, 345-352; Kamenetsky and Crawford, 1998, EPSL, 160, 115-132). Because ultracalcic liquids ( $\text{CaO} \geq 14$  wt%;  $\text{CaO}/\text{Al}_2\text{O}_3 \geq 1.0$  by weight) are exceedingly rare in the global mid-ocean ridge basalt population, these inclusions have been interpreted as partial melts of exotic mantle lithologies. To evaluate the extent to which an olivine-hosted melt inclusion preserves its initial CaO content, we determined experimentally the diffusivity of Ca in San Carlos olivine and the partitioning of CaO between magnesian olivine and basalt. The experimental results demonstrate efficient communication between a melt inclusion and the melt outside of its host crystal with respect to CaO and significant reequilibration over relatively short timescales. Therefore, the reliability of olivine-hosted melt inclusion CaO content as an indicator of mantle heterogeneity is questionable.

Diffusion experiments were carried out at 1 bar and 800-1100 °C using synthetic anorthite powder as a Ca source. Diffusion profiles in experiments carried out at  $T \leq 1000$  °C were measured using Rutherford Backscattering Spectroscopy (RBS). Experiments carried out at higher T were depth profiled using Secondary Ion Mass Spectroscopy (SIMS). The Arrhenius relation for diffusion of Ca parallel to the *c* crystallographic axis of  $\sim\text{Fo}_{90}$  olivine at an oxygen fugacity along the Ni-NiO buffer is:

$$D_{\text{Ca}} = 2.284 \exp(-55010/T(\text{K})) \text{m}^2 \text{s}^{-1}$$

The olivine/basalt partition coefficient for CaO was determined to be relatively insensitive to temperature at 1 bar, decreasing from 0.030 at 1225 °C to 0.027 at 1325 °C.

Diffusive reequilibration of the CaO content of an olivine-hosted melt inclusion following magma mixing was investigated by using our experimental data in the model of Qin et al. (1992, Am. Mineral. 77, 565-576) for equilibration of a 200  $\mu\text{m}$  melt inclusion centered in a spherical host olivine 2 mm in diameter. The melt inclusion was assumed to have an initial CaO content of 10 wt%, while the external melt contained 14 wt% CaO. At 1225 °C, the melt inclusion will retain its original concentration of CaO for  $\sim 10$  years, after which it increases rapidly. Following 20 years of diffusive reequilibration, the CaO content of the inclusion has increased to 11.4 wt%; after 50 years the inclusion contains 13.5 wt% CaO and by 70 years reequilibration is nearly complete.