

## An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50° C

STEPHAN J. KÖHLER, FABIEN DUFAUD, AND ERIC H. OELKERS

Laboratoire de Géochimie, Université Paul Sabatier/CNRS-UMR 5563, 38 rue des Treize Six Ponts, 31400 Toulouse, FRANCE; (kohler@lmtg.ups-tlse.fr)

The reactivity of clay surfaces are particularly significant in controlling the chemistry of surface waters due to their ubiquity and high surface area. To address these potential affects, natural illite (Illite du Puy) dissolution rates were measured from Si release rates during closed system experiments at pH ranging from 1.4 to 12.4 and temperatures ranging from 5 to 50 °C. Si release rate decreased with time during all experiments. This phenomena can be attributed to either 1) change in reactive surface area, 2) the affect of initial fine particle dissolution or 3) a sub-zero order of the illite dissolution reaction with respect to aqueous Al and/or aqueous Si (Oelkers et al., 2001). As such, illite dissolution rates generated from Si release rates measured during the initial parts of the experiments are significantly higher than those generated during latter stages of each closed system experiment. Such also seems to be the case for all published closed system clay mineral dissolution experiments reported in the literature (c.f. Heurtas et al., 1999).

After an initial preferential release of aluminum relative to silicon, the reactive fluid Al/Si concentration ratio evolution was consistent with stoichiometric illite dissolution for all experiments conducted at  $4 < \text{pH} < 11$ . Measured dissolution rates exhibited a typical variation with pH; rates decrease with increasing pH at acid conditions, minimize at near to neutral pH and increase with increasing pH at basic conditions. The degree to which measured illite dissolution rates increased with temperature depends strongly on pH; apparent activation energies decreased from 18 to 5 kcal/mol with increasing pH from 1.6 to 4.8, but increase with increasing pH at basic conditions.

### References

- Huertas, F.J., Chou, L., and Wollast, R. (1999) Mechanism of kaolinite dissolution at room temperature and pressure. Part II: Kinetic study. *Geochim Cosmochim. Acta*, **63**, 3261-3276.
- Oelkers, E.H., Schott, J., and Devidal, J.-L. (2001) On the interpretation of closed system mineral dissolution experiments; Comment on "Mechanism of kaolinite dissolution at room temperature and pressure Part II: Kinetic Study" by F. J. Huertas, L. Chou, and R. Wollast. *Geochim Cosmochim. Acta*, **65**, 4429-4432.

## Shearing Melt out of the Mantle

DAVID L. KOHLSTEDT AND BENJAMIN K. HOLTZMAN

Department of Geology and Geophysics  
University of Minnesota, Minneapolis, MN 55455 USA  
(dlkohl@umn.edu) (holtz007@umn.edu)

To extract melt quickly enough from beneath a mid-ocean ridge to satisfy geochemical constraints on transport times, melt must segregate from grain-scale pockets into melt-rich, high-permeability channels. As indicated by the occurrence of ductile shear zones in ophiolites and demonstrated by our laboratory experiments on partially molten rocks, such channels can develop during shear deformation. Melt organizes into melt-rich planar bands separated by melt-depleted, low-permeability zones provided the compaction length for the melt-solid system is less than the thickness of our sheared samples. Here, compaction length,  $\lambda_c = \frac{\eta}{k \rho \Delta \rho}$ , is defined in terms of the permeability,  $k$ , and the ratio of the solid to the melt viscosity,  $\frac{\eta_s}{\eta_m}$ . If the compaction length is significantly larger than the sample thickness, stress-induced pressure gradients cannot develop to drive melt segregation. In shear experiments, channels contain up to 20 vol% melt and are aligned antithetic to the shear direction at  $\sim 20^\circ$  to the shear plane. Bands are already clearly present after a shear strain of  $\gamma < 1$ , and segregation becomes more intense with increasing strain reaching a steady-state microstructure by a shear strain of  $\gamma \sim 2$ . The spacing between the channels is controlled by the amount of melt available in the sample. Throughout formation, the orientation of the bands is independent of strain.

Two lines of evidence demonstrate that shear strain localizes on these melt-rich bands. First, samples of anorthite + 3 vol% melt sheared at constant rate weaken dramatically at shear strains  $\gamma \sim 2$ . Second, in samples of olivine + basalt, which do not form bands, the normal to the slip plane (b-axis) in the olivine grains is perpendicular to the overall sample shear direction. In contrast, in samples of olivine + chromite + basalt, which do form melt-rich bands, the b-axes are rotated backward by  $\sim 20^\circ$  relative to the slip direction (i.e., the slip planes in the melt-depleted regions form an angle of  $\sim 40^\circ$  with the melt-rich bands). Hence, the direction of shear in the melt-depleted regions compensates for that in the melt-rich bands to permit the sample to obtain a bulk shear consistent with the applied state of stress. In addition, the seismically fast a-axes in samples without bands are parallel to the overall shear direction, while the fast axes in samples with bands are rotated  $90^\circ$  from the shear direction.

Deformation-driven melt segregation will dramatically influence the physical properties of rocks. The presence of melt-rich bands will affect seismic anisotropy directly through their presence and indirectly through their influence of lattice preferred orientation. The redistribution of melt will modify the permeability network and create an anisotropic viscosity structure. If melt-rich bands occur in partially molten regions of the Earth, they will have important consequences for the flow of both solid and melt.