



The effect of small amounts of water on reaction kinetics between silicates in experiments (and rocks)

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The system MgO-SiO₂-(H₂O), and especially pyroxene reaction rim growth between olivine and quartz has become the best studied system aiming at the effect of small amounts of water on the kinetics of diffusion-controlled reaction-rim growth. A recent compilation of the square law rate constants for Opx rim growth from several labs, using various techniques and a broad range of pressure media reveals the existence of just two kinds of data sets, that can be termed "dry" and "wet".

All "wet" data come from solid media high P experiments in piston cylinder devices in the temperature range from 750 to 1100 °C (Yund 1997; Milke et al. 2001; Milke et al. 2009). The spread of pressures from 0.7 to 1.9 GPa is virtually without effect. Initially these experiments range from vacuum dried to 5 wt% H₂O added, but the initial state of the loads affects the growth rates only weakly, if at all, thus indicating a water flux from the pressure media into the sealed capsules during the experiments. FTIR measurements of initially practically water-free olivine and quartz after initially dry runs show them to be saturated with intracrystalline H-defects after experiment.

The "dry" data cover the T range from 1000 to 1350 °C and come from single-crystal reaction couples (Fisler et al. 1997) and thin film setups (Milke et al. 2007) at 0.1 MPa, and from piston-cylinder experiments at 1.5 GPa using water-absorbing alumina as pressure medium (Gardès et al. 2010). All rate constants define a sharp line plotted against reciprocal temperature. This observation is in line with the very small activation volumes determined for grain boundary diffusion in silicates.

"Wet" experiments lead to activation energies around 200 kJ/mol, whereas "dry" experiments yield values around 400 kJ/mol. Extrapolated to higher temperatures the "dry" and "wet" lines would cross far above the melting point of all involved phases. In the geologically relevant T regime the reaction constants in "wet" experiments are 4 to 6 orders of magnitude larger than in "dry" ones.

Reaction constants between water-bearing (f.ex. initially vac.dried) and water-rich (f.ex. 5 wt% H₂O added) "wet" experiments show a difference by a factor of 5. Water-rich conditions can be defined by the presence of pores on the scale of BSE images. FIB-FEG-SEM investigations including 3D imaging of quartz-orthopyroxene interfaces on the sub- μ m-scale reveal the mechanism behind this difference. At water-rich conditions the Opx crystal tips grow along fluid-filled micropores that migrate into quartz driven by the chemical potential gradient in SiO₂(aq) between local equilibration with dissolving quartz (higher) and growing orthopyroxene (lower).

The absence of any experimental results between "dry" and "wet" hints to the fact that even very small amounts of water (tentatively in the 10 to 100 ppm range) have a major effect on diffusion-controlled reaction kinetics, whereas the presence or absence of pores in water-saturated systems seems only to induce a second order effect. The range achieved in experiments ranging from "dry" to water-rich is largely identical to what can be assumed for rock metamorphism, thus making the effect of small amounts of water on reactions between silicates and the quantification of these effects a continuing research topic among rock scientists.