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Experimental determination of Mg removal rates from seawater-like fluids due to reaction with plagioclase and clinopyroxene at 200°C and 32.5 MPa

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It is well known that seawater circulating through mid-ocean ridge (MOR) hydrothermal systems is stripped of Mg and SO_4 and accumulates Ca. The broad features of this process have been documented in many laboratory experiments, mostly using basalt or diabase bulk rock compositions. To provide more generalizable constraints we have carried out fluid-mineral hydrothermal experiments using just two minerals, plagioclase (PLAG, An_{80}) and clinopyroxene (CPX,Ca_{47},Mg_{35},Fe_{18}), in differing proportions, to gain insight into mineral-specific reactivity for the purpose of advancing reactive transport models of MOR processes. A flexible gold reaction cell system in a rocking furnace is used, which allows for detailed recording of fluid chemistry with time. We report the results of experiments at 200°C and 32.5 MPa using CPX/PLAG proportions of 80/20, 20/80, and zero (PLAG only). Fluid initially has seawater values of Na, Cl, and Mg, zero Ca, SO_4, and Sr, and fluid/solid ratios are 5 to 6. In all experiments, Mg is systematically removed from the fluid and replaced by Ca in almost exact proportion. The time required to remove 50% of initial Mg is 10 days for the 80:20 experiment, 45 days for 20:80, and > 200 days for PLAG-only. CPX appears to dissolve much faster than PLAG, but modeling using TOUGHREACT suggests instead that the two minerals dissolve at similar rates but both minerals dissolve faster when there is a higher proportion of CPX. The simulations also suggest that the reaction rate constant for PLAG (using geometric surface area) is close to that suggested at pH 5 and 200°C in [1], but the rate constant for CPX is much lower than those for diopside and augite in [1]; roughly the value for bronzite. Secondary minerals are predicted to be mostly chlorite and montmorillonite. These results suggest that the degree of match between the Mg-Al stoichiometry of reactants and products can substantially affect dissolution rates, which was unexpected, but captured by the TOUGHREACT simulations with no change in rate constants. Experiments at other temperatures have also been done to evaluate activation energies.

[1] Palandri & Kharaka (2004) USGS Open File Report 2004-1068.