

Chlorite dissolution experiments under CO₂ saturated conditions

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The injection and long-term storage of supercritical CO₂ (scCO₂) into geological reservoirs is seen as an important option to mitigate rising levels of atmospheric CO₂. Predicting what changes take place to geochemical and petrophysical properties of a reservoir once CO₂ has been injected requires an understanding of how mineral dissolution and precipitation proceed. The dissolution of CO₂ in groundwaters in contact with an scCO₂ plume leads to a decrease in the pH of pore fluids, driving the system far from equilibrium and accelerating the dissolution of minerals in the reservoir. Experiments exposing a siltstone to CO₂ saturated fluids have shown that the dissolution of carbonates and clays, including chlorite, lead to increased porosity and permeability in a sample of a siltstone caprock [1].

The dissolution kinetics of chlorite have been extensively studied [2], but not under CO₂ saturated conditions. Here we present the results of batch reactor experiments on a clinoclone chlorite (CCa-2, The Clay Minerals Society); testing the potential effects of pH, chloride and bicarbonate concentration, temperature and pressure (pCO₂) on the dissolution rate of the mineral. The dissolution rates observed are of a comparable magnitude (c. -12 log mol m⁻² sec⁻¹ at 50°C) to previous studies, but the proton promoted dissolution normally observed is not as prominent. The results suggest that dissolved bicarbonate affects the dissolution mechanism and new rate laws are presented accounting for the effect of [HCO₃⁻]. An apparent activation energy for the dissolution process of 19 kJ mol⁻¹ is calculated assuming a simple empirical rate law with an Arrhenius form. This result is much lower than the activation energy of 88 kJ mol⁻¹ previously reported under acidic conditions [3], and often used in geochemical models under all pH regimes. However, it is consistent with the results of a recent study using flow-through techniques [4].

[1] Armitage *et al.* (2013) *Nature Geosci.* **6**, 79-80. [2] Lowson *et al.* (2007) *Geochim. Cosmochim. Acta*, **71**, 1431-1447. [3] Ross, G.J. (1967) *Can. J. Chem.* **45**, 3031-3034. [4] Smith *et al.* (in press) *Chem Geo.*

U-Pb thermochronology and the thermal history of planetary crusts

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U-Pb accessory phase thermochronology (minerals: apatite, titanite and rutile) allows estimates of cooling rates of rocks as they pass through moderate temperatures (400-800 °C). Despite a growing number of datasets employing these techniques, these data--like all thermochronologic data-- are highly non-unique and can often be interpreted as the result of any number of geologic scenarios. This problem of non-uniqueness can largely be resolved by exploiting the U-Pb system's dual decay scheme, where two parent isotopes, ²³⁸U and ²³⁵U, decay to daughter isotopes ²⁰⁶Pb and ²⁰⁷Pb respectively. The difference in decay rates between parent isotopes imposes a time-variant parent and instantaneous daughter isotopic composition for any point in Earth's history. This new thermochronologic methodology works to capture this isotopic evolution using the variation in the time of Pb retention between both: 1) samples of different crustal depths, where variations in the timescale of cooling result from the thermal gradient within a conductively cooling crust, and; 2) crystals of different size, where volume diffusion behavior, in particular for slowly cooled systems, result in larger crystals retaining lead at higher temperatures and over a longer and older timescales in comparison to smaller crystals, which retain lead at lower temperatures and at younger times. The differences in U/Pb and ²⁰⁷Pb/²⁰⁶Pb among samples from different depths, and within each sample—between grains of different size — can be used to reconstruct the long-term thermal histories within planetary crusts. By moving beyond assigning nominal closure temperatures to dated minerals one can avoid the cooling rate uncertainties that propagate from experimental diffusion kinetics. The sensitivity to cooling rate lies in the topology of U-Pb data and has been demonstrated using forward modelling to be highly insensitive to diffusion kinetics. I'll work to demonstrate how this methodology can be employed to reconstruct the thermal histories of: 1) the continental lithosphere through reconstruction of thermal histories of lower crustal xenoliths, and; 2) the chondrite parent bodies, through reconstruction of chondrite meteorite thermal histories. In each example, I'll focus on interpreting thermochronologic data with the aid of thermal models in order to elucidate the relative roles of heat conduction, production and advection (erosion/burial) and in doing so provide constraints on the timing and processes controlling continent stabilization and the assembly of planetesimals.