Geochemical Reactions during Geologic Sequestration of CO_2 in the Rose Run Formation, Ohio USA

BEVERLY SAYLOR, GERALD MATISOFF, PHIL MORRISON, NICK JANDA, AND BINIAM ZERAI

Department of Geological Sciences, Case Western Reserve University, Cleveland, OH 44106-7216 USA
bzs@po.cwru.edu

Major concerns for CO_2 sequestration in both petroleum reservoirs and aquifers are the impacts of mineral-brine-CO_2 reactions on the integrity of the seal, the permeability of the formation near the injection site, and the storage capacity of the formation. Experimental and geochemical modeling investigations were conducted for the carbonate and siliciclastic members of the Upper Cambrian Rose Run Formation, a deep saline aquifer in eastern Ohio USA.

Dissolution rate experiments are conducted for silicate and carbonate minerals, including Na-feldspar, K-feldspar, and calcite, in CO_2-pressurized KCl brine solutions, at a range of pressures and temperatures representative of deep aquifer conditions. Results from inexpensive tube- reactor experiments are compared with results from experiments run under identical operating conditions in a commercial Parr stirred reactor, and with results from the published literature.

Equilibrium modeling is conducted using Geochemists Workbench^{TM} to simulate the experiments and to simulate expected reactions for mineral-brine assemblages typical of the Rose Run. Geochemical modeling of mineral-brine-CO_2 mixtures makes it possible to evaluate the impact of temperature, pressure, mineralogy, brine composition, CO_2-fluid-rock ratio, and CO_2 fugacity on mineral dissolution and precipitation, amount of CO_2 sequestered, and the form of sequestration. For a representative Rose Run carbonate, injection of CO_2 causes dissolution of calcite, but precipitation of siderite. Increasing the CO_2-to-brine ratio lowers the pH and increases carbonate dissolution. For silicate minerals, geochemical reactions convert some of the CO_2 to carbonate minerals such as siderite, calcite, dolomite, and dawsonite, absorbing more of the CO_2 than for the comparable carbonate case. The reactive minerals are consumed by the reactions and the CO_2 that remains free in the system is very small as compared to the carbonate case. An important finding of the numerical modeling work is the prediction that dissolution of Na-feldspar can lead to the precipitation of the carbonate mineral dawsonite ($NaAlCO_3(OH)_2$). This finding is significant because it means that reaction with Na-feldspar, which is widespread in the Rose Run sandstone, can lead to mineral trapping of CO_2.

Boron and chlorine cycling in the subducted hydrous oceanic mantle

[1]SCAMBELLURI M., [2]MUENTENER O., [3]OTTOLINI L., [4]PETTKE T., [5]VANNUCCI R.

[1]Dipartimento Studio del Territorio e sue Risorse, Genova, Italy
[2]Geological Institute, University of Neuchatel, Switzerland
[3]CNR-IGG, Sezione di Pavia, Pavia, Italy
[4]Department of Earth Sciences, ETH-Zentrum, Zuerich, Switzerland
[5]Dipartimento di Scienze delle Terra, Pavia, Italy

The serpentinized oceanic mantle acts as repository of oceanic B, Cl and as fluid carrier to great depth during subduction. Oceanic serpentinites are richer in B (up to 85 ppm; Bonatti et al., 1984; Earth Planet. Sci. Lett., 70, 88-94.) than unaltered mantle (0.1 – 0.3 ppm; Chaussidon and Libourel, 1993, Geochim. Cosmochim. Acta, 57, 5053-5062), and chlorine dissolved in seawater can be incorporated in oceanic serpentine (0.2 – 0.5 wt% Cl; Scambelluri et al., 1997, Earth Planet. Sci. Lett.,148, 485-500). Boron behaviour during subduction was only investigated in mafic and metasedimentary rocks from melange terrains buried to P < 1.5 GPa along relatively hot gradients (Moran et al., 1992, Earth Planet. Sci. Lett., 111, 331-349; Bebout et al., 1993 Geochim. Cosmochim. Acta, 57, 2227-2237; Domanik et al., 1993, Geochim. Cosmochim. Acta, 57,4997-5010). These studies indicate the progressive decrease in the B content of rocks and minerals at increasing depths. Still lacking is the analysis of coherent slices of hydrated oceanic mantle buried along cold gradients to high and very high pressures.

We measured B and Cl concentrations in ultramafic rocks, representative of oceanic mantle subducted at increasing depths: (i) oceanic serpentinites from non-subducted ophiolites (Northern Apennine and Alps), with secondary serpentine and chlorite after original mantle assemblages; (ii) high pressure Alpine serpentinites, with stable antigorite, olivine, diopside, chlorite and Ti-clinohumite; (iii) olivine + orthopyroxene rocks (Betic Cordillera), derived from high- to very high-pressure breakdown of antigorite serpentinites. Oceanic serpentines have the highest Cl and B concentrations (max Cl 6210 ppm; B 200 ppm), which progressively decrease in high pressure antigorite (max Cl 1031 ppm; B 54 ppm) and in higher grade olivine, orthopyroxene, and chlorite (max Cl 18 ppm; B 39 ppm). Estimated bulk rock B and Cl decrease from oceanic serpentinites (B 48.54 ppm; Cl 774 ppm), to high pressure antigorite serpentinites (B 18 ppm; Cl 98 ppm) to olivine-orthopyroxene-chlorite rocks (B 11 ppm, Cl 74 ppm). These data indicate a depth-related decrease of Cl and B in bulk rocks and minerals, and point to their partitioning in the evolved fluids. Metamorphic harzburgites and olivine formed after antigorite at the highest grade still contain boron amounts an order of magnitude higher than the average B content of mantle peridotites and olivine.