Stable isotope studies of Manus basin hydrothermal vent fluids and deposits

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Hydrothermal vents in Manus backarc basin, Papua New Guinea, have strong chemical and light stable isotopic evidence of direct magmatic influence on vent fluid composition. Many samples have very low pH and fluid chemistry is consistent with magmatic volatiles (H_2O, CO_2, SO_2, HCl, HF) mixed into seawater. Vent fluid samples have normal $\delta^{18}O$ values (0.2-2.2 ‰) compared to other vent fluids worldwide. However, vent fluid δD values are as low as -7.6 permil, which suggests a magmatic water component with δD of -24 permil. This is consistent with island-arc related magmatic water values.

Sulfur isotope data ($\delta^{34}S$) for dissolved sulfate and sulfide and for elemental sulfur precipitates at the vent sites is consistent with disproportionation of magmatic SO_2. $\delta^{34}S_{H2S}$ values range from -4.4 to -7.0 ‰, with corresponding $\delta^{34}S_{SO4}$ ranging from 15.8-20.9 ‰. $\Delta^{33}S$ values support magmatic sulfur derivation. Extremely acidic systems (pH 0.8-1.2) tend to have abundant So and no H2S. Elemental sulfur has $\delta^{34}S_S$ from -3.8 to -10.5 ‰ or even lower values, and associated $\delta^{34}S_{SO4}$ ranges from 9.8-15.3 ‰. All of these sulfur isotope values are consistent with disproportionation of SO_2 that originally had magmatic $\delta^{34}S_{SO2}$ values near 0-3 ‰.

Mineral dissolution and nanoparticle evolution on phlogopite surfaces under CO_2 geologic sequestration conditions

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To effectively apply geologic CO_2 sequestration (GCS), a better understanding of the interactions between CO_2/saline water/rocks is necessary. Especially at the early injection stage, the dissolution of pre-existing minerals and precipitation of secondary mineral phases may potentially change the permeability of rocks, thus altering the injectivity of CO_2. In this work, we used both fluid/solid chemistry analysis and interfacial topographic studies to investigate the interactions between CO_2-saline water-phlogopite under simulated GCS conditions (1500 psi, 95 °C, and 1 M NaCl solution). Phlogopite ($KMg_3Si_3AlO_{10}$ (F, $OH)_2$), served as a model of the clay minerals that are present in both formation rocks and caprocks in potential CO_2 sequestration sites.

We found that introduction of CO_2 significantly enhanced the dissolution of phlogopite, compared to the control experiment conducted under nitrogen gas. With atomic force microscopy (AFM), we observed that the predominant surface feature on phlogopite after reaction was dissolution pits. However, although chemical analysis indicated that the dissolution of phlogopite was far from equilibrium, and although the theoretical calculation based on MINEQL+ showed that the aqueous species were not oversaturated with respect to any potential secondary mineral phases, we did observe the formation of nanoscale precipitates on phlogopite surfaces in 1 M NaCl solution after only 5 hours, based on AFM images. Nanoscale particles first appeared on the edges of dissolution pits and then relocated to other areas and started to aggregate to form larger particles. When we used pure water instead of 1 M NaCl in this experiment, we found that the nanoparticles of the secondary mineral phase formed after only 3 hours, and the precipitates were not observed on the edges of the dissolution pits, suggesting that the salinity of the pre-existing solution influenced the reaction mechanisms. The formation of nanoscale precipitates after such short reaction times, together with the relocation of those particles when phlogopite was in a 1 M NaCl solution, suggests that the permeability of rocks can be changed by pore throat clogging. Thus, the injectivity and transport of CO_2 through formation rocks or sealing properties of caprocks may be influenced. This research provides new key information on the kinetics and mechanisms of the interfacial reactions between CO_2 and sequestration rocks. This information will aid in designing secure and environmentally acceptable CO_2 sequestration techniques.