

Geochemical monitoring and geochemical modeling of the CO₂CRC Otway Project CO₂ storage pilot, Victoria, Australia

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Formation fluid monitoring and geochemical modeling of the CO₂CRC (Cooperative Research Centre for Greenhouse Gas Technologies) Otway Project carbon storage pilot site was undertaken to understand the physical and chemical processes taking place during the injection of CO₂ into a depleted gas reservoir. The collection of high quality samples of the supercritical and aqueous phases was enabled using a multilevel U-tube downhole assembly. A total of 11 water samples from U-tube 2 (2041.8 m) and 26 from U-tube 3 (2046.3 m) were collected covering a period from pre-injection to self-lift. The initial water chemistry data from the two U-tubes is very similar and follows the same trends for major and minor dissolved species analyzed. However, just prior to U-tube 2 self lift a change in composition is observed that is not consistent with the expected changes due to gas-water-rock interactions. The similarity in the water chemistry suggests that the initial water produced was dominated by a higher permeability zone in the upper portion of the perforated interval. Integration of the fluid compositional data with numerical modeling of the system indicates the pH is buffered by CO₂-water-rock interactions both prior to and after the arrival of the CO₂. Simulations of the filling of the reservoir show ferroan dolomite dissolution resulting in increases in the pH, Ca, Mg, Fe and HCO₃ content. These results are consistent with the U-tube data indicating that some of the variations in the water chemistry may reflect the effects of carbonate dissolution.

Improvement of SIMS oxygen isotope analyses on magnetite

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Crystal Orientation Effect in SIMS Analysis

Magnetite is common in many rocks and useful for oxygen isotope geothermometry [1]. Accurate temperatures are often precluded by zoned or altered grains, so that *in situ* analysis of δ¹⁸O by SIMS promises improved temperature estimates. However, magnetites show a significant range of analytical bias (≥5‰) due to crystal orientation [2-3], which is caused by channeling of the primary ions and focusing of the secondary ions when the primary Cs⁺ beam is parallel to planes of atoms in the crystal lattice [3]. In routine δ¹⁸O analysis using IMS-1280 at WiscSIMS (multicollector Faraday Cup; 10µm spot [4]), magnetite standard grains show reproducibilities of 0.4‰ (2SD) within single grains, but ~3‰ (2SD) from grain-to-grain due to crystal orientation effects [3]. Except magnetite and hematite, no other silicate, oxide and carbonate minerals have been found with measurable crystal orientation effects for δ¹⁸O [5].

Test Analyses with 13keV Impact Energy

In normal operating conditions (primary/secondary accelerating voltages of +10kV/-10kV), primary ion impact energy is 20keV with an incident angle of 21°. We examined the reproducibility of oxygen isotope analyses on standard magnetite grains at the lower impact energy of 13keV. Three analytical conditions were applied for primary and secondary voltages; +3kV/-10kV, +6.5kV/-6.5kV and +10kV/-3kV, corresponding to the primary ion incident angles of 14°, 21° and 26°, respectively. The best results were obtained from the +3kV/-10kV condition, showing improved grain-to-grain reproducibility of 0.8‰ (2SD). For +6.5kV/-6.5kV, the reproducibility of analyses was only moderately improved to 1.8‰ (2SD), comparable to the amount of reduction in impact energy. The +10kV/-3kV test did not improve the reproducibility. The above results indicate that the crystal orientation effect in SIMS isotope analyses depends on both impact energy and incident angle of primary ion beam. Using the optimized (+3kV/-10kV) condition, SIMS magnetite-quartz thermometry can be applied to crystals as small as 10 µm with temperature resolution better than 50° at ≤500°C.

[1] Valley (2001) *Rev. Min. Geochim.* **43**, 365–414. [2] Lyon *et al.* (1998) *Int. J. Mass Spec. Ion Proc.* **172**, 115–122. [3] Huberty *et al.* *GCA* **73**, A562. [4] Kita *et al.* (2009) *Chem. Geol.* **264**, 43–57. [5] Valley & Kita (2009) *MAC short course* **41**, 19–63.