



An experimental study of basaltic glass-H₂O-CO₂ interaction at 22 and 50 °C: Implications for subsurface storage of CO₂

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A novel high pressure column flow reactor (HPCFR) was used to investigate the evolution of fluid chemistry along a 2.3 meter flow path during 37-104 days of pure water- and CO₂-charged water- (0.3 M CO_{2(aq)}) basaltic glass interaction experiments at 22 and 50 °C. The scale of the HPCFR, the ability to sample a reactive fluid at discrete spatial intervals under pressure and the possibility to measure the dissolved inorganic carbon and pH *in situ* all render the HPCFR unique in comparison with other reactors constructed for studies of CO₂-charged water-rock interaction.

During the pure water-basaltic glass interaction experiment, the pH of the injected water evolved rapidly from 6.7 to 9-9.5 and most of the dissolved iron was consumed by secondary mineral formation, similar to natural basaltic groundwater systems. In contrast to natural systems, however, the dissolved aluminium concentration remained relatively high along the entire flow path. The reactive fluid was undersaturated with respect to basaltic glass and carbonate minerals, but supersaturated with respect to zeolites, clays, and Fe hydroxides.

Basaltic glass dissolution in the CO₂-charged water was closer to stoichiometry than in pure water. The mobility of metals increased significantly in the reactive fluid and the concentration of some metals, including Mn, Fe, Cr, Al, and As exceeded the WHO (World Health Organisation) allowable drinking water limits. Iron was mobile and the aqueous Fe²⁺/Fe³⁺ ratio increased along the flow path. Basaltic glass dissolution in the CO₂-charged water did not overcome the pH buffer capacity of the fluid. The pH rose only from an initial pH of 3.4 to 4.5 along the first 18.5 cm of the column, then remained constant during the remaining 2.1 meters of the flow path.

Increasing the temperature of the CO₂-charged fluid from 22 to 50 °C increased the relative amount of dissolved divalent iron along the flow path. After a significant initial increase along the first metre of the column, the dissolved aluminium concentration decreased consistent with its incorporation into secondary minerals. The dissolved chromium concentration evolution mimicked that of Al at 50 °C, suggesting substitution of trivalent Cr for Al in secondary phases. According to PHREEQC calculations, the CO₂-charged fluid was always undersaturated with respect to carbonate minerals within the column, but supersaturated with respect to clays and Fe hydroxides at 22 °C and with respect to clays and Al hydroxides at 50 °C.

Substantial differences were found between modelled and measured dissolved element concentrations in the fluids during the experiments. These differences underscore the need to improve computational models before they can be used to predict with confidence the fate and consequences of carbon dioxide injected into the subsurface.