REE-chloride complexing in hydrothermal fluids with new data on Lanthanum chloroaqua complexes

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Direct investigations of the speciation and complex formation of rare earth elements (REEs) in chloride-bearing aqueous fluids at high temperatures (T) and pressures (P) are needed for a greater understanding of the transport and deposition of rare earths in hydrothermal systems. We present new data on La^{3+}-chloride complexing in low-pH aqueous solutions up to 500 °C and 230 MPa. Synchrotron x-ray absorption spectroscopy (XAS) measurements were made on a 0.02 *m* La/0.12 *m* HCl aqueous solution on the PNC-ID 20 beam line at the Advanced Photon Source, Argonne National Laboratory in the 25 - 500 °C T-range and up to 230 MPa. Analysis of the XAS spectra shows that the La^{3+} aqua ion is the predominant species in the aqueous solution at 25 °C. From 150 to 500 °C, stepwise inner sphere chloroaqua complexes of the type $La(H_2O)_{\delta-n}Cl_n^{+3-n}$ are formed in the aqueous solution. The average total ligand number (δ) of the lanthanum chloroaqua complex species decreases from roughly 10 to 7 whereas the average number of Cl^- ligands (n) increases steadily from 1.5 to 3.1 with increasing temperature over this temperature range. These results indicate that the degree of chloride complexation for La is slightly greater than for Nd and significantly greater than for Gd and Yb, in acidic aqueous solutions under similar P-T conditions. The greater stability of light REE (LREE) chloride complexes in high-temperature acidic aqueous solutions suggests that LREE may be transported more effectively than heavy REE (HREE) under similar conditions in chloride-rich hydrothermal fluids. Because simple ionic interactions alone are insufficient to account for the greater stability of LREE over HREE in acidic chloride-bearing hydrothermal fluids, additional REE-ligand interactions or steric effects may have to be invoked. The results from our XAS studies of REE (including La) in aqueous solutions up to 500 °C show negligible pressure dependence for pressures up to about 0.5 GPa.

Comparison of isotopic trends revealing the fate of injected CO_2 in two geological storage projects in mature oilfields in Canada

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Monitoring and verification of CO_2 storage is an essential component of geological storage projects. We present evidence from two enhanced oil recovery projects in Canada that geochemical and isotopic techniques can be successfully used to trace the fate of injected CO_2. Geochemical and isotopic data for fluids and gases obtained from multiple wells at the International Energy Agency Greenhouse Gas Weyburn CO_2 Monitoring and Storage Project (Saskatchewan, Canada) and from the Penn West Pembina Cardium CO_2-Enhanced Oil Recovery Monitoring Pilot (Alberta, Canada) were collected before and throughout the CO_2 injection phase. Carbon isotope ratios of injected CO_2 in the Weyburn project were significantly lower than those of background CO_2 in the reservoir. In contrast, $\delta^{13}C$ values of injected CO_2 at Penn West's Pembina Cardium CO_2-Enhanced Oil Recovery Monitoring Pilot were markedly higher than those of background CO_2. After commencement of CO_2 injection, the concentrations and $\delta^{13}C$ values of CO_2 and HCO_3^- in fluids and gases repeatedly obtained from monitoring wells were determined. Increasing CO_2 and HCO_3^- concentrations in concert with $\delta^{13}C$ values trending towards those of the injected CO_2 revealed effective solubility and ionic trapping of injected CO_2 at several monitoring wells at both study sites [e.g. 1]. In addition, changes in the $\delta^{18}O$ values of reservoir fluids provided independent evidence for dissolution of injected CO_2 in the produced waters. We conclude that geochemical and isotopic monitoring techniques, in concert with other monitoring approaches, can play an essential role in verification of CO_2 storage, provided that the isotopic composition of the injected CO_2 is distinct.

[1] Raistrick *et al*. (2006) *Environmental Science & Technology* **40**(21), 6744-6749.