# Formation fluids-$CO_2$-sediment interactions: Minimizing environmental impacts of $CO_2$ storage

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Sedimentary basins in general and deep saline aquifers in particular are being investigated as possible long-term repositories for large volumes of anthropogenic $CO_2$ to mitigate global warming and related climate changes. Detailed chemical and isotopic analyses of water, gases, and added tracers obtained from Frio field tests, near Houston, Texas, proved powerful tools in: 1- Tracking the successful injection and flow of $CO_2$ in Frio C, the reservoir sandstone; 2- showing that injected $CO_2$ was not detected in shallow groundwater; 3- detecting that some $CO_2$ leaked into the overlying Frio B sandstone that is separated from C by 15 m of shale and siltstone; 4- showing mobilization of metals (Fe, Mn, Pb, etc) and toxic organic compounds (BTEX, PAHs, etc) following $CO_2$ injection; 5- showing major changes in chemical and isotopic compositions of formation water, including a dramatic drop in calculated brine pH, from 6.3 to 3.0. Geochemical modeling, chemical data and Fe isotopes indicate rapid dissolution of minerals, especially calcite and Fe-oxyhydroxides, and show that some of the metal increases were caused by corrosion of well pipe. Significant isotopic and chemical changes, including mobilization of metals and BTEX, were also observed in shallow groundwater following $CO_2$ injection at the ZERT site, Bozeman, Montana. Geochemical techniques, which have sensitive chemical and isotopic tracers for tracking water-$CO_2$–sediment interactions, are recommended for $CO_2$ injection sites to monitor injection performance, and for early detection of any leakage.

# REEs in high p$CO_2$ groundwater from volcanic-sedimentary bedrocks of Sikhote-Alin ridge (Russia)

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Abundance and distribution of rare earth elements (REEs) was determined for volcanic-sedimentary bedrocks and related high p$CO_2$ groundwater from three spas of Sikhote-Alin ridge, Far East of Russia.

*Lastochka spa* is located in the northwestern part of the Sikhote-Alin ridge. Bedrock consists of Jurassic sandstones, siltstones and shales. Groundwater circulation occurs in the upper fractured zone of sandstones and in the shatter zones. High p$CO_2$ water has TDS ranged from 3.7 to 4.7 g/l, pH 5.8-6.4 and belongs to Na-Ca-$HCO_3^-$ type.

*Gornovodnoe spa* is placed in the eastern part of the Sikhote-Alin ridge, inside the Eastern Sikhote-Alin volcanic belt. Groundwater circulation occurs in the upper zone of Mesozoic volcanic sediments (ignimbrites, tuff-lava, persilicic tuffs). High p$CO_2$ groundwater belongs to Ca-Mg-$HCO_3$ type and has TDS 1.4-3.5 g/l, pH 6.6.

*Ivanovskoe spa* is located in the central part of Sikhote-Alin ridge, in the volcanogenic sediments of Upper-Jurassic - Lower-Cretaceous ages. Groundwater is Ca-Mg-$HCO_3$ type with pH 5.7-6.1 and TDS up to 3 g/l.

Our data indicate that whole-rock REEs concentrations decrease from the surface to the deepest bedrock layers. This could possibly caused by leaching REEs from primary silicate minerals and gained by secondary precipitated minerals such as phosphate, clay and Fe-oxides.

The concentration of the REEs in groundwaters is approximately five to seven order of magnitude lower than in bedrock. All studied high p$CO_2$ groundwaters are relatively enriched in MREEs and HREE compared to LREE.

The enrichment of bedrock in LREEs and depletion in HREEs compared to groundwater samples are probably caused by preferential leaching of the HREEs from material during water-rock interaction and retention of LREEs. Positive Eu/Eu* in groundwater and negative Eu/Eu* in rock are the result of hydrothermal alteration of albite during water-rock interaction and the consequent increase in concentration of aqueous $Eu^{3+}$. Comparison profiles of NASC-normalized groundwater with their bedrocks indicate that profiles of REEs in these groundwaters do not reflect the REEs profiles of bedrock.