An experimental study of brine-CO_2 metal fractionation: Applications to the geological storage of CO_2

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In this study, we have measured the fractionation of Fe, Cu, Zn and Na between brine and carbon dioxide at pressure-temperature conditions applicable to the saline aquifers used for the geological storage of CO_2, in order to evaluate the potential for trace element remobilization within the injected CO_2 plume. The experiments were carried out at 6.5-16 MPa and 60°C in a Ti autoclave loaded with a 20 wt% NaCl solution containing a known concentration of Fe, Cu or Zn, in addition to pressurized CO_2. Paired samples of brine and CO_2 were extracted from separate capillary lines and analyzed for metal concentrations.

The vapour-brine partition coefficients $(D_i^{V/L} = C_i^V/C_i^L)$ ranged from $4x10^{-4}$ - $2x10^{-3}$ for Fe, $8x10^{-5}$ - $4x10^{-4}$ for Cu, $4x10^{-6}$ - $2x10^{-4}$ for Zn, and $1x10^{-6}$ - $1x10^{-3}$ for Na. The fractionation of these elements into the CO_2 did not cause a measureable decrease of their concentrations in the brine. The total element concentrations in the CO_2 samples ranged from 0.2 to 1.4 mg/kg (ppm) Fe, 0.1 to 0.6 mg/kg Cu, 0.004 to 0.4 mg/kg Zn and 0.6 to 92 mg/kg Na, and generally displayed a small positive correlation with CO_2 density. The values of $D_i^{V/L}$ in a CO_2 storage reservoir at 7-28.5 MPa and 35-98°C, in which the density of CO_2 is ~0.3-0.7 g/cm^3 (as compared to 0.1-0.6 g/cm^3 in this study), could be expected to be approximately equivalent to those determined from these experiments.

Considering the metal concentrations typical of brines in CO_2 storage aquifers that have reacted with CO_2 and sandstone (20-200 mg/kg Fe, 0.3-1 mg/kg of Cu, 3-5 mg/kg Zn), and neglecting the increased solvent capability of higher-density CO_2, these results suggest that a plume of injected CO_2 could contain up to 0.1 mg/kg Fe, 0.3 µg/kg Cu and 1 µg/kg (ppb) Zn, in addition to 16 mg/kg Na. At a Sleipner (North Sea)-sized reservoir used to store 14 Mt of CO_2, this would lead to the mobilization of about 1 t Fe, 5-10 kg Cu and Zn, and 200 t Na. In terms of long-term CO_2 storage, the potential consequences of these results include the precipitation of carbonate minerals in shallower, more distal regions of the aquifer and the transferral of metals to adjacent aquifer systems.

Combining NanoSIMS with STXM/TEM imaging to shed new light on organic matter contained in micron-sized particles

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During the past 10 years, NanoSIMS has opened a new window on the study of the spatial distribution of light elements and their isotopic composition in natural samples. This instrument, with its high sensitivity, high precision and high spatial resolution, is suitable to study organic matter (OM) in meteorites and soil aggregates. Nevertheless, this technique suffers from the influence of the nature and the topography of the sample surface on the ion yield (the so called matrix effect) making the unambiguous characterization of the carbonaceous phases sometimes problematic. Moreover, the intrument cannot deliver molecular information, often required for the study of OM.

We illustrate here, through several examples, the benefits to combine NanoSIMS imaging with TEM and STXM, in order to improve the characterization of the carbonaceous materials and to strengthen the conclusions arisen from NanoSIMS images. This is a challenging task because these cutting edge techniques, while sharing high spatial resolution capabilities, have very different intrumental constrains.

The combination TEM+NanoSIMS was used to characterize the carbonaceous phases isolated from an Enstatite chondrite by HF/HCl dissolution. Graphite and poorly organised OM were identified by TEM (and Raman spectroscopy). With NanoSIMS, we measured the D/H and $^{13}C/^{12}C$ isotopic ratios along with the H/C and N/C elemental ratios of each phase, without ambiguity. Hence, we entirely characterized the carbonaceous phases separately to understand their relationship and origin.

We could also assess the fate of labelled OM after a 10 years *in situ* incubation experiment in a natural forest by combining NanoSIMS and STXM. While NanoSIMS was able to map ^{15}N-labelled OM in soil microaggregates recovered from this forest, it has to be combined with STXM imaging (of the same aggregates) to reveal the molecular structure of the organic constituents. The combination of these instruments allows us to follow, at the submicron scale, the processes leading to the soil OM recycling.