Measurement of the isotopic composition of dissolved Fe in seawater

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Since the advent of multi collector ICPMS, the number of studies of the iron isotopic composition in the environment has dramatically increased. This interest is due to the major role of this element in the bio-geo-chemical cycles. In particular, iron is a major component of our planet, it is sensitive to redox conditions and it is essential for life.

In the ocean, the iron cycle is especially important since, unlike on the continents, large areas of the surface ocean are iron depleted, which has been shown to limit phytoplankton growth. The iron oceanic cycle is therefore linked to the carbon cycle and hence to climate. However, our present knowledge of the oceanic iron cycle is limited. In particular, the relative importance of the different potential sources of iron for the surface ocean is still a matter of debate. Whereas aerosol dissolution is usually considered as the dominent source, some works (e.g. Elrod *et al.* [1]) suggest that sediment remobilization could play a significant role.

As for other isotopic systems (e.g. C, N or Si), Fe isotopic composition data in seawater could bring new insight in our understanding of the oceanic iron cycle. Such measurements are very challenging however, due to the very low Fe concentration and to the high salt content of seawater. Such analysis requires extraction and purification of iron from seawater, with a high yield, low blanks, a complete separation from interfering elements (Cr and Ni) and no isotopic fractionation, or a means to correct for it.

We will present our results concerning this analytical development. We are currently testing the double spiking technique with a Neptune MC-ICPMS (Thermo Scientific) coupled with an Aridus desolvating system. Comparison of different preconcentration and purification methods (including coprecipitation and chelating resins) will be presented. Preliminary Fe isotopic composition data from the Southern Ocean (Kergelen area) and/or Equatorial Pacific Ocean will also be presented.

[1] Elrod, V. A. & W. M. Berelson *et al.* (2004) *Geophysical Research Letters* **31**, doi,10.1029/2004GL020216.

Noble gases as precursors of CO_2 deep storage leaks towards surface

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We are developping the use of noble gases as tools to survey the integrity of CO_2 geological storages. The advantage of using noble gases stems from their chemical inactivity which dont delay them when they migrate in leaking pathways. Using the aquifers located above the CO_2 deep storages as leak integrators and monitoring them for noble gase contents could make it possible to forecast a future CO_2 arrival. To achieve this possibility, the CO_2 in place in the storages must contain noble gases. Noble gases can be present naturally in geological reservoirs as a mantle-derived signal, or could be injected with CO_2 as helium spikes or as atmospheric argon.

As an analogue of a CO_2 reservoir, we have studied the Montmiral CO_2 accumulation (about -2500m, near Valence, France) using the new analytical procedure described in [1]. The CO_2 gas phase was first analyzed to describe its noble gas content. Our results present a high volume fraction of helium (^{4}He= 301±29 ppm) and high helium versus neon ratios (^{4}He/^{20}Ne= 364±48). In the CO_2 reservoir, the origin of helium is described by a R/Ra ratio of 0.75±0.12. Then, above the CO_2 reservoir, we spatially collected and analyzed samples from shallow aquifers at depths of about -100m. In the deeper water samples, we have recognized the reservoir noble gas signal. Using the ^{4}He/Ne ratios vs. the distance to the CO_2 reservoir wells, we are able to detect a trend which is interpreted as a leak of the reservoir gas towards the surface via a poorly sealed well (abandoned in 1956).

This work wants to promote the use of noble gas geochemistry as an efficient subsurface monitoring tool to survey the CO_2 geological storages and to trace possible gas leaks.

[1] S. Lafortune, M. Moreira, P. Agrinier, H. Schneider & H. Catalette (2007) *GCA* **71**(15, I) A535 Abstract of the 17th annual Goldschmidt Conference (Cologne, August 2007)