

Yttrium and rare earth element composition of the Rapitan Iron Formation (Northwest Territories, Canada)

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The Neoproterozoic represents a time in Earth's history when significant environmental changes took place, including global glaciations that led to ocean stagnation and an apparent build-up of dissolved ferrous iron. As the ice receded and ocean circulation became re-established, the iron became oxidised and formed a suite of iron formations (IFs) in the oxic zone of upwelling areas. However, the ultimate source of iron is still a matter of intense debate.

Rare earth elements plus yttrium (REY) concentrations in IFs have been successfully used as proxies to study secular trends in Precambrian ocean chemistry. Despite a number of previous geochemical studies on Cryogenian IFs, complete REY datasets are virtually absent. Here we examine bulk and mineral phase trace-element geochemistry (REY) of the Rapitan Iron Formation, Northwest Territories, Canada. Samples for geochemical analysis were selected on the basis of extremely low, if any, Th, Zr, Hf and Sc concentrations and lack of co-variations between Zr vs. Y/Ho, Y/Ho vs. Ce/Ce* and Th vs. La/La*. The results show: (1) REY profiles with distinctive seawater-like signatures (i.e., LREE-depletion relative to HREE, superchondritic Y/Ho ratios and positive anomalies of both La and Gd); (2) precipitation under oxygen-deficient conditions (no to slightly positive Ce anomaly); and (3) iron being sourced from hydrothermal vents (positive Eu anomaly). Of particular interest, along with Ce, is the identification of an Eu anomaly in all of the samples analyzed. The latter might be explained either by precipitation in an open stratified ocean involving ferruginous deep waters -through which hydrothermally sourced Eu (and iron) could travel long distances- or by deposition taking place in a somewhat restricted basin where the Eu signature is more easily retained. In the first scenario, our results might confirm, as previously proposed, that ferruginous conditions dominated during the Sturtian "snowball glaciation". Alternatively, a semi-isolated basin should be considered for the deposition of the Rapitan IF.

Zinc sorption on carbonate reservoir system, implications on CO₂ geological storage.

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Geological storage is one of the solutions envisaged to reduce greenhouse gases concentration in atmosphere, and storage in underground saline aquifers is of major interest considering their high storage capacity. One of the main question still unanswered regards the consequences of the supercritical CO₂ injection on the metals mobility; from the storage formation to the sub-surface. Indeed, supercritical CO₂ injection (over 31 °C and 74 bar) acidifies the aquifer and induces metals release from rock matrix. In consequences, geochemistry (dissolution/precipitation phenomena, sorption of metals...) and petrophysical properties (porosity and permeability) of each compartment impacted will be changed.

In this study, two natural carbonates (from Lavoux and St-Emilion) were used to carry out zinc sorption experiments (initial concentration equal to 10⁻⁵ mol/L) at 40 °C and four different CO₂ pressures (3.5e⁻⁴, 30, 60 and 90 bar) in saline solutions (100g/L NaCl) in batch reactors.

Results obtained for the different pressure conditions investigated on Lavoux carbonate show that: (i) in atmospheric conditions, the zinc adsorption phenomenon is clearly put in evidence and matches well with a Freundlich adsorption isotherm model [1]; (ii) at 30 bar of CO₂, the dissolution of Lavoux carbonate [2] induces a zinc release in the system, with no adsorption observed; (iii) at 60 bar, a strong decrease of zinc concentration is observed (factor 2) over 70 days and after, it goes back close to its initial value; (iv) with a CO₂ pressure of 90 bar, adsorption is observed but in lower proportions and slower kinetic than in atmospheric conditions. Comparative studies with St-Emilion carbonate are being carried out and will be discussed with these previous results obtained with the Lavoux carbonate.

Though more investigations have to be carried out to better understand the coupling and competition of rock dissolution and metals adsorption phenomenons, these results are very important in order to better understand the behavior of metals in the {carbonate/saline-solution/CO₂} system in a geological storage context. Indeed, the CO₂ pressure implies very different compartment on metals sorption, which will occur in natural context. These results will allow us to predict by reactive modelling the future behavior of metals in CO₂ geological storage sites, their potential mobilization up to surface aquifers and their impact on surface potable aquifers.

[1] Limousin et al. (2007) *Applied Geochemistry* **22**, 249-275.

[2] Pokrovsky et al. (2005) *Chemical Geology* **217**, 239-255