

Non-traditional stable isotopes and surface complexation models for ion binding to humic substances (NICA-Donnan) and oxide mineral surfaces (CD-MUSIC)

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Non-traditional stable isotopes (i.e. Zn, Fe, Ni and Cu) are increasingly used for environmental studies [1]. Considering the wide range of possible sorbents (Mn or Al oxides, phyllosilicates, carbonates, biologic surfaces...), the importance of the reactions at the sorbent/water interface for these numerous studies emphasized the importance of modelling approaches that are needed to quantify the isotopic fractionation of these elements caused by their sorption at mineral/water, organic moieties/water interfaces.

The present work will show how the use of EXAFS spectroscopy and CD MUSIC and NICA Donnan modelling can help to better understand the changes in isotopic ratio. Zn isotopic fractionation upon sorption onto Hydrated Ferric Oxide (HFO) and goethite will be discussed to assess the influence of reactions at the Fe-(hydr)oxide/water interface on the isotopic distribution of Zn [1]. The Zinc isotopic fractionation during interaction onto natural organic matter will be discussed. The Donnan Membrane device was successfully adapted for isotopic measurements and used to separate Zn bound to the PHA from free Zn²⁺ ions in solution and allowed the measurement of isotopic ratios of free Zn²⁺. The NICA-Donnan model, is used to simulate the corresponding isotopic fractionation and the composition of free Zn in the Seine river, France and allows a better understanding of Zn isotope fractionation mechanisms associated with organic matter binding [2].

[1] D.M. Borrok, R.B. Wanty, W. Ian Ridley, P.J. Lamothe, B.A. Kimball, P.L. Verplanck, *et al.*, *Applied Geochemistry*, **24** (2009) 1270–1277. [2] F. Juillot, C. Marechal, M. Ponthieu, S. Cacaly, G. Morin, M. Benedetti, *et al.*, *Geochimica Et Cosmochimica Acta*, **72** (2008) 4886–4900 [3] D. Jouvin, P. Louvat, F. Juillot, C.N. Maréchal, M.F. Benedetti, Zinc Isotopic Fractionation: Why Organic Matters, *Environ. Sci. Technol.* **43** (2009) 5747–5754.

In-situ IR spectroscopic study of forsterite carbonation in wet-scCO₂

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Capturing and storing CO₂ in basaltic formations is one of the most promising options for reducing the effects of energy production from fossil fuel on the Earth. These geologic reservoirs have high reactive potential for CO₂-mineral trapping due to an abundance of divalent-cation containing silicates, such as forsterite (Mg₂SiO₄). Recent studies [1-4] have shown that carbonation of these silicates is more effective in wet scCO₂ conditions, encountered near a CO₂ injection well, than in dry and/or CO₂-saturated aqueous fluids. More interestingly, formation of magnesite under supercritical fluid conditions has been reported in some of these previous studies at temperatures as low as 35°C [3], in spite of its known sluggish formation under aqueous scenarios.

In this study, we used high pressure IR spectroscopy to investigate the carbonation of nanometer-sized forsterite at 35 and 50°C by systematically titrating water that subsequently dissolves in scCO₂ at 90 bar. The results show that at low total dissolved water concentrations, only highly structured adsorbed water and bicarbonate are detected at the forsterite surface. However, as the water concentration increases up to a critical value, but below H₂O-saturated scCO₂, a more liquid-like water film is detected on the forsterite particles, the bicarbonate concentration decreases and magnesite precipitates, as shown in our *in situ* IR spectra, as well as from *ex-situ* XRD, TGA and SEM analyses.

The results of these studies provide important insights into metal silicate carbonation mechanisms in low water scCO₂ environments. They reinforced the concept of a water threshold for carbonation to occur, which has also been demonstrated for steel corrosion in the presence of wet scCO₂ [5]. These results will also constrain thermodynamic models and molecular dynamic simulations used to predict mineral trapping extent in basaltic host rocks.

[1] Kwak *et al.* (2011) *Int. JGGC.*, **5**, 1081-1092. [2] Loring *et al.* (2011) *ES&T*, **45**, 6204-6210. [3] Felmy *et al.* (2012) *GCA*, **91**, 271-282. [4] Schaefer *et al.* (2013), *ES&T*, **47**, 174-181. [5] McGrail *et al.* (2009) *Energ. Proc.*, **1**, 3415-3419.