

COMBINING μ SXRF, EXAFS AND ISOTOPIC SIGNATURE TO UNDERSTAND THE NI CYCLE IN IMPACTED ULTRAMAFIC SOILS

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Biogeochemical cycles of metals have been deeply modified by anthropogenic activities since the industrial revolution [1]. Since the end of the 90's, the development of metal isotopic ratios analysis provides crucial information about their biogeochemical behaviour. In the case of mining or smelter activities, extracted metals can be clearly followed through their isotopic signatures [2; 3]. Only few publications [4; 5] report the use of Ni isotopes for environmental studies, in spite of its high potential for tracing anthropogenic Ni. The combination of isotopic tools with microspectroscopic techniques (μ SXRF and XAS), to unravel metal local distribution and speciation, should improve our understanding of Ni behavior and predict its mobility and bioavailability.

Samples from the ultramafic massives of Barro Alto and Niquelândia (Goiás State, Brazil), constituted in ores, fly ash, slags and natural and waste impacted soils were characterized for their Ni speciation and isotopic signatures. Ni concentrations range from 0.5 to 22.9 g.kg⁻¹

Ni K-edge XAS data were collected in bulk and microbeam modes for Ni ore, pristine pyrometallurgical wastes (fly ash and slags) before and after leaching (TCLP and DTPA procedures), to evaluate Ni extractability. TCLP or DTPA leaching leads to the extraction of 0.3 to 8.1% of Ni depending on samples. XANES spectra show that Ni is octahedrally coordinated. Linear Combination Fitting of EXAFS oscillations suggests that Ni in the ore is mainly involved in Ni-phylosilicates and less than 20% in Ni bearing goethite. The Ni speciation in wastes is dominated by olivine and ferronickel, and leaching procedures only slightly impact Ni speciation.

The relatively high temperature processes occurring during pyrometallurgy processes may be responsible of strong isotopic fractionation [2]. Hence, Ni species from slags and fly ash should be easily distinguished from natural Ni species by their different isotopic signatures. Thus, all anthropogenic materials (ores, fly ash and slags) and soils will be carefully studied for isotopic signatures, in order to trace anthropogenic Ni in this ecosystem.

[1] Rauch & Pacyna (2009) *Glob. Biogeochem. Cycles*, **23**, 1-16. [2] Sivry et al. (2008), *Chem. Geol.*, **255**, 295-304. [3] Juillot et al. (2011), *Geochim. Cosmochim. Acta.*, **75**, 2295-2308. [4] Sergeev et al. (2006), *Geochim. Cosmochim. Acta.*, **70**, suppl., A570. [5] Sergeev et al. (2007), *Geochim. Cosmochim. Acta.*, **71**, suppl., A918.

Insights into biomineral growth from atomistic simulations of clusters and nanocrystals

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Introduction

The common biomineral calcium carbonate (CaCO₃) appears in nature as a variety of crystalline polymorphs and morphologies, exhibiting structure on a hierarchy of length scales which cannot be reproduced synthetically. Molecular simulation has a key role to play in elucidating the earliest stages of biomineral growth where length scales prohibit direct observation by experiment.

Nanoparticle simulations

Our previous free energy calculations based on metadynamics [1,2] have established that amorphous structure is energetically competitive with crystalline calcite for particles smaller than 2nm, with calcite structure increasingly preferred at sizes of 5nm and larger. This confirms experimental evidence that CaCO₃ growth can proceed via amorphous precursor phases.

Substantial improvements in the quality of force-fields for CaCO₃ [3] are enabling new questions to be addressed. Specifically water content and dehydration of the amorphous phase, and the stability of nanocrystals with aragonite or vaterite structure. The latter of these questions is a necessary step in elucidating the mechanisms of polymorph selection during nucleation and growth.

The traditional method of generating atomic representations of crystalline nanoparticles is the Wulff construction, in which a bulk crystal is cleaved such that the total surface energy is minimised. Our most recent work has demonstrated that such an approach fails for models which correctly capture the CaCO₃-water interfacial energetics. Surface *enthalpies* are found to be negative, with the entropic penalty of tightly-bound surface water being sufficient to generate a net interfacial free energy penalty.

We have developed an alternative Monte-Carlo method for generating nanocrystal configurations and applied this to the three CaCO₃ polymorphs. A discussion of magic-number effects will be presented, along with simulations comparing the energetics of these particles over a range of sizes in explicit water. Some progress toward simulating transitions between nano-crystalline polymorphs will be presented, along with challenges to calculation of transition kinetics.

Pre-nucleation clusters

Improved atomistic models have also allowed larger scale simulations to probe the earliest stages of ion aggregation, suggesting an explanation for the formation of stable pre-nucleation clusters [4]. This talk will present recent attempts to capture this phenomenon in simple lattice models of nucleation and growth.

[1] Quigley & Rodger (2008) *J. Chem. Phys.* **128**, 221101. [2] Quigley et al (2011) *J. Chem. Phys.* **134**, 044703. [3] Raiteri et al (2010) *J. Phys. Chem. C*, **114**, 5997-6010. [4] Demichelis et al (2011) *Nature Comms.* **2**, 590.