

Neutron Diffraction: Applications in Environmental Issues

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INTRODUCTION.

Maintaining and remediating the quality of water, air and soil, so that Earth will be able to sustainably support human population growth, is one of the great challenges of our generation. The scarcity of water, both in terms of quantity as well as quality, poses a significant threat to the man's well-being. Environmental technology is set to play a key role in the shaping of current environmental engineering and policy. Our ability to study materials at the nano-scale has stimulated the understanding of environmental systems, as well as the development and use of novel and cost-effective technologies for remediation, pollution detection, and catalysis, to name but three. There is now a huge expectation that these applications and products will lead to a cleaner and healthier environment. New developments in neutron sciences to enhance our understanding of environmental relevant concepts such as bioavailability and toxicity of single molecules, heavy metals or nanoparticles, and to develop technological-oriented processes such as transformation and sequestration of these pollutants (Wenk, 2006).

Toxic heavy metals in soil and water are global problems that are directly and indirectly threatening humanity. Industrial and agricultural activity has increased their release and made them available to fish and wildlife in aquatic and terrestrial ecosystems around the globe (Bradl, 2005). Heavy metal pollution is therefore often the result of human activities such as mining, metallurgy and metal surface treatment. The toxicity of a given element depends mainly on the bioavailability of the toxic element, i.e. on the fraction of the total soil, air or aqueous concentration of the element which can be taken up by the organism. Agreement on the definition of bioavailability seems unlikely in the near future (Reeder 2006) as it involves many chemical, physical and biological aspects. In general terms, "bioavailability studies"

deal with processes occurring at the interface between the environmental matrix and the surface of an organism. The most important factors controlling bio-availability are: (i) metal concentrations in solution, (ii) solute and particles metal speciation, (iii) metal partitioning among solid and aqueous ligands, (iv) pH, (v) redox potential, (vi) influence of other cations, and (vii) temperature.

NEUTRON DIFFRACTION.

Thermal neutrons are a uniquely powerful probe of the microscopic-scale structure of condensed matter systems. Their wavelengths are well matched to the atomic distances, while the lack of charge makes them deeply penetrating and non-destructive. Moreover, the neutron interacts primarily with the nuclei, rather than electrons. Light atoms such as H are therefore relatively strong scatterers of neutrons, in contrast to the situation when using X-ray techniques, and in many cases the different isotopes of the same element have very different neutron scattering properties. This last characteristic is the basis of isotopic labelling techniques, whereby the structure around one particular species can be isolated from all others.

Over the last decades neutron scattering has become an important method for the study of geological materials. To a significant extent this is due to the ability of neutrons to locate H, an important and common element in minerals: because of its large coherent scattering cross section, H can be resolved much more clearly with neutrons than with X-ray based techniques such as EXAFS. Neutron diffraction experiments yield data up to much larger scattering vectors, because the atomic form factor is independent of the scattering vector. This in turn provides higher real-space resolution than X-ray scattering, particularly when analysing the complex low-symmetry crystal structures of many minerals, and when looking at thermal movement and atomic occupancy of la-

ttice sites. In comparison with other isotopic substitutions, the use of heavy water (D₂O) instead of light water (H₂O) is relatively easy and low cost. Neutron scattering therefore complements X-ray techniques, and is rapidly broadening its use in environmental related studies. For instance, Neutron Diffraction with Isotopic Substitution (NDIS) is a very useful technique for the study of the water structure around a specific cation, using contrast variation through H₂O/D₂O exchange. This provides a detailed knowledge of the atomic positions and number of both O and H atoms around a given metal ion, and thus allows distinguishing surface O atoms from hydration water (or hydroxyl atoms). This kind of information is very valuable in the study of surface complexation of pollutants on mineral surfaces (Cuello et al., 2008).

SURFACE PROCESSES.

The NDIS technique has attracted much interest in the study of ion uptake mechanisms in clay interlayers. The water structure and counterion coordination in the interlayer region of smectite clays such as montmorillonite is fundamental to many of the important properties of the clays and important for understanding applications such as radioactive waste disposal. The NDIS has allowed the study of the hydration of hazardous cations in the interlayer of clay minerals (Pitteloud et al., 2003, Sobolev et al., 2007). The hydration shell structure of the aqua-ions may change when they are adsorbed on the clay interlayer, as shown in the case of Nd³⁺ and Yb³⁺ exchanged Wyoming Montmorillonite (Pitteloud et al., 2003). The lanthanide (Ln)-exchanged forms are of interest in the context of the migration of radionuclides in clay containment barriers and in the environment. This is possible assuming that these Ln and their equivalent actinides are isomorphous (Pitteloud et al., 2003). The Nd and Yb were chosen because of their positions among the early larger Ln and later smaller Ln, respectively, and for the

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availability of isotopes with contrasting neutron scattering lengths. In aqueous solution, Nd^{3+} and Yb^{3+} are found by neutron diffraction to be hydrated by 9 and 8 water molecules, respectively (Cossy et al., 1995). Using the NDIS technique with ^{172}Yb , ^{174}Yb , ^{144}Nd , ^{143}Nd , H_2O and D_2O substitutions it was possible to probe in detail the local environment of water molecules and cations in the interlayer region of smectite clays. The ability to separate the ion-H and ion-O pair distribution functions enabled to distinguish between binding to water molecules and binding to other oxygen atoms. It was shown (Pitteloud et al., 2003) that a mild heat treatment produces a dehydration of the ions, suggesting that the Ln(III) ions may bind to the clay layers under burial conditions.

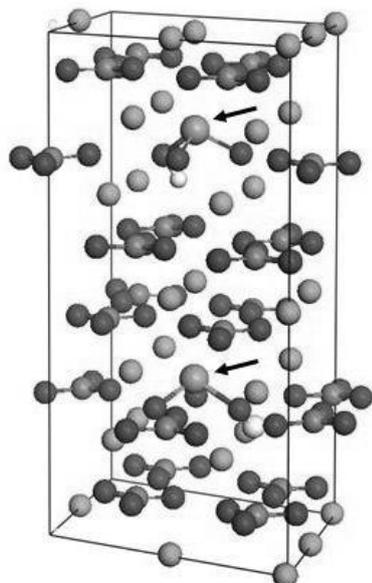


fig 1. Incorporation of an arsenite molecule HAsO_3^{2-} in the calcite unit cell. The arrows show As atoms.

POLLUTANTS IN BULK MINERALS.

Neutron scattering techniques have been proved to be very useful for quantifying the degree of substitution of As anions in the bulk of mineral phases. The non-electromagnetic character of the neutron-nuclei interaction makes the neutron an ideal probe for bulk properties. This is the case for the study of arsenite (HAsO_3^{2-}) incorporation into calcite crystals. Following several studies on the adsorption of arsenic in calcite surfaces, it has been shown (Román-Ross et al., 2006) that the mechanism of incorporation of arsenite anions into the bulk of calcite, through the substitution of carbonate molecules (Fig 1). A volume expansion has been found for synthetic calcite samples co-precipitated with

As(III), as revealed by neutron diffraction. Density Functional Theory simulations proved that this substitution produces an expansion of the lattice cell compatible with the expansion observed in the experimental data (Fernández Martínez et al., 2006). In a previous study, it was demonstrated experimentally with the use of X-ray Standing Waves how arsenite molecules can adapt to the surface of calcite by replacing a carbonate. The incorporation of arsenite to the bulk of calcite plays a very important role in the quantification and immobilization of arsenic in natural environments.

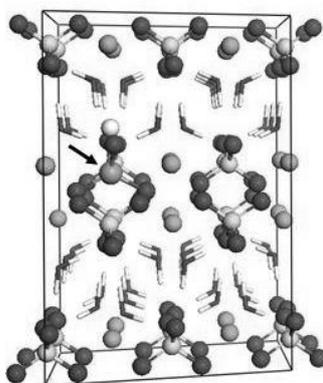


fig 2. Incorporation of an arsenate molecule HAsO_4^{2-} in the gypsum unit cell. The arrow shows As atom.

There are industrial activities where mineral ores are smelted generating As-rich gypsum sludges, produced upon neutralization of As-rich acidic solutions and quite often gypsum from those sludges appears associated to Ca arsenates. However, little information is usually obtained from the incorporation of arsenic into the bulk of gypsum, which may potentially lead to its long term immobilization into the mineral structure. A combined neutron diffraction and X-ray absorption spectroscopy study has revealed the ability of gypsum to host up to 1 mol_{As}/kg (Fernández Martínez et al., 2006, 2008). Rietveld refinement of neutron powder diffraction data combined with DFT-based calculations revealed the structure and properties of the substitution process of a sulphate (SO_4^{2-}) by an arsenate molecule (HAsO_4^{2-}) (Fernández Martínez et al., 2006, 2008). The gypsum structure is formed by layers of ionic bonded sulphate molecules (SO_4^{2-}) and calcium atoms (Ca^{2+}). Water molecules are intercalated between the layers, holding them together through hydrogen bonds. The trapping process relies on the substitution of a sulphate by an arsenate molecule (Fig 2). Neutron powder diffraction

experiments have revealed an expansion of the unit cell volume proportional to the concentration of arsenic present in the gypsum samples. Two factors make neutron diffraction the better adapted technique to follow this volume expansion: its neutral electronic character makes the neutron an ideal probe for probing the bulk of the material under study and the fact that deuterium is a good scatterer of neutrons make possible to determine the exact atomic positions for all the deuterium atoms of a highly hydrated structure as gypsum.

REFERENCES.

- Bradl H. (ed.) (2005): *Heavy Metals in the Environment: Origin, Interaction and Remediation*, Interface Sci. Techn. 6, Acad. Press
- Cossy C., Helm L., Powell D.H., Merbach A.E. (1995): A change in coordination from 9 to 8 along the lanthanide(III) aquaion series in solution: a neutron diffraction study, *New J. Chem.* 19, 27
- Cuello G.J., Román-Ross G., Fernández-Martínez A., Sobolev O., Charlet L., Skipper N.T. (2008): Pollutant speciation in water and related environmental treatment issues in "Neutron Applications in Earth, Energy, and Environmental Sciences", L. Liang L., Rinaldi R., Schober H.R. (Eds.), Springer, in press.
- Fernández-Martínez A., Román-Ross G., Cuello G.J., Turrillas X., Charlet L., Johnson M. R., Bardelli F. (2006): Arsenic uptake by gypsum and calcite: Modelling and probing by neutron and X-ray scattering, *Physica B* 935, 385-386.
- Fernández-Martínez A., Cuello G.J., Johnson M.R., Bardelli F., Charlet L., Román-Ross G., Turrillas X. (2008): Arsenate Incorporation in Gypsum Probed by Neutron, X-ray Scattering and Density Functional Theory Modeling, *J. Phys. Chem. A.* 10.1021/jp076067r
- Pitteloud C., Powell D.H., González M.A., Cuello G.J. (2003): Neutron diffraction studies of ion coordination and interlayer water structure in smectite clays: lanthanide(III)-exchanged Wyoming montmorillonite, *Colloids Surf. A: Physicochem. Eng. Aspects* 217, 129
- Reeder R.J., Schoonen M.A.A., Lanzirotti A. (2006): Metal Speciation and Its Role in Bioaccessibility and Bioavailability, in *Medical Mineralogy and Geochemistry*, Sahai N., Schoonen M.A.A. (eds.), *Rev. Mineral. Geochem.* 64, 59
- Román-Ross G., Cuello G.J., Turrillas X., Fernández-Martínez A., Charlet L. (2006): Arsenite sorption and co-precipitation with calcite, *Chem. Geol.* 233, 328
- Sobolev O., Charlet L., Cuello G.J., Gehin A., Brendle J., Geoffroy N. (2008): Hydration and hydrolysis of samarium (III) in montmorillonite clay: a neutron diffraction study, *J. Phys. Cond. Matter* 20, 104207
- Wenk H.-R. (ed.) (2006): *Neutron Scattering in Earth Sciences*, *Rev. Mineral. Geochem.* 63.