

X-ray Pair Distribution Function Studies of Nanosize Minerals

/ ALEJANDRO FERNANDEZ-MARTINEZ (1, 2, *), GABRIEL J. CUELLO (2), JOHN E. DANIELS (3), LAURENT CHARLET (1)

(1) Laboratoire de Geophysique Interne et Tectonophysique, Université de Grenoble - CNRS. Maison des Geosciences, B.P.53. 38041 Grenoble Cedex 9 (France)

(2) Institut Laue-Langevin, B.P. 156, 38042, Grenoble Cedex 9 (France)

(3) European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble Cedex 9 (France)

INTRODUCTION.

Much effort has been devoted in the last decade to determine the effects of the reduced size of nanomaterials in their physico-chemical properties. The study of size-dependent properties of nanosize minerals is now an emerging discipline in the field of mineralogy [Hochella et al., 2008]. Some examples of size-specific effects which are relevant to the environmental sciences include structural relaxation [Gilbert et al., 2006], enhanced photo-chemical reactivity [Sakai et al., 2005] or increase of the sorption strength by stabilization of the surface-tension [Auffan et al., 2008]. The development of new experimental techniques for structural determination with atomic resolution has allowed gaining a better understanding of processes occurring at the nanoscale. Between these techniques, the Pair Distribution Function (PDF) method has revealed itself as very powerful to describe the short and medium-large order in nanosize minerals [Michel et al., 2005; Michel et al., 2007]. Although extensively used in the past for the study of liquids and amorphous solids [Fischer et al., 2006], it has been only in the last decade, in parallel with the development of nanotechnology, when it has shown its power and usefulness in this field.

THE PAIR DISTRIBUTION FUNCTION METHOD.

The PDF is a diffraction technique which involves the use of (1) high energy radiation (high energy X-rays, electrons or hot neutrons) and (2) the use of a Fourier transformation mediated real space analysis of the data. Classical diffraction analyses are performed usually in the reciprocal space, through the use of convolution methods as the Rietveld refinement, or following deconvolution strategies, as the Warren-

Averbach method. The theoretical basis of the PDF technique can be understood from this equation:

$$I_N(Q) \propto S(Q) = 1 + \frac{1}{N} \sum_{i,j \neq i}^N f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

This expression, called the 'Debye equation for diffraction' [Debye], holds for randomly oriented systems in which the isotropic approximation can be made [Fischer]. It links the observed scattered intensity, I_N , with a sum over all the pairs of atoms in the sample, r_{ij} . $S(Q)$ is called the 'static structure factor', being Q the norm of the scattering vector:

$$Q = \frac{4\pi \sin(\theta)}{\lambda}$$

where θ is the diffraction angle and λ the wavelength of the incident radiation, and f_i is the atomic form factor. A real-space analysis of this intensity distribution in series of sinus functions can be made through a Fourier transformation:

$$g(r) - 1 = \frac{1}{2\pi^2 r \rho} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dr$$

The function $g(r)$ is called the Pair Distribution Function. It is proportional to the probability of finding two atoms separated by a distance of r . In contrast with the partial-PDF obtained with other spectroscopic methods such as Extended X-ray Absorption Fine Structure (EXAFS), the PDF function obtained from diffraction experiments is not centered in any specific atom, thus giving a structural description of local ordering around any atom in the structure. Nanosize minerals present structural features that make them difficult to be studied by classical analysis methods of diffraction. Atoms in their surfaces are exposed to

interactions with solvents and ionic species, which cause relaxation effects and so deviations from the bulk periodic structure. Moreover, the ratio of surface atoms vs. bulk atoms scales with $1/R$, being R the radius of the mineral nanoparticle (assuming spherical shape). This implies that for very small nanoparticle sizes relaxation effects will be very relevant to the mean structure. On the other hand, reduced number of atoms in the bulk implies that only few atomic planes will be participating coherently in the diffraction. This translates into ill-defined Bragg peaks in the diffraction patterns, and a not-negligible diffuse scattering. Classical diffraction analysis methods are limited under these conditions, as they rely on the Bragg peaks' positions and intensity. The advantage of the PDF method is that all the diffuse scattering is integrated as well within the Fourier transform, and so the structural information inherent to it is recovered.

NANOSIZE MINERAL PRECIPITATES.

We present here the application of the PDF method to the structural study of Fe^{2+} bearing fresh precipitates forming under anoxic conditions: FeS (mackinawite) and Fe_3O_4 (magnetite). These nanosize minerals are present in suboxic soils and sediments. They show very high reactivity towards redox sensitive oxyanions like selenite [Scheinost]. However, little is known about the substrate's size dependence of these redox reactions. Within this context, we have performed real-space PDF analyses of both minerals, with the aim of obtaining structural information on their local ordering. High-energy X-ray diffraction experiments have been carried out at the ID15B beamline of the European Synchrotron Radiation Facility, in Grenoble. A X-ray energy of 90 keV was used. The samples were loaded in 0.8 mm diameter capton capillaries,

sealed under anoxic conditions. Data treatment (background subtraction, and corrections for Compton scattering, fluorescence, X-ray polarization, absorption and normalization procedures were carried out using the PDFGetX2 software (<http://www.totalscattering.org>). PDF obtained for two of the precipitates and for one reference standard (LaB₆) are presented in Figure 1 (points: experimental PDF; lines: fitted structures; bottom line: difference).

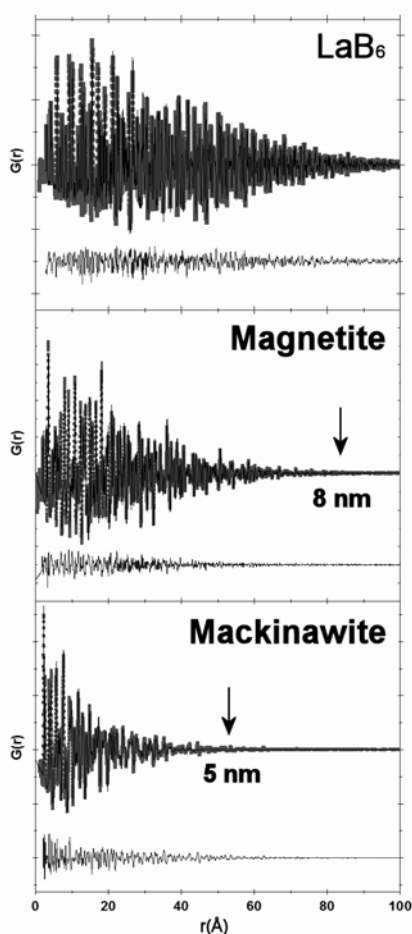


fig. 1. PDF of a crystalline standard, and two nanosize minerals: magnetite and mackinawite.

The PDF of the highly crystalline standard material LaB₆ shows an exponential decay of the intensity of the atomic correlations only due to the instrumental resolution; a precise characterization of it is needed in order to isolate structural features from instrumental ones. Both the PDFs for FeS and Fe₃O₄ show a decay of the intensity at medium distances (5–8 nm), that can be assigned to the limited particle size (assuming spherical shape), giving an idea of the so called 'coherent domain size' of the sample. Note that this size does not account for

aggregation effects. A second important feature observed in the PDFs is the effect of bond length relaxation at the particle/water boundaries. FeS and Fe₃O₄ fresh precipitates show nanoparticle diameters of around 5 nm and 8 nm respectively. This translates in percentages of atoms in the surface of 26% for FeS and 18% for Fe₃O₄. Both percentages are significant enough to think that relaxation effects may be important in the structure. Fitting of the PDF yields lattice parameters for mackinawite solids slightly increased in a 2% respect to their bulk counterparts. Any remarkable difference in lattice parameters is found for magnetite. The explanation for this effect in mackinawite has been hypothesized by Wolther *et al.* [wolthers]: FeS is a layered mineral, formed by sheets of Fe and S covalently bonded atoms that are held together by H-bonds. Relaxation effects may be possible if water molecules get into the interlayer spaces of the first atomic sheets. This effect could be an explanation for the increasing observed. Magnetite is a valence-mixed compound formed by Fe³⁺ octahedral and Fe²⁺ tetrahedra. All the structural units are covalently bonded to their neighbours, thus making more difficult any expansion of the lattice parameters by surface relaxation effects. However, some bond length relaxation can be observed if the first peaks of the PDF are examined with caution. The use of crystallographic supercells in the fitting procedure of the PDF function allows introducing different bond distances for the same atom-pair correlation. This practice helps in reducing the residue of the fit, which validates the hypotheses made on the bond relaxation effects. One of the difficulties associated with the application of this technique to 'environmental' samples is that these are usually not pure phases. This makes data analysis more difficult since corrections as the one accounting for Compton scattering is strongly dependent on the sample composition. In addition, samples usually contain water, which gives as well an incoherent background in the case of neutron diffraction, and adds some Compton scattering in the case of x-ray diffraction.

For this reason, a good estimation of the water content is required for good data treatment and reduction steps. In our case, the samples were filtered and dried. An estimated value of five water molecules per asymmetric unit formula was added in all the calculations.

CONCLUSIONS.

PDF analyses have revealed as a powerful method for the study of nanosize minerals, in spite of their sometimes inherent defective structures and reduced sizes. Classical diffraction methods, although very useful for mineral identification and size evaluation (mainly by the use of the Scherrer equation), fail when a quantitative structural description of a nanosize mineral is needed. The PDF method offers a useful alternative to classical methods by allowing a real-space representation of the information hidden in a diffraction patterns, including the diffuse scattering that is usually considered as meaningless background. Further work in the study and reactivity of nanosize minerals can help to understand problems as solubility of nanoparticles, problems related to kinetics of crystal growing (by *in-situ* PDF studies of crystal precipitation) or vacancy level estimation in defective materials.

ACKNOWLEDGMENTS

R. Kirsch and A.C. Scheinost are greatly acknowledged for enriching discussions.

REFERENCES

- Auffan M., Rose J., Proux O., Borschneck D., Masion A., Chaurand P., Hazemann J. L., Chanéac C., Jolivet J. P., Wiesner M. R., Van Geen A. and Bottero J. Y. (2008): Enhanced adsorption of arsenic onto maghemite nanoparticles: As(III) as a probe of the surface structure and heterogeneity. *Langmuir*, **24**, 3215.
- Fischer E. E., Barnes A. C. and Salmon P. S. (2006): Neutron and x-ray diffraction studies of liquids and glasses. *Rep. Prog. Phys.*, **69**, 233.
- Gilbert B., Huang F., Lin Z., Goodell C., Zhang H. Z. and Banfield J. F. (2006): Surface chemistry controls crystallinity of ZnS nanoparticles. *Nano Letters* **6**, 605.
- Hochella M. F. Jr., Lower S. K., Maurice P. A., Penn R. L., Sahai N., Sparks D. L. and Twining B. S. (2008): *Nanomaterials, Mineral Nanoparticles and Earth Systems. Science*, **319**, 1631.
- Michel F. M., Antao S. M., Chupas P. J., Lee P. L., Parise J. B. and Schoonen M. A. A. (2005): Short to medium range atomic order and crystalline size of the initial FeS precipitate from PDF analysis. *Chem. Mater.*, **17**, 6246.
- Michel F. M., Ehm L., Antao S. M., Lee P. L., Chupas P. J., Liu G., Strongin D. R., Schoonen M. A. A., Phillips B. L. and Parise J. B. (2007): The structure of ferrihydrite, a nanocrystalline material. *Science*, **316**, 1726.
- Sakai N., Ebina Y., Takada K and Sasaki T. (2005): Photocurrent generation from semiconducting manganese oxide nanosheets in response to visible light. *J. Phys. Chem. B*, **109**, 9651.