New concepts in XAFS analysis

FRANÇOIS FARGES[1,2]

[1] Laboratoire des Géomatériaux, FRE CNRS 2455 and Univ. de Marne la Vallée, France (farges@univ-mlv.fr)
[2] Department of Environmental Sciences, Stanford University, USA

The extraction of robust structural information from the x-ray absorption fine structure (XAFS, including XANES and EXAFS regions) spectra is highly dependent on the methods used to extract the desired information. We present here a variety of new methods to further reduce the XANES and EXAFS spectra.

Deconvolutions

Pre-edge, XANES and EXAFS deconvolutions (see Filipponi, 2000) are used to enhance spectral features such as electronic transitions in the pre-edge region. Application to the case of Fe in glasses suggests that Fe(II) do not form any 6-coordinated environment, but a mixture of 4-, and 5-coordinated Fe(II). Using deconvolutions, one can also shows that the enhanced pre-edge (Fe-K) for ferrihydrite is related to some extra transition, which is not related to crystal-field splitting (probably a Fe-Fe transition, as in epidote: Farges, 2002). Finally, deconvolutions of the EXAFS region help to evidence multi-electronic transitions, as it will be shown for Th in zircon.

Fourier modelling of the XANES

Analysis of the XANES can now be performed using FT methods, considering single-, and multiple scattering paths of the photo-electron (Bugaev et al., 2002) to get speciation information such as for Ti in radiation damaged titanites or in silicate glasses. Despite of the intrinsic limitations, the obtained information is consistent with that obtained from pre-edge or EXAFS analysis and other methods such as scattering methods (Bugaev et al., 2002).

Principal Component Analysis

In order to get the components composing the XAFS spectra of a mixture, principal component analysis provides some statistics on the number of end members to model. By inversion, the spectra for the end members can then be derived. An application to the photo-reduction of Au on ferrihydrite will be presented as well as for Fe in glasses synthesized under variable redox conditions.

References

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Using proton-induced ^{3}He to study He diffusion kinetics and rock thermal histories

K.A. FARLEY[1], D.L. SHUSTER[1], D.S. BURNETT [1] AND J. SISTERSON[2]

[1] Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125; farley@gps.caltech.edu; dshuster@gps.caltech.edu; burnett@gps.caltech.edu
[2] Northeast Proton Therapy Center, Massachusetts General Hospital, Boston, MA 02114; janet_sisterson@dfci.harvard.edu

We have investigated He release kinetics by step-heating of minerals in which we introduced artificial ^{3}He with a beam of ~150 MeV protons in a particle accelerator used primarily for cancer therapy. This process mimics cosmic-ray spallation, and produces He with a ^{3}He/^{4}He ratio of about unity. The induced helium is homogeneously distributed within the target crystals, and because it is emitted with few MeV energies, the ^{3}He should reside in sites indistinguishable from those of radiogenic ^{4}He. As a consequence it is reasonable to use ^{3}He as a proxy for radiogenic ^{4}He during step heating. The advantage of this procedure is that we can measure He diffusion coefficients from essentially any mineral, even those for which there is little or no natural He or He retention. In addition, diffusion coefficients computed using standard step-heat procedures would be erroneous if the He is not uniformly distributed within the diffusion domain. For example a slowly cooled apatite sample will have a highly rounded ^{4}He concentration profile which would retard the early He release in a step heating experiment, thus yielding erroneously low apparent diffusion coefficients. By using the artificial ^{3}He we can invert for the ^{4}He concentration profile *and* helium diffusivity simultaneously (e.g., see Albarede, 1978). This may prove useful as a technique for narrowing down permitted rock thermal histories.

Experiments on Durango apatite reveal excellent agreement between induced ^{3}He and radiogenic ^{4}He diffusion, supporting our approach. In contrast, probable slowly cooled apatites yield ^{4}He/^{3}He ratios that rise as the step heat proceeds, consistent with rounded ^{4}He concentration profiles. However in the first few steps the ^{3}He diffusion is anomalously high; we do not yet understand the origin or implications of this phenomenon.