

Experiment title (#08-01-899): Characterization of a new biomineral from Ingurtoisu mine (Sardinia)

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Report

Introduction

Biomineralization can be generally defined as the production of minerals by living organisms (Medina et al., 2011). The resulting biominerals have unique morphologies, hierarchical structures and specific functions, and often exhibit remarkable properties. Different studies (Towe and Lowenstam 1967; Lowenstam and Weiner, 1989; Becker et al., 2003) demonstrated that the first-formed mineral may be relatively disordered and over time transforms into more stable crystalline phases (Ostwald's Rule of Stages) (Weiner et al., 2009). These materials, usually, are characterized by a local order of a few Ångstroms or more (Addadi et al., 2003), and tend to be amorphous to X-ray because of their short-range order and other microscopy and spectroscopy techniques are required to study them.

The purpose of the experiment was to investigate, by X-ray absorption spectroscopy (XAS), the structural state of Zn associated to the X-ray amorphous biomineralization occurring at Ingurtoisu (SW Sardinia, Italy), along the Naracauli stream (Zuddas et al., 1998; Medas et al., 2012). Preliminary results are reported.

Experimental

We collected the spectra of eighteen natural samples (signed WM), collected along the Naracauli stream between summer 1994 and summer 2010. The reference samples were: i) willemite, ii) hemimorphite, iii) hydrozincite, iv) smithsonite, and v) zinc oxide. XAS experiments were carried out at the Zn K-edge (9,659 eV) and spectra were measured in transmission geometry. Standard procedures were used for data normalization and to extract the structural EXAFS (extended X-ray absorption fine structure) signal $\chi(k)$. The EXAFS data refinement was performed using the FITEXA code (Meneghini et al., 2012).

Results

Figures 1a and b report the near edge region of the normalized spectra of reference compounds and selected samples.

All biomineral samples depict similar Zn K-edge XANES spectra, then they have similar Zn local environment- On the other hand all the natural XANES spectra are significantly different from those collected on smithsonite and ZnO, suggesting definitive local structure differences.

Interestingly all the XANES of natural samples reassemble closely to the data measured in Hemimorphite while a close look allow to distinguish clear differences with the Willemite spectra. This finding is important because Hemimorphite and Willemite Zn local structure are closely similar in the EXAFS regions and cannot simply distinguished on the basis of EXAFS analysis.

Only the Zn K edge XANES of WM3 sample are similar to the data collected in Hydrozincite reference, in this sample the presence of Zn in this phase is evident. Figures 2a and b reports the Zn EXAFS spectra of selected natural samples and reference compounds with the best fit curves, and the Fourier transforms(FT). If compared with reference compound spectra, the data of natural samples presents weakly structured EXAFS signal and nearly absent next neighbour shells (FT) pointing out an amorphous nature of Zn in these samples. Only the WM3 data depict some high frequency contribution (EXAFS) and relatively intense next neighbour peak (FT) pointing out some degree of medium range order as expected in Hydrozincite environment. Quantitative analysis demonstrate 4-coordinated Zn-O ($R \pm 1.96 \text{ \AA}$) in all the natural samples; in some of them a weak next neighbour Zn-Zn shell is found around 3.2 \AA . The quantitative analysis of WM3 EXAFS data confirms the Hydrozincite-like environment.

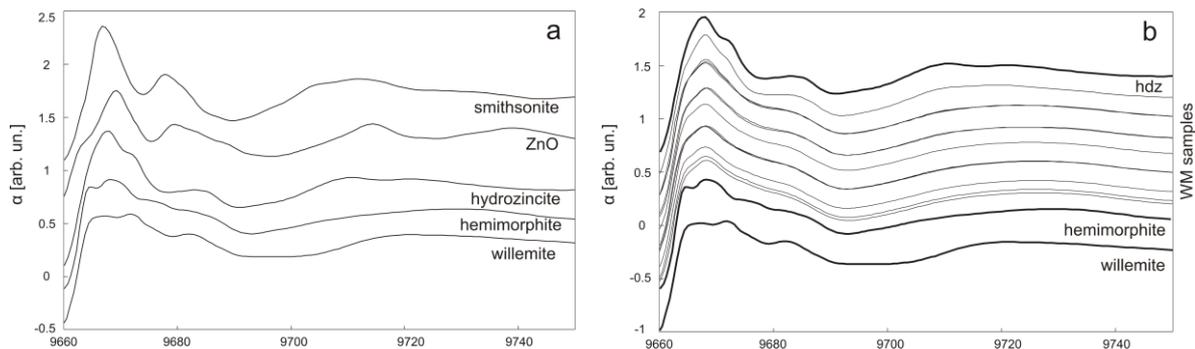


Fig. 1. Near-edge region of the XAS spectra collected on the measured samples, vertically shifted for the sake of clarity. a) reference compounds and b) biomineral samples (WM) compared to hydrozincite (hdz), hemimorphite, and willemite reference compounds.

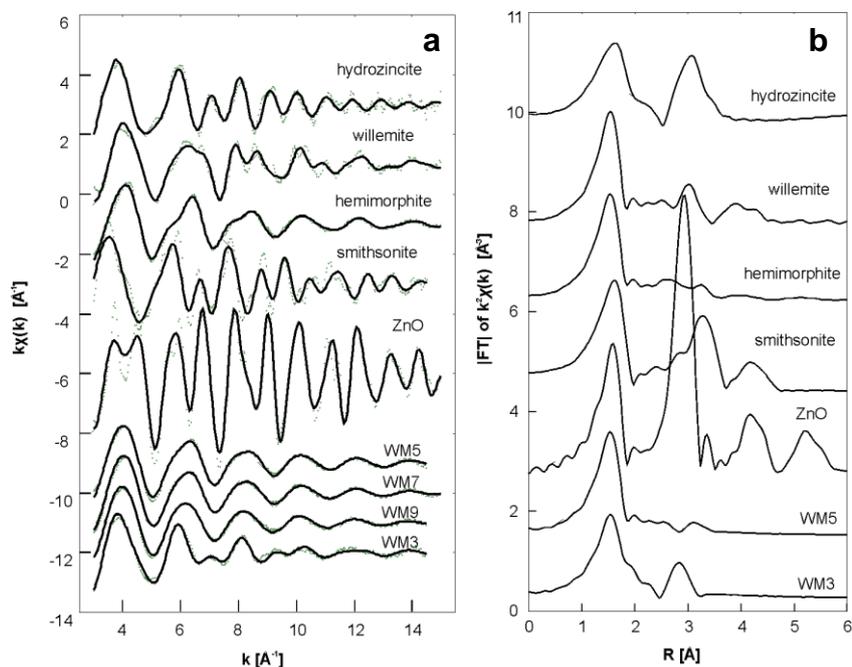


Fig. 2. a) Best fits of experimental EXAFS spectra for references compounds and some biomineral samples (WM), vertically shifted for the sake of clarity. b) Fourier transforms of EXAFS spectra.

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