



	<b>Experiment title:</b> Structural state of Pb in bioprecipitated hydrozincite from mine contaminated waters, Sardinia	<b>Experiment number:</b> ME-1126
<b>Beamline:</b> BM-08	<b>Date of experiment:</b> from: 13.06.2005 to: 17.06.2005	<b>Date of report:</b> 23.01.2006
<b>Shifts:</b> 9	<b>Local contact(s):</b> Chiara Maurizio	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Pierfranco Lattanzi, Università di Cagliari* Giovanni B. De Giudici, Università di Cagliari* Francesca Podda, Università di Cagliari Chiara Maurizio, ESRF (on leave for maternity)		

## Report:

### Introduction

This is the continuation of the experiment 08-01-659. The purpose of the experiment was to investigate, by means of X-ray absorption spectroscopy, the structural state of “heavy metals” associated with biologically mediated precipitation of hydrozincite –  $Zn_5(CO_3)_2(OH)_6$  from the metal-contaminated stream waters of Rio Naracauli, Sardinia, Italy [1]. The results should give indications on the mechanism of heavy metal trapping by hydrozincite, and therefore on its capability of long term removal of contaminants from polluted waters. The previous experiment was addressed to Cd; of specific interest to this experiment was Pb.

### Experiment

Materials for the experiment included (Table 1): two natural hydrozincite samples from the study area; a sample of natural cerussite ( $PbCO_3$ ): a set of synthetic materials, comprising Pb-bearing calcite ( $CaCO_3$ ), and three hydrozincites synthesized from solutions containing different amounts of Pb. These materials were synthesized in our laboratories in Cagliari. Specifically, Pb-calcite and hydrozincite 5 were synthesized at room temperature with the procedure described by Reeder et al. [2], whereas hydrozincites 3 and 9 were synthesized at about 100° C. Table 1 reports the analytical bulk concentrations of Pb in these materials, as determined by ICP-OES (for  $PbCO_3$ , the nominal concentration is shown).

Table 1

Sample description	Operational label at ESRF	Pb ppm	Pb atoms %
Pb-hydrozincite, hot synthesis	3	14800	<b>0.17</b>
Pb-calcite, Reeder synthesis	4	532	<b>0.005</b>
Pb-hydrozincite, Reeder synthesis	5	4070	<b>0.039</b>
Pb-hydrozincite, hot synthesis	9	1950	<b>0.022</b>
Natural hydrozincite (ING4 26-06-2001)	19	3700	<b>0.042</b>
Natural hydrozincite (ING0N 07-05-1997)	20	6500	<b>0.075</b>
Natural cerussite ( $PbCO_3$ )	22-16		<b>20</b>

Most materials were prepared at the beamline as thin films deposited onto Millipore paper disks from aqueous (deionized water) suspensions. Because the solubility of hydrozincite in deionized water is not negligible, small amounts of  $Na_2CO_3$  were added to the suspensions to obtain an alkaline environment. The amount of deposited material was not determined exactly, but was in the order of 100 mg for each disk. After deposition, the films were sealed by Kapton tape. The cerussite sample was prepared by weighing the amount expected to give the optimal absorbance (16 mg). This amount was then mixed with cellulose and prepared as a pressed pellet. The spectra were collected at the Pb L edge (13035 eV). Both transmission and

fluorescence mode were attempted; the best results were obtained in fluorescence mode, except for cerussite. A 13-element HP-Ge detector was employed. To minimize instrumental noise, the chamber was cooled with liquid nitrogen down to about 80° K. For hydrozincite, the strong fluorescence Zn peak would rapidly lead to detector saturation. Therefore, attenuation of the Zn signal was achieved by interposition of an aluminum foil. Because of the comparatively low Pb concentration of most samples, and signal attenuation due to the aluminum foil, spectra collection was relatively lengthy. Spectra were acquired from 12855 to 13800 eV, in 1 to 10 eV steps, counting times 3 to 15 seconds per step. For samples with low counting rates, scans were repeated 2 to 5 times. The overall data acquisition for each sample required 1 to 10 hrs.

## Results

The quality of XAS is good (fig. 1), and should provide the basis for meaningful results; in this sense, the experiment can be regarded as successful. XAS data were treated using standard methods for background subtraction and data normalization in order to extract structural XAFS signals. Quantitative structural analysis (preliminary at this time) was performed by fitting the total XAFS signals (fig. 2) using theoretical amplitude and phase functions calculated with the FEFF8.2 code. A more advanced refinement and a detailed interpretation of the results is currently under way. The preliminary comparison of the XANES part of spectra (fig. 1) suggests that all hydrozincites, both natural and synthetic, are very similar to each other, and markedly different from cerussite and (to a lesser extent) from Pb-calcite. In cerussite, Pb is in 9-fold coordination with oxygen, whereas in Pb-calcite it is in a distorted octahedron [2]. In the hydrozincite structure Zn occurs in three sites. The best fit for hydrozincite (fig. 2a,b) is obtained assuming that Pb occurs in two distinct sites. Work is in progress to refine these observations.

## Acknowledgments

Fabrizio Bardelli, ESRF, and Pilar Costagliola, Università di Firenze, provided assistance during the experiment. Carlo Meneghini, Università di Roma 3, assisted with data elaboration.

## References

1. Podda F, Zuddas P, Minacci A, Pepi M, Baldi F (2000). *Appl. Environm. Microbiol.*, 66, 5092-5098.
2. Reeder R J, Lamble GM, Northrup PA (1999). *American Mineralogist*, 84, 1049-1060.

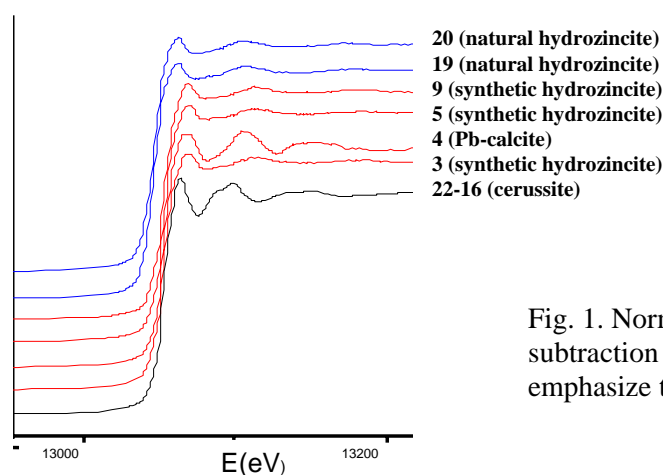


Fig. 1. Normalized spectra, after pre-edge subtraction (only a portion is shown, to emphasize the XANES part)

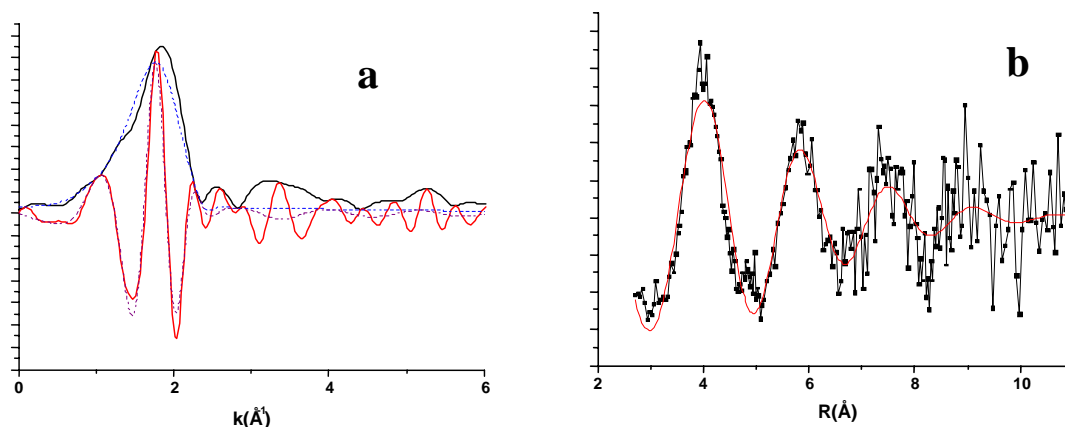


Fig. 2. Fits (in red and blue) in K (a) and R (b) spaces of experimental data (in black) for sample 9