

**Experiment title:**

Structural state of "heavy metals" (Cd, Cu, Pb) in hydrozincite

Experiment**number:**

08-02-636

Beamline: BM-08	Date of experiment: from: 02.09.2006 to: 04.09.2006	Date of report: <i>Received at ESRF:</i>
Shifts:	Local contact(s): Marco Merlini	

Names and affiliations of applicants (* indicates experimentalists):***Pierfranco Lattanzi, Università di Cagliari****Giovanni B. De Giudici, Università di Cagliari****Francesca Podda, Università di Cagliari*****Carlo Meneghini, Università Roma 3****Francesco Di Benedetto, Università di Firenze****Report:****Introduction**

The purpose of the experiment was to refine, through synchrotron-based X-ray powder diffraction, the structural position of "heavy metals" (Cd, Cu, Pb) in natural and synthetic hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, complementing previous XAS data (see Reports of experiments 08-01-659 and ME-1126). Pure synthetic hydrozincite was included in the sample set as a reference material. The following Table lists the material used in this experiment.

Sample number	Type of sample	Pb/Cd/Cu content (mg/kg) in the sample
Synthetic		
Pb-3	Pb-bearing hydrozincite, hot synthesis	14800
Pb-5	Pb-bearing hydrozincite, cold synthesis	4070
Pb-9	Pb-bearing hydrozincite, hot synthesis	1950
Cd-10	Cd-bearing hydrozincite, hot synthesis	261
Cd-12	Cd-bearing hydrozincite, hot synthesis	20000
13 Hyd-Hot	Pure hydrozincite, hot synthesis	-
14 Hyd-Ree	Pure hydrozincite, cold synthesis	-
Cu-1	Cu-bearing hydrozincite, hot synthesis	480
Cu-2	Cu-bearing hydrozincite, hot synthesis	10410
Cu-3	Cu-bearing hydrozincite, cold synthesis	356
Naturali		
Nat-INGOM	Natural hydrozincite from Naracauli, Sardinia	3800 / 630 / 120
Nat-INGON20	same	6500 / 540 / 260
Nat-NR2	same	1650/640/150
Nat-ING4	same	3700 / 750 / 100
Nat-18	same	2600 / 850 / 60

Hot synthesis according to Garcia Clavel et al., Thermochim. Acta 1989; cold synthesis according to Paquette & Reeder, Geochim. Cosmochim. Acta 1995

Experiment

Samples were prepared as powders deposited on Millipore membranes sealed within Kapton tape. Angle dispersed 2D X-ray powder diffraction data were collected using a monochromatic radiation of energy 15.5 KeV and the Imaging Plate (IP) detector. Set-up calibration (beam energy, sample to IP distance, etc...) was accomplished refining diffraction pattern of a LaB₆ standard. For sample Cd-12, having the highest Cd content, an anomalous diffraction experiment was done, collecting XRD patterns near the Cd K edge at the energies 26.713 KeV (near) and 26.300 KeV (far).

Results

All patterns show well defined peaks corresponding to those of hydrozincite. No additional phase was evident in any of the spectra. Cell parameters were determined by Rietveld full pattern refinement analysis (GSAS package), and the results are resumed in the table below:

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	volume(Å ³)
Pb_3	13,7607	6,33529	5,39245	90	96,20	90	467,358
Pb_5	13,8264	6,34729	5,39529	90	96,13	90	470,786
Pb_9	13,6801	6,34988	5,37175	90	95,17	90	464,733
Cd_10	13,7180	6,33961	5,38619	90	96,13	90	465,745
Cd_12	13,7130	6,34009	5,38294	90	96,08	90	465,370
HYD_13	13,6242	6,33844	5,37336	90	95,18	90	462,130
HYD_14	13,7914	6,34445	5,37827	90	95,98	90	468,026
Cu_1	13,6796	6,35597	5,36974	90	95,44	90	464,783
Cu_2	13,6826	6,36404	5,36746	90	95,12	90	465,512
Cu_3	13,7300	6,34326	5,37168	90	95,39	90	465,764
Nat-Ingom	13,8769	6,34091	5,39589	90	96,37	90	471,865
Nat-Ingon20	13,8163	6,33183	5,37687	90	96,10	90	467,717
Nat-NR2	13,8568	6,33822	5,38843	90	96,49	90	470,221
Nat-Ing4	13,9577	6,34905	5,40394	90	96,75	90	475,573
Nat_18	13,9783	6,34317	5,40048	90	96,89	90	475,387

It appears that the metal content has little influence on cell parameters, whereas samples synthesized at room temperature and all natural samples have much larger values of *a*, and consequently of volume, than samples synthesized at high temperature. Rietveld refinement has evidenced some discrepancies between our diffraction patterns, including the two of pure hydrozincite, and the structure of “standard” hydrozincite as reported in literature (Ghose, Acta Cryst. 1964): there are systematic peak shift and intensity discrepancies. This probably reflects the well known fact that hydrozincite structure may vary largely depending on stacking defects. On the other hand, the literature on hydrozincite shows a quite broad dispersion of lattice parameters, occupancies and ion positions. The difficulties on Rietveld refinement prevent obtaining reliable results on host ion site occupancies even in the case of Cu, that is known from literature to occupy the Zn sites.

Anomalous diffraction at the Cd K edge showed no meaningful residue; this means that Cd is not regularly hosted in a long range ordered (crystallographic) environment.

We can combine these XRD results with previously acquired XAS data (exp. N. 08-01-659 and ME-1126) to confirm that: Cd is present in hydrozincite as surface (inner-sphere) adsorbate, or as an amorphous surface precipitate; Pb is present both as a surface adsorbate, and as a surface precipitate with a local environment similar to cerussite, that however does not form a separate, X-ray recognizable, phase.

Data elaboration is in progress in combination with previously acquired evidence from EPR spectra.