

**Experiment title:**

Refinement of the crystal structure of hydrozincite with respect to the incorporation of cadmium

Experiment**number:**

CH-2898

Beamline: ID-31	Date of experiment: from: 15.05.2009 to: 19.05.2009	Date of report: 22.06.2010
Shifts: 12	Local contact(s): Irene Margiolaki	<i>Received at ESRF:</i>
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Report:**Introduction**

The experiment is a continuation of a study of structural state of “heavy metals” in hydrozincite, $Zn_5(CO_3)_2(OH)_6$, previously carried out by XAS and XRD experiments at the BM-08 line ([1,2]). Specifically, the main objectives were 1) a confirmation/amendment of the published reference structure of hydrozincite; 2) a systematic definition of stacking sequence varieties, and their dependence from formation /synthesis conditions; 3) an unambiguous definition of the structural state of Cd in synthetic and natural hydrozincites. The results confirmed structural complexities of these material, so that a full refinement is still under way. Preliminary results are reported here.

Experimental

Having been allocated 12 shifts, during which all components worked properly, we were able to run more samples than expected in the proposal. Specifically, we collected the spectra of four natural hydrozincites from supergene zinc deposits (D), five natural bioprecipitated hydrozincites from Naracauli, Sardinia (N), and 25 synthetic “hydrozincites” (S) prepared with two different synthesis methods (“hot” H, and “cold” C – see [1,2] for details), with variable amount of Cd (~0-59% wt.) in the starting bulk composition. As detailed below, several S samples contain otavite ($CdCO_3$) in addition to hydrozincite, and two contain only otavite. Samples were measured in standard capillary sample holders at room temperature. Monochromatic x-ray wavelength ($\lambda=0.4 \text{ \AA}$) was calibrated using c-Si reference powders (NIST). Diffraction patterns were refined using GSAS package.

Results

All patterns show well defined peaks corresponding to those of hydrozincite and/or otavite. Specifically, the two phases coexist for bulk Cd contents of ~ 5-20% wt., whereas for Cd > 35% only otavite was found. No additional phase was evident in any of the spectra. Cell parameters calculations gave the following results:

	<i>type</i>	<i>phase</i>	<i>Cd</i> (<i>bulk</i>)	a_o	b_o	c_o	β	<i>V</i>
Eve2	D	h	n.a.	13,5801	6,32124	5,40143	95,4672	461,565
Malfi_Fi	D	h	n.a.	13,5639	6,30383	5,40251	95,6425	459,701
Saduc	D	h	74	13,5785	6,31193	5,40463	95,628	460,977
Malfi Ca	D	h	116	13,6323	6,30420	5,39918	95,5411	461,841
n2	N	h	547	13,8218	6,34940	5,38218	95,7593	469,958
n10	N	h	561	13,8319	6,35013	5,38414	95,8175	470,475
n11	N	h	636	13,8371	6,34409	5,38628	95,9245	470,303
n12	N	h	647	13,8342	6,34188	5,38627	95,9967	469,976
n13	N	h	811	13,8332	6,33895	5,36746	96,0548	469,371
s10	SH	h	261	13,6923	6,35074	5,38771	95,0534	466,676
s13	SH	h	~0	13,6871	6,35261	5,38742	94,9432	466,686
s14	SC	h	~0	13,6680	6,36203	5,37713	94,5193	466,120
s15	SH	h	38800	13,7369	6,37438	5,38896	94,9826	470,096
s16	SH	h+o	76700	13,7239	6,36751	5,39011	94,8921	469,309
s17	SH	h+o	131600	13,7246	6,36704	5,38951	95,0772	469,113
S18	SH	o	348900	-	-	-	-	-
S19	SH	o	587000	-	-	-	-	-
s20	SC	h	2087	13,6992	6,36391	5,37494	94,4670	467,166
s21	SC	h	1041	13,6765	6,36177	5,37653	94,3087	466,473
s22	SH	h	~0	13,7150	6,35509	5,38795	95,1284	467,734
s23	SC	h	~0	13,7145	6,37181	5,37335	94,5209	468,096
s25	SC	h	18971	13,7223	6,35913	5,38441	94,6260	468,323
s26	SC	h	29719	13,7435	6,35797	5,37872	94,6752	468,431
s27	SC	h+o	55589	13,7580	6,35623	5,38792	94,9023	469,444
s28	SC	h+o	192966	13,7875	6,36006	5,41130	94,2795	473,191
s29	SC	h	2000	13,7844	6,36786	5,37730	94,9866	470,219
s30	SC	h	1400	13,7783	6,36293	5,37615	95,0476	469,499
s31	SC	h	1880	13,7658	6,35949	5,37745	95,0627	468,925
s33	SC	h	19700	13,8089	6,36649	5,38306	95,2786	471,241
s34	SC	h+o	77400	13,8603	6,35229	5,38786	96,2492	471,552
s35	SH	h	10400	13,7496	6,36401	5,39207	95,2052	469,874
s36	SH	h	5090	13,7476	6,35916	5,39183	95,3315	469,330
s37	SH	h	2260	13,7299	6,36010	5,39027	95,1115	468,825

D = hydrozincite from mineral deposits; N = hydrozincite from Naracauli; SH = “hot” synthetic hydrozincite; SC = cold” synthetic hydrozincite; h = hydrozincite, o = otavite
Cd contents in mg/kg; a , b and c in Å; β in degrees; volume in Å³

It appears that the metal content has little influence on cell parameters. Samples from mineral deposits have comparatively smaller values of a , b , and V , and slightly larger values of c , than all other samples. These samples show the best fit to published structures for this phase [3,4,5]. Naracauli samples show consistently high values of a . The absence of any correlation between Cd content and cell parameters is in full agreement with the previous conclusion [2] that this metal is not hosted in the hydrozincite structure. Except for mineral deposit samples, all other patterns cannot be simply fit to the published hydrozincite structures; a full refinement is therefore a complex task, and it is still under way.

[1] – Lattanzi P. et al., J. Hazardous Mater. 177, 1138 (2010)

[2] – Lattanzi P. et al., Eur. J. Mineral., in press

[3] – Ghose S., Acta Cryst. 17, 1051 (1964)

[4] - Jambor J.L., Pouliot G., Can. Mineral. 8, 385 (1965)

[5] – Effenberger H., Pertlik F., Osterreich. Akad. Wiss. Math. Natur. Kl. Anzeiger 122, 9 (1985)