



Experiment title:
LEAD WHITE RECIPES REVEALED BY
SYNCHROTRON X-RAY POWDER DIFFRACTION

**Experiment
number:**
CH 1728

Beamline: ID31	Date of experiment: from: 19/11/2003 at 8:00 to: 24/11/2003 at 8:00	Date of report: 01/02/06 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): François FAUTH	

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(all experimentalists)

Report:

The mineral composition of lead white is generally considered to be hydrocerussite $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ but our analyses of Ancient cosmetics have shown that it could also be a mixture of hydrocerussite and cerussite, or only cerussite PbCO_3 . Following the different recipes of synthesis, various mixtures can be obtained. We have studied various samples to better understand the chemical conditions of hydrocerussite synthesis in various contexts: (1) From make-up containers of the Hellenistic period (museum of Volos and Thessaloniki in Greece) between 400 and 200 B.C. (2) From artificially produced hydrocerussite, for comparison with the above-mentioned archaeological specimens. (3) From the Isenheim Altarpiece, which was painted by Matthias Grunewald (ca. 1513-1515), Museum of Colmar (France) (4) From the palette of Théodore Rousseau, one of the painters of the School of Barbizon (ca. 1850-1860).

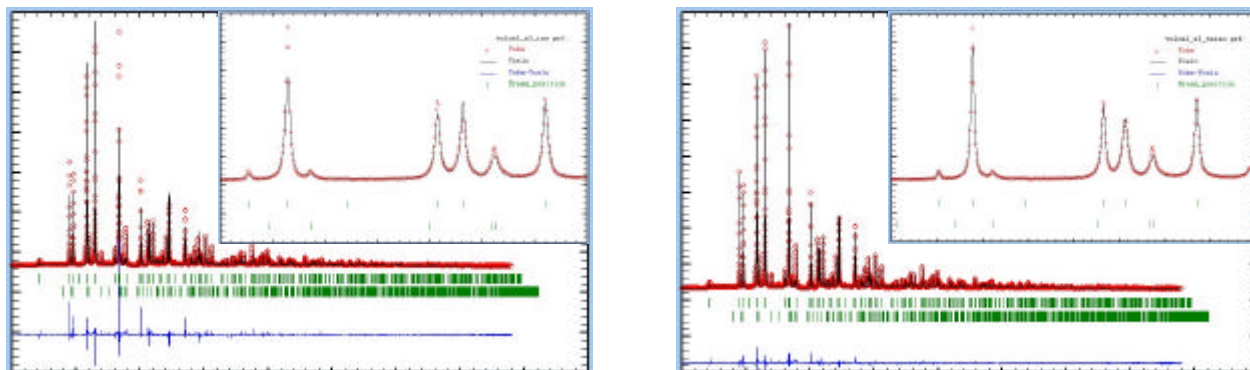
- Experimental method:

The different powders were analysed in 0.3mm glass capillaries, in the high-resolution mode at the wavelength: $\lambda=0.04$ nm. The 300 μm -thick slices of paints of the 16th and 19th centuries were analysed in transmission mode. Thanks to the quality of patterns collected at ID31, the refinement of structure of the synthetic hydrocerussite and the Rietveld quantitative and microstructural analysis of archaeological samples have been realised.

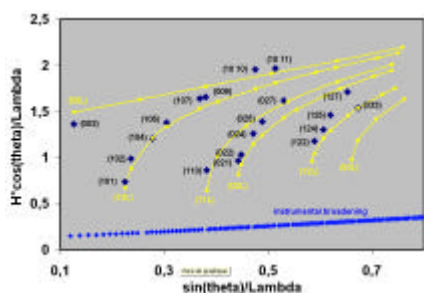
- **Quantitative powder diffraction** is now possible since the structural model of hydrocerussite has been recently elucidated by our group [1]. The atomic arrangement is closely related to the structures of other lead hydroxide carbonates. The hydrocerussite structure can be viewed as a sequence of two types of layers stacked along [001]. Layer A is composed of Pb and CO_3 , and layer B is composed of disordered Pb and OH. The stacking sequence is BAABAA. The quantitative analysis is required to compare ancient pigments, i.e. Greco-roman cosmetics between us and with modern powders synthesised in the lab according to the ancient recipes. Results on archaeological samples have revealed that the ratio of the two lead carbonate phases can be very different depending on the sample [2,3]. In some cases, the cerussite is present as the major phase.

- **The microstructural aspect (strain and crystallite size)** must to be considered too. We aim at correlating the microstructure of the mineral with the chemical condition of the wet synthesis (method, pH and carbonate concentration of the solution). These conditions affect the microstructure of hydrocerussite, and was studied through the X-ray line breadths. The peak breadth variation on the Williamson-Hall plot has shown the presence of significant

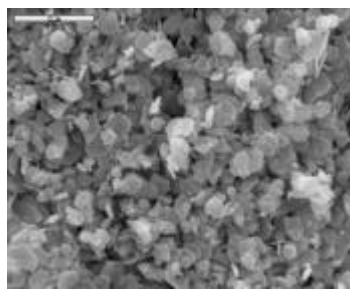
strain with a large anisotropy as a function of (hkl) in an ancient Greek cosmetic powder. We have considered a size anisotropy correction in the Rietveld refinement for archaeological lead samples containing mainly hydrocerussite. In this way, it has been possible to correlate these results with scanning electron microscopy observations. The visualisation of calculated shape of crystallites is possible using the software GFourier.



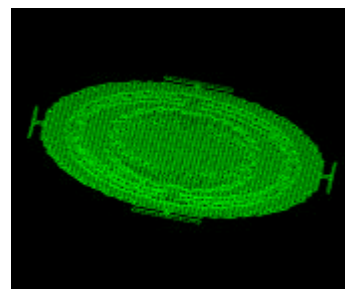
Rietveld refinement of an archaeological lead white using model from synthetic hydrocerussite: (left) without size anisotropy correction, $R_p=7.77$, $R_{wp}=10.4$, $R_{exp}=3.46$, $\chi^2=8.95$; (right) with size anisotropy correction, $R_p=5.75$, $R_{wp}=7.34$, $R_{exp}=3.48$, $\chi^2=4.45$.



A



B



C

(A) Platelet-like size effect : $HL \cdot \cos(q) = Y + e \cos(f)$ where $f = [hkl]^2/[001]$, Average apparent size = 500 \AA along $\langle 001 \rangle$, aspect ratio ~ 2 ; (B) Observations by SEM of a synthetic hydrocerussite sample; (C) Visualisation using the software GFourier of the calculated shape of crystallites

Bibliography :

- [1] MARTINETTO P., ANNE M., DOORYHEE E., WALTER P., TSOUCARIS G. (2002) – Synthetic hydrocerussite by powder X-ray Diffraction. *Acta Crystallographica* C58, 83-83.
- [2] WELCOMME E., WALTER Ph., VAN ELSLANDE E., TSOUCARIS G., (2006) – Investigation on white pigments used as make-up during the Greco-Roman period. To release in *Applied Physics A – Materials Science & Processing*.
- [3] E. DOORYHÉE, MARTINETTO, PH. WALTER AND M. ANNE (2004) - Synchrotron X-ray analyses in art and archaeology. Radiation Physics and Chemistry. Special issue: 9th International Symposium on Radiation Physics (ISRP-9) - Edited by M.J. Cooper and D.C. Creagh 71, pp. 863-868.

Communications :

- * Matériaux du Patrimoine et synchrotron SOLEIL – Colloque “Imagerie Synchrotron SOLEIL, Orsay, 26-28 novembre 2003. P. Walter
- * Identification of the painting techniques in Northern Europe at the beginning of the Renaissance by Synchrotron microimaging, Ph. Walter, E. Welcomme, E. Laval, M. Menu, A. Principaud, E. Van Eslande, M. Cotte, F. Fauth, A. V. Sole, J. Susini, E. Dooryhee, J.L. Hodeau, P. Martinetto, M. Anne, Synchrotron Radiation in Art and Archaeology (SR2A-2005), ESRF-CNRS joint workshop, Grenoble, France, 9-11 Fév. 2005
- * Identification of paints pots by Synchrotron microanalysis - The example of Ancient cosmetics, E. Welcomme, J. Salomon, E. Van Eslande, Ph. Walter, M. Cotte, J. Susini, A. Simioniovici, P. Martinetto, E. Dooryhee, Synchrotron Radiation in Art and Archaeology (SR2A-2005), ESRF CNRS joint workshop, Grenoble, France, 9-11 Fév. 2005
- * Investigation on white pigments used as makeup during the Greco-roman period, E. Welcomme, Ph. Walter, E. Van Elslande, G. Tsoucaris, E-MRS Spring meeting, juin 2005, Strasbourg (France)
- * Powder Diffraction in Art and Archaeology – XX Congress of International Union of crystallography E. Dooryhée, P. Martinetto, M. Anne, J.-L. Hodeau, P. Walter, M. S. del Rio, juillet 2005, Florence (Italie).