Experimental report

29/03/2016

Proposal:	**5-24-565**	**Council:**	4/2015
Title:	Study of synthetic and biogenic Vaterite from low to high temperature		
Research area:	Chemistry		

This proposal is a new proposal

Main proposer:	**Davide LEVY**
Experimental team:	Michela BRUNELLI Davide LEVY
Local contacts:	Emmanuelle SUARD

Samples: CaCO3 vaterite

Instrument	Requested days	Allocated days	From	To
D2B	3	3	10/11/2015	13/11/2015

Abstract:

Calcium carbonate is a material largely diffuse in nature as geological mineral and as biological phase. Despite the minor stability, vaterite is the principal polymorph in the biological systems. The hexagonal structure of vaterite is reported to have the CO32- disordered on three sites around the three-fold axis. From an unpublished thermal expansion experiment on biogenic and synthetic vaterite samples, we have noticed that: (1) The thermal expansions are different in the two sample; (2) it is possible to highlight a change in the slope of the thermal expansions curves of the two samples at about 150°C; (3) the thermal expansion is anisotropic.
We propose to collect neutron powder diffraction patterns on synthetic and biogenic vaterite from in the between 150-525 K in order to study different features of vaterite: (1) Accurate determination to the atomic positions; (2) super-structure determination (3) study of the thermal expansion of vaterite on an extended temperature range; (4) determination of the thermal ellipses of the oxygen atoms to understand their role in the thermal expansion anisotropy; (5) understanding difference between synthetic and biogenic vaterite.

Experimental report: Study of synthetic and biogenic Vaterite from low to high temperature

Introduction and aims

Calcium carbonate, $CaCO_3$, in its three polymorphic modifications calcite, aragonite and vaterite, represents one of the most important inorganic materials with respect to the global carbon cycle: it is noteworthy that calcium carbonate is probably the most important sink for the immobilization of CO, during the generation of the present atmosphere. Of the three modifications, calcite is thermodynamically the most stable, followed by aragonite and then vaterite, which is the least stable. Despite the minor stability, vaterite is the principal polymorph in the biological systems. The structure of the vaterite is based on a close packing of Ca^{2+} ions bonded by the CO_3^{2-} molecules. Differently to the calcite structure where the CO_3^{2-} molecule are perpendicular to the stacking vector, in the vaterite the CO_3^{2-} groups are parallel to the stacking vector. While a disordered structure of vaterite was proposed long time ago by Kamhi (*1*), different ordered structures were proposed by different authors (*2*) in recent times. The best structure that fit the X-ray diffraction data is the triclinic structure proposed da Mugnaioli et al. (*3*), but the very low symmetry and the very big cell do not allow a fine refinement of the structure. Moreover, a new study shows that there is a difference between natural and synthetic vaterite (*4*). Another important issue about the vaterite is its transformation in calcite as it is fundamental to understand why the biological systems prefer crystallize the calcium carbonate in one polymorph in respect the other. This transformation begins at relatively low temperature (225-250°C). The structural features of this transformation have not been studied yet.

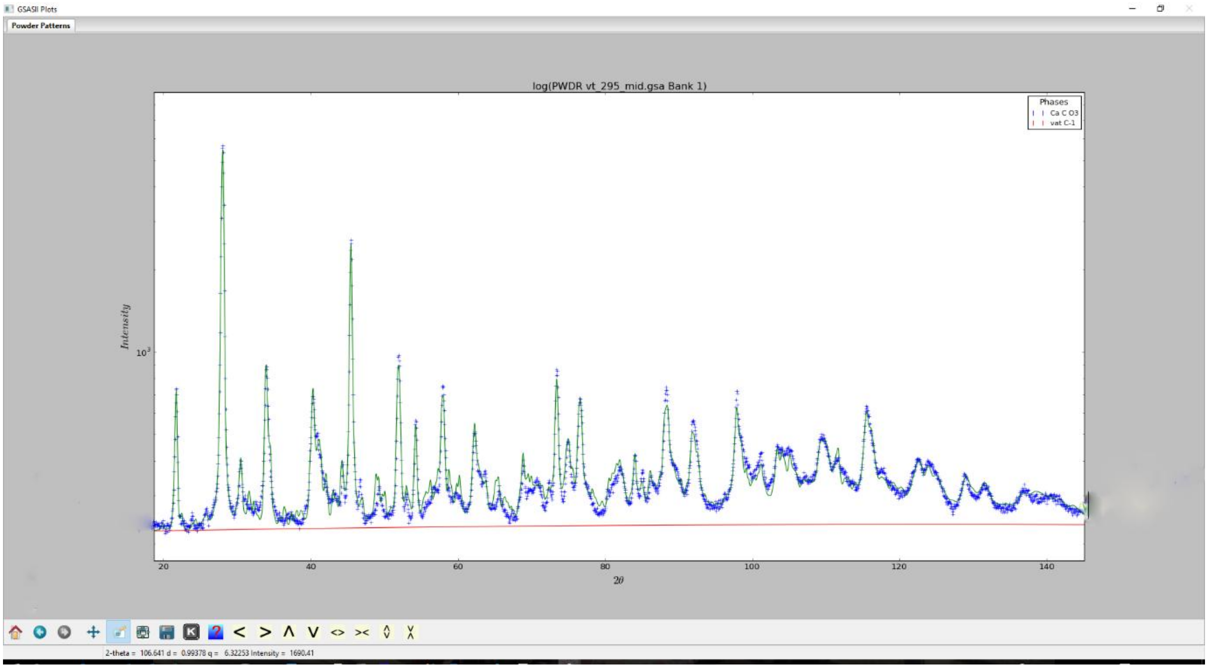
In this experiment a neutron powder study has been performed on a synthetic sample of vaterite from low temperature (120 K) to high temperature (540 K) in order to obtain:

1) an accurate determination to the atomic positions as Ca, C, and O atoms have similar scattering length (4.70, 6.64, 5.80 fm respectively)
2) an accurate study of the thermal expansion of vaterite on an extended temperature range together with a study of the evolution of the thermal vibration ellipses of the oxygen atoms in order to understand their role in the thermal expansion anisotropy of vaterite

The experiment was conducted at the D2B diffractometer, at a wavelength λ= 1.594 Å, using medium resolution in order to optimize data collection time and obtain an optimized resolution considering the not good crystallinity of the sample, which naturally limited the reciprocal space resolution of the diffraction patterns. Sample was loaded in a Vanadium can and then placed into a standard ILL orange cryostat. Data were collected at 14 different temperatures, from 120 to 540 K, for about 4 hours each temperature. The 2D data were treated with the standard procedure using Lamp in order to obtain 1D diffractograms at different temperatures.

Rietveld refinements (using GSAS-II, *(5)*) were performed on the collected data using the different structures reported in letterature. As the main difference between of these structures is the orientation of the CO_3^{2-} around the staking vector, the final refinament agreement factors are reported to be good for refinements performed using x-ray data. On the opposite, neutron diffraction is sensitive to the position of carbon and oxygen atoms and so the refinement results with these same structures are quite poor . The only structure that gives an adequate result is the triclinic structure (wR=6.55%, GoF=4). Moreover, the observation of the experimental and calculate diffractograms show mismatch in the peak intensities (see figure below). Attepts to obtain a better fit were unsucccesfull because the symmetry is very low and there are 46 indipendent atoms in the unit cell and – as a consequence – the refinement is instable. With this triclinic structure is not possible to obtain any accettable information of the structure.

At present, we are trying to find a relativelly simple structure that fit well the experimental data in order to extract structural information and in particular the thermal vibration ellypsoids.



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2-theta = 106.641 d = 0.99378 q = 6.32253 Intensity = 1690.41
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2. R. Demichelis, P. Raiteri, J. D. Gale, R. Dovesi, The Multiple Structures of Vaterite. *Crystal Growth & Design* **13**, 2247-2251 (2013).
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