ESRF	**Experiment title:** **Thermal Behaviour of Natural Zeolites from Mt. Adamson (Antarctica)**	**Experiment number**: 08-02-267
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Report:

Introduction

The goals of this work was to undertake the thermal behaviour of two rare natural zeolite form Mt. Adamson (Antarctica): tschernichite, firstly described by Boggs et al. [1] and more recently by Alberti et al. [2] is the natural counterpart of synthetic zeolite beta [3,4]; boggsite, a high-silica zeolite with the first three-dimensional channel system bounded by both 12- and 10-rings [5].

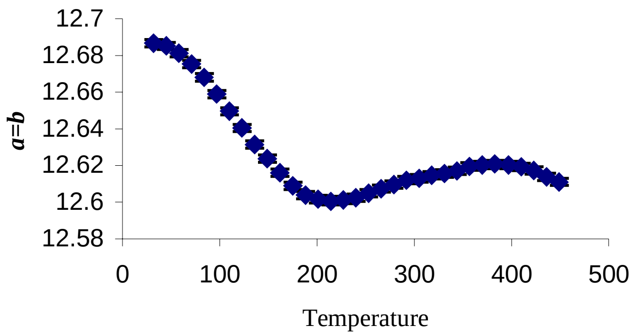
Experimental

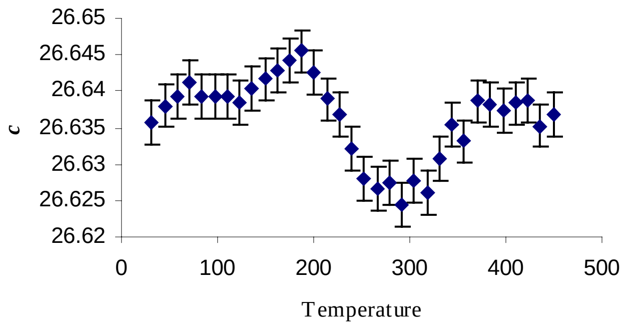
Temperature resolved powder data were collected at GILDA beamline using a Debye-Scherrer geometry with an angle dispersed set up based on a 2D Imaging Plate (IP) detector (200X400mm^2). The powder samples were packed in a 0.3 mm capillary open at both ends and heated in situ up to 1000 °C with a heating rate of 4.7°C/min using a hot air stream controlled by an Eurotherm controller. During the heating process the two dimensional diffraction patterns were recorded on the 4mm slit-delimited portion of the translating IP. The capillary containing the samples powder were mounted horizontally on a goniometer head and rotated during acquisition in order to improve the grain statistics. The incident beam wavelength was chosen equal to 0.72932 and the IP detector was positioned perpendicular to the sample at a distance of 205 mm from it. The powder diffraction patterns were extracted from the two dimension image integrating on strips corresponding to 10°C with an integration step of 20°C using the program FIT2D. The extracted patterns were analysed using Rietveld structure refinement approach as implemented in the GSAS package [6]

Results

Tschernichite: it is know that zeolite beta as well as its natural counterpart tschenichite is a highly intergrown hybrid of distinct, but closely related structures. According to Newsam et al. [3], zeolite beta can be described as a disordered sequence of only two polytypes, one tetragonal with symmetry $P4_122$ (or $P4_322$) and a=b≈12.5 Å and c≈26.4 Å (polytype A), the other monoclinic with symmetry *C*2/*c* and *a*≈*b*≈12.5x √2 Å, *c*≈14.4 Å and β≈114° (polytype B). According to Higgins et al. [4], a third polytype is present in zeolite beta with monoclinic symmetry, space group *P*2 (actually *P*2/*c*), with *a*≈*b*≈12.5 Å, c≈27.6 Å and β≈107° (polytype C). According to this the diffraction pattern of zeolite beta is characterized by a set of sharp reflections at *h* = 3n and *k* = 3n, and a set of diffuse maxima for *h* ≠ 3n and *k* ≠ 3n, frequently superimposed to continuous streaks parallel to **c***.

The structure description reported so far suggests that the refinement of the tschernichite structure using powder diffraction data is very hard; for this reason here we report only the variation of the unit cell parameters. The diffraction patterns showed that there was no evidence for a lowering of symmetry or phase transition as a consequence of the thermal treatment. The crystallographic structure of the polytype A[3,4] of zeolite beta was adopted as starting structural model for cell refinement.





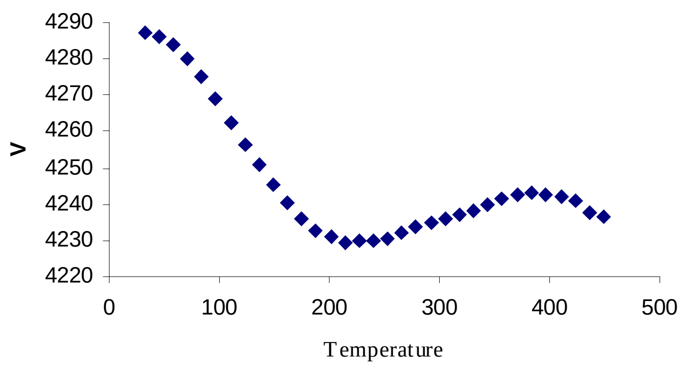
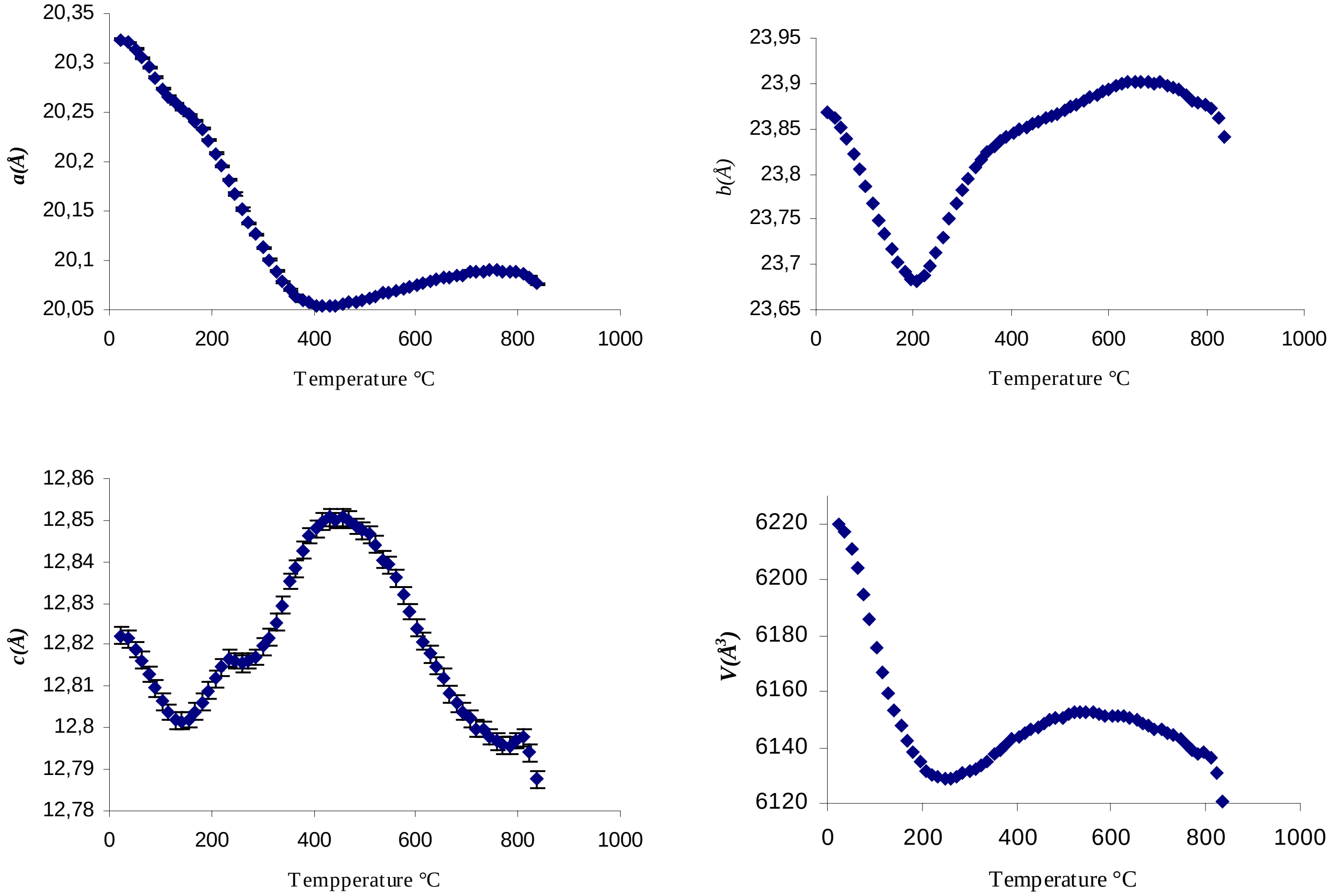


Figure 1. Cell parameters of thernichite *vs.* temperature; the “negative thermal expansion” is evident.

The decreasing of the cell parameters *a*, *b* and volume contraction are due to the rapidly flow of the water molecules from the zeolite channel and the subsequent readjustment of the extraframework cations. The complete removal of the water occurred at about 200÷250 °C; after that, an increase of the cell parameters (see figure 1) was observed. The thermal stability of zeolite tschernichite is very low, in fact the collapse of the structure occurred at 450°C.

Boggsite: also for boggsite the diffraction patterns showed that there was no evidence for a lowering of symmetry or phase transition as a consequence of the thermal treatment. The orthorhombic structure model proposed by Pluth and Smith [5] was adopted as starting structural model for the refinement of the unit cell parameters.



In figure 2 has been reported the variation of the cell parameters, it is important to note the very similar pattern of cell volume of boggsite and tschernichite.

The considerable contraction of all cell parameters between 0 and ~200°Cis clearly related to the main water loss of the system. After the removal of water, the decrease of the cell parameter *a* continued, whereas *b and c* (and volume) increased. It is interesting to note that after 500°C *c* cell parameter (and volume) decreased once more. Detailed structure refinement is in progress to clarify this pattern. The collapse of the structure appeared at about 800°C.

References

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