| | **Experiment title:** **Structural transformations induced by high pressure in the natural zeolites scolecite and heulandite** | **Experiment number**: CH-831 |
|---|---|---|
| **Beamline**: ID09 | **Date of experiment**: from: 06/02/2000     to:      10/02/2000 | **Date of report**: 1/08/2000 |
| **Shifts:** 12 | **Local contact(s)**: Davide Levy | *Received at ESRF:* |

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**Report:**

Zeolites are framework aluminosilicates, whose structure is characterised by cavities and channels, where exchangeable cations and water molecules are hosted. These structural features are responsible of the wide industrial applications of zeolites as catalysts and selective absorbers. The literature on the effect of pressure on zeolites is very poor [1,2,3] and few quantitative information on the structure and cell parameters of the possible pressure induced polymorphic phases are reported. The aim of this study is the investigation of the pressure induced structural modification in scolecite and heulandite.

The diffraction experiments have been performed at ID09 beamline, at the fixed wavelength of 0.4103 Å. High pressure structures have been obtained placing the powdered zeolite samples in a Diamond Anvil Cell, using silicon oil as non penetrating pressure medium [1]. Data collection has been performed from 0 to 10 GPa and some pressure points have been collected decompressing the samples. The pressure calibration has been performed by the ruby-fluorescence method [4]. The diffractograms, obtained by the integration of the image plate images, using FIT2D software [5] have been employed for the determination of the cell parameters  using GSAS package [6].

The refinement of the cell parameters of <u>scolecite</u> was carried out up to 7.5 GPa, since above this pressure the diffraction patterns exhibit large peaks and intense background due to the X-ray amorphous phase coexisting with the crystalline one. In the range  0-2 GPa, the contraction of the unit cell parameters (Fig. 1) is quite uniform, while in the range 2-9.6 GPa *a* and *b* cell edges reduce of 5% and 6% respectively, while *c* reduces of 1%. In the studied  pressure range a volume contraction of 14% is observable; an increase in the slope of  the linear pressure-volume dependence is observable at about 6.5 GPa, suggesting an increase of the compressibility with  pressure. This anomalous behaviour has been recently observed by Miletich [7] in gillespite-type phases. The compression process appears to be essentially irreversible. The structure of

scolecite under different pressure conditions has been simulated by means of Density Functional pseudopotential calculations, relaxing all the atomic positions by the Car-Parrinello method [8]. Both the results of the calculations and the experimental cell parameter values, indicate that the HP-induced structural modifications in scolecite framework are interpretable on the basis of a rotation of the tetrahedral chains along their elongation axis and of the associated channel squashing, as observed during the dehydration process of fibrous zeolites [9,10]. Moreover, the results of the simulations show a significant deformation of the first coordination shell of the extra-framework cations, and well defined transformations in the hydrogen bonding configuration, induced by the channel squashing under pressure.

The study of <u>heulandite</u> revealed, up to 3 GPa, an uniform contraction of the unit cell parameters and a linear dependence of the volume with the external pressure is observable (Fig.2). At 3 GPa, *a* exhibits a relative contraction greater than that of *b* and *c*; above this pressure, the linear pressure-volume dependence changes in slope, suggesting a decrease of the structure compressibility. In the range of pressure considered (0-6.5 GPa), the compression process is essentially reversible. The cell parameter contraction percentages and the results obtained by Comodi et al. [11] on a heulandite single-crystal studied by HP-XRD, suggest that the HP-induced geometrical modifications of heulandite framework are significantly different from those undergone at high temperature [12]: in particular, the small relative contraction of *b* parameter observed under pressure is related to the permanence of the water molecules in the channels.
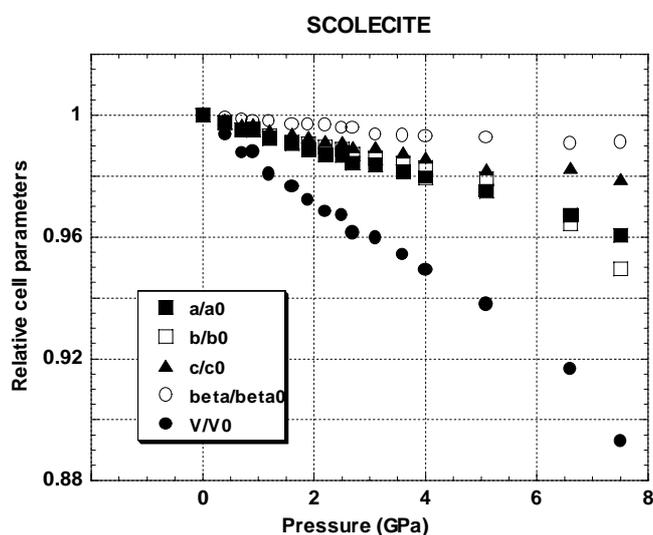


Fig. 1- Relative cell parameters of scolecite as a function of pressure.
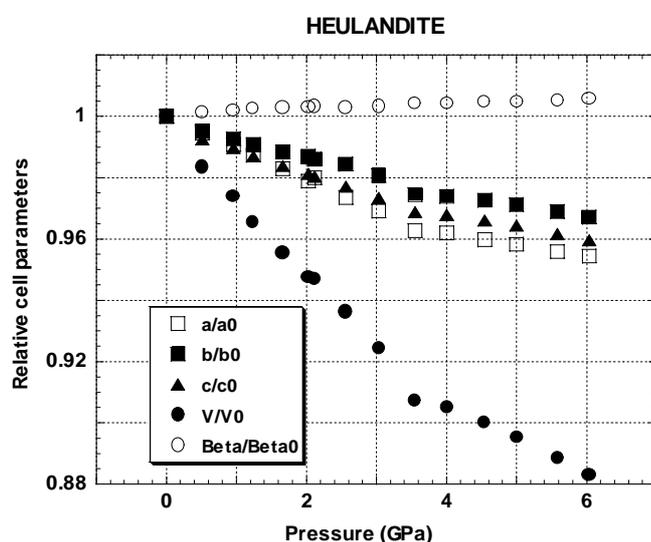
Fig. 2 - Relative cell parameters of heulandite as a function of pressure.

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