ESRF	**Experiment title:** **Single-crystal X-ray diffraction study of a new zeolite with ZSM5-type topology.**	**Experiment number:** **CH187**
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Report:

Recently, a new natural zeolite, named Mutinaite, has been recognized in the Jurassic Ferrar dolerites of Mt. Adamson, Antarctica. Chemical analysis yielded the following schematic formula: $Na_3Ca_4Al_{11}Si_{85}O_{192} \cdot 60H_2O$. The Si/AI ratio, equal to 7.7, is the highest up to now found in a natural zeolite. The water content was determined by TG analysis and the reversible dehydration was tested on the mineral up to 1100°C. The mineral quickly regained nearly 95% of its weight loss at temperature of up to 900°C; whereas its rehydration capacity became zero at 1100°C. A preliminary diffraction data collection was carried out on a Siemens four-circle diffractometer using a rotating anode generator. The very small dimensions of the crystal resulted in only 25% of observed reflections, a percentage inadeguate for an accettable crystal structure refinement. However, it was possible to verify that mutinaite has the same topology, and therefore is the natural counterpart, of synthetic zeolite ZSM-5[1,2], as was foreseeable from the cell parameters (a = 20.223(7), b = 20.052(8), c = 13.491(5) Å) and powder pattern. Systematic extinctions were consistent with the space group Pnma.

The synchrotron radiation experiments were performed on a single crystal of 0.03x0.03x0.015 mm^3 mounted on a Siemens diffractometer; wavelength 0.87 A, crystal-detector (CCD camera) distance of 300 mm, resolution $(sen\theta/\lambda)$ 0.76 $Å^{-1}$, exposure time 15 sec, scan axis ω, frame width 0.05. The cell parameters, determined by synchrotron X-ray powder diffraction and refined by Rietveld method are: *a* = 20.201(2), b = 19.991(2), c = 13.469(2).

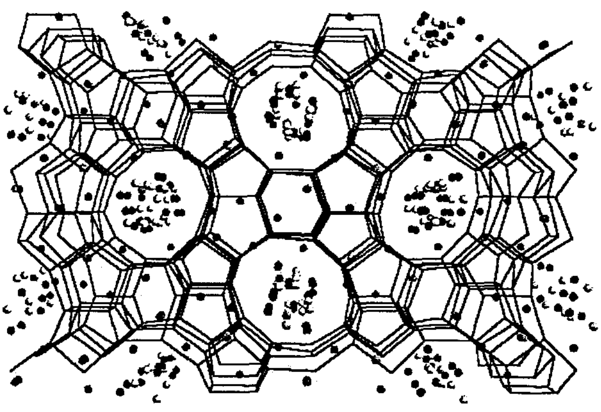
12692 intensities were collected in the θ range 5.1 - 71.5 and corrected for Lorentz-polarization and air absorption. The unique reflections were 6207 with an R_{int}=6.75. Of these, 3868 with 1 > 5σ (I) were used in the structure refinement. Least-squares refinement (SHELX-763) was carried out in the space group *Pnma*, starting from the positional parameters of the framework atoms of the synthetic zeolite ZSMS. Atomic scattering factors for neutral atoms were used for both framework and extra-framewok species.

As shown in Fig.1, the preliminary results of the structure refinement confirmed that the new natural zeolite mutinaite has the same topology of the synthetic ZSM5. The mean T-O tetrahedral distances are rather short with respect to the Al content of the zeolite, and do not give any clear indication of Si,Al ordering in the tetrahedral sites. Moreover, 17 extra-framework sites were localized, all with partial occupancy. They account only for 54% of the electrons obtained from the chemical analysis.

At present, the structure refinement with anisotropic framework gives R and Rw discrepancy factors of 10.90% and 9.6%, respectively. These rather high values and the low percentage of extra-framework electrons found from the structure refinement are not surprising results, since they are similar to those obtained for other new natural zeotites (gottardiited and terranovaite[5]) found in the same locality of Antarctica. These two zeolites are characterized by a strong extra-framework disorder, that precluded the unambigous chemical identifications of the channel sites during the structure determinations.

An accurate structural refinement of mutinaite, besides the interest given by the knowledge of the structure of a new zeolite, may potentially furnishes information useful to the comprehension of the characteristics of ZSMS not jet completely known.

Fig. l- Projection of mutinaite onto the ac plane



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