ESRF	Experiment title: Structure determination of M^+-Fe-silicalites ($M^+ = NH_4^+, Na^+, K^+, Cs^+$) by single crystal diffraction	Experiment number: CH-733
Beamline: BM1	Date of experiment: from: 17/09/1999 to: 21/09/1999	Date of report: 29/02/2000
Shifts: 12	Local contact(s): K. Knutsen	*Received at ESRF:*

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Report: Within the obtained beamtime, we were able to collect high quality data on Na^+-, K^+-, NH_4^+-Fe-silicalites with template at 120 and 300 K. The refinements of the Na^+-Fe-silicalite structure is now complete, and the main results can be summarized as follows:

(1) We have been able to locate the TPA template at the intersection of the straight and sinusoidal channels, in comparable positions with respect to those observed on ZSM-5 [1].

(2) A number of convincing indications on the possible substitution sites, *i.e.* the most challenging goal of our experiment, have been obtained: (i) The localization in the difference electron density maps of a relevant peak (2.28 e/Å^3 Figure 1) attributed to the extra-framework Na^+ counterion, implies that framework Fe^{III} species must be inserted in the adjacent T sites. Besides, a second smaller peak (0.67 e/Å^3 Figure 1) can also be interpreted as a less populated site (let refer to them as $Na1^+$ and $Na2^+$ respectively). When this information was introduced in the refinement, a significant improvement of the agreement factors was observed. It is worth pointing out that the total population of Na^+ cations was found to be of about 2.1 atoms per unit cell, a very reasonable value, slightly lower than the value of 2.5 indicated by elemental analysis. (ii) A significant lengthening of the T-O distances (Figure 2), with respect to ZSM-5 [1], is a second indication of the most probable substitution sites. (iii) The detection of an excess of electron density due to Fe^{III} substitution is problematic, because of its spread probably due to the slightly different location of Si and Fe in the tetrahedral sites. Nevertheless, it has been possible to localize some residual electron density on some of the T sites.

From these evidences we can derive the following conclusions: i) Site T9 is the most probable substitution site, because is located at 1.97(1)Å from the $Na1^+$ cation (Figure 1), and the lengthening of the T9-O distances is maximum; besides, a residual electron density of 0.34 e/Å^3 is present. Besides T9 shows the maximum anisotropy in the thermal displacement parameters. ii) Site T10 is the second most probable substitution site, because is at 1.92(5)Å from $Na2^+$ and at 2.64(1)Å from $Na1^+$ and shows a less marked but significant lengthening of the T10-O distances; besides, the residual electron density at the site is of 0.19 e/Å^3. All other T sites are far away from $Na1^+$ and $Na2^+$ and the lengthening of the T-O distances is less significant [$\Delta d < 3\sigma(d)$]. A small degree of substitution at some of these sites is not detectable, but can not be excluded. In particular the relatively large Δd value and the residual electron density of 0.28 e/Å^3 at T3 may suggest this site as a possible substitution site. Some degree of random substitution is suggested by the positive Δd value found for all T sites. The here summarized results have been recently submitted for publication [2], while preliminary results on the K^+- and NH_4^+-Fe-silicalites confirm the results obtained for the sodium form. Acknowledge are due to K. Knutsen and H.P. Weber, for the constant technical support during data collection and analysis.

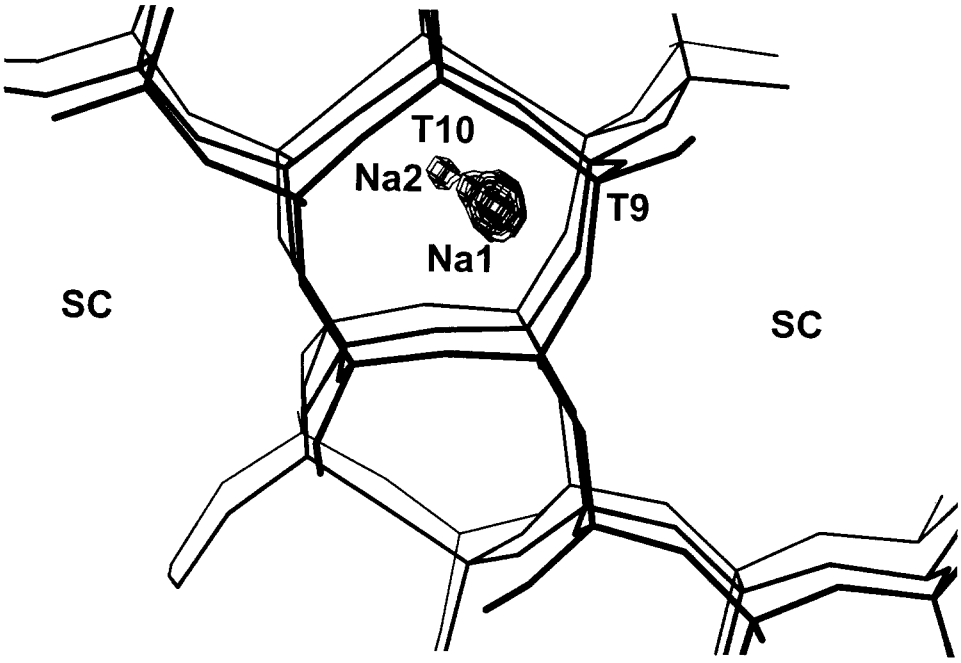

Figure 1 – Maxima in the difference electron density map corresponding to the two positions of the counterions, $Na1^+$ and $Na2^+$. The framework skeleton around these peaks is also shown. SC indicates the straight channels almost normal to the projection plane.

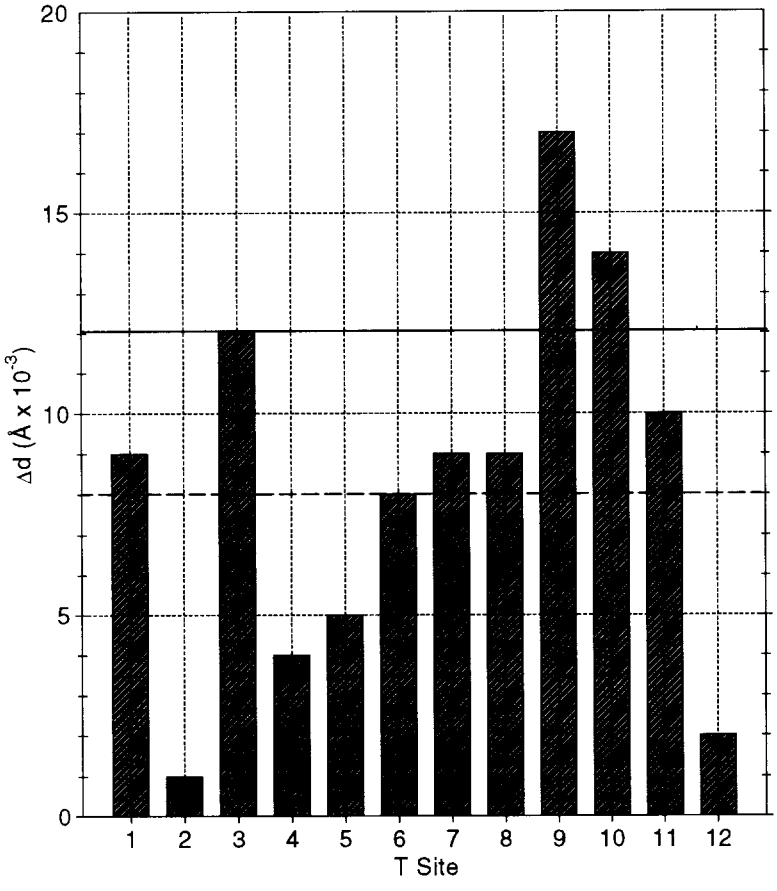

Figure 2 – Differences Δd between the average T-O distances found in the present Fe-silicalite and the corresponding average distances in ZSM-5 [1], for the 12 independent T sites. Dotted and continuous horizontal lines represent $2\sigma(d)$ and $3\sigma(d)$ values respectively.

References

[1] H. Van Koningsveld, H. Van Bekkum, J.C. Jansen, *Acta Cryst.* **1987**, *B34* , 127-132

[2] M.Milanesio, C.Lamberti, R.Aiello, F.Testa, M.Piana, D.Viterbo, *Angew. Chem. Int. Engl. Ed.*, submitted