by hydrothermal synthesis starting from a reaction mixture of silica, boric acid, water, and pyridinedimine as the template. After heating the mixture at 200°C for two months clear colorless crystals of nonasil(pyrr) were obtained. 3595 intensities (Mo Kα, 2θmax. = 60°) of a single crystal of nonasil(pyrr) were collected using omega scan mode on a Syntax R3 diffractometer (Rint = 0.031). 1697 reflections having 1>3σ were used for the refinement procedure with the XLS system.

The structure refinement (R = 0.092, Rw = 0.068) revealed that nonasil(pyrr) possesses the space group Cmca which is a subgroup of Pnma. 7 symmetrically inequivalent silicon and 14 inequivalent oxygen positions are present in the structure.

Silica and pyridinedimine are corner-linked via common oxygen bridges and form a 3-dimensional silica framework. The framework consists of three different types of cages: the [546]- and the [458]-cages which are too small to house guest molecules and the [5612]-cages which contain the pyridinedimine molecules.

The silica framework of nonasil(pyrr) shows unusually short Si-O distances and high Si-O-Si angles which are associated with unusually large temperature factors of the oxygen atoms. The mean values of δ(Oi-Oj) and δ(Oj-O-Si) (Table 1) differ considerably from those of the dense silica polymorphs δ(Oi-Oj) = 1.608 Å, δ(Oj-O-Si) = 144° but are compatible with the values of other clathrasil structures like
dodcasil 3C
(δ(Oi-Oj) = 1.586 Å, δ(Oj-O-Si) = 174.5°),
dodcasil HP
(δ(Oi-Oj) = 1.556 Å, δ(Oj-O-Si) = 170.4°),
and melanochlore
(δ(Oi-Oj) = 1.576 Å, δ(Oj-O-Si) = 168.8°). These unusual values are interpreted as due to static or dynamic disorder.

Table 1: Selected distances and angles of nonasil(pyrr).

<table>
<thead>
<tr>
<th>Distance or angle</th>
<th>range of values</th>
<th>mean values</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ(Oi-Oj)</td>
<td>1.554(8) - 1.625(9) Å</td>
<td>1.579 Å</td>
</tr>
<tr>
<td>δ(Oj-O-Si)</td>
<td>141.9(6) - 171.9(5)°</td>
<td>159.9°</td>
</tr>
</tbody>
</table>

Difference Fourier syntheses showed that the guest molecules are positioned disorderly. Therefore, the guest molecules were simulated by carbon and nitrogen atoms located in six different positions. The coordinates of these positions were obtained from the highest maxima of the difference syntheses.

A detailed analysis of the disorder of the framework atoms and guest molecules is in progress.

**PS-09 02.13 STRUCTURAL REFINEMENTS OF CATION-EXCHANGED GEMLINITES.**
By M. Sacerdote(1), L. Passaggia(2) & R. Carnevali (2). (1) Istituto di Mineralogia, Università di Ferrara, Italy; (2) Istituto di Mineralogia, Università di Modena, Italy.

The prevailing exchangeable cation in the natural gemlinites (hexagonal zeolite) is normally Na, but also Ca and K. To point out the crystallographic variations induced by the exchangeable cations, three natural samples have been exchanged with Na, K and Ca, and the structures of the corresponding forms have been refined. The crystals before X-ray data collection were tested by electron microprobe analysis in order to ascertain the exchange degrees. The exchanged forms show quite different unit cell dimensions with a and c parameter values inversely correlated with each other.

The structural refinements show that the cell dimensions depend on the type of cation in C1 site, located in the gemline cubic cage just outside the double 6-ring. The occupancy of this site by the different exchangeable cations (Na, K, Ca) noticeably modifies the diameters of the 6-ring channel (normal to c) as defined by the following O1-O1 (in direction) and O3-O3 (in a direction) distances:

- d(O1-O1) = 5.76 Å
- d(O3-O3) = 3.11 Å
- d(C1-C1) = 5.65 Å
- d(O1-O3) = 3.79 Å

The C2 site in the main 12-ring channel parallel to c is partially occupied only in the monovalent cations (Na, K) exchanged forms.

**PS-09 02.14 THE ANALYSIS OF THE PATHWAYS FOR SOME MOLECULES IN PENTASIL CHANNELS.**
By L. M. Voronina, 1. A. Zastourskaya, Department of Chemistry, Moscow State University, 119899, Moscow, Russia.

The structure of empty (not filled by van der Waals spheres) space in pentasil 2SM-5 was investigated (L. A. Zastourskaya, L. M. Voronina. Vestn. Mosk. Univ., Ser. 2, Khim., 1999, 31, N5, 454(457)). It was found that particles can move most
freely through the straight channels, the diameter of which is in the range from 2.64 to 3.30 Å. In this work the calculations, which allow to geometrically estimate the possibility of the location and movement of the molecules of xylene isomers and benzene in straight channels in zeolite ZSM-5 were carried out. We used the scanning method in 3 rotational and 3 translational degrees of freedom. All the distances between the atoms in a molecule and the surrounding atoms of the crystal were calculated for each scanning point and were compared with the normal van der Waals contacts. It was assumed that a molecule may be located in the scanning point if considerably shortened intermolecular contacts are absent. The calculation showed, that any of the considered molecules can be placed in a straight channel. However, only benzene and p-xylene molecules can move through such channel, because the overlapping of their van der Waals spheres with those of the channel atoms is acceptable (less 0.35 Å). The identity of the results obtained for the molecules of benzene and p-xylene indicates that the presence of substituent in para-position does not obstruct the movement of the molecule through the channel. Such calculations permit to estimate the geometry of available space.

08-03.02a STUDY ON HOKUTOLITE SYNTHESIS AND ITS CRYSTALLOGRAPHIC ANALYSIS. Shu-Cheng Yu and Jian-Shing Lee, Department of Earth Sciences, National Cheng-Kung University, Tainan, Taiwan

Hokutolite is a mineral of hot spring deposit and considered to be a solid solution of barite (BaSO₄) and anglesite (PbSO₄). Natural occurrences of hokutolite reported in literature include Hokuto, Japan and Shikokure near Akita, Japan. The chemical composition of hokutolite from Taiwan was found to be from 21 mol% PbSO₄ to 32 mol% PbSO₄.

Synthetic hokutolite samples with different chemical composition were grown in the present study with the starting materials of solutions of Pb(NO₃)₂, Ba(NO₃)₂ and (NH₄)₂CO₃. Two different growth processes were carried out at 95-100°C and ambient pressure conditions, with growth time of 3-4 days.

Optical microscopy and X-ray diffraction analysis suggest that the growth process significantly affects the crystallinity, growth rate and crystal size of the synthetic hokutolite. With two different growth processes, one process produced the sample with 59-71 mol% PbSO₄, and the other 73-80 mol% PbSO₄, with their corresponding average crystal size being less than 0.5 um and greater than 0.5 um, respectively. Extinction anomaly observed in optical microscopy study suggests that the grown materials may exhibit chemical/structural domain in the hokutolite crystal lattice.

08-03.02b THE X-RAY STUDY OF Fe₂I ORE MINERALS FROM THE PACIFIC OCEAN. By M.T. Dmitrieva, Institute of oree deposits. geology, mineralogy, petrology and geochemistry. Russian Acad. Sci., Moscow.

The samples of natural Fe₂I oxide minerals from different types or oceanic basaltb have been studied by X-ray and electron microprobe analyses. It is estimated that the dominating