# Final project report

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| *Project ID* | **2004/4.07** |
| *Title* | Pentasil zeolites from Mt. Adamson: natural analogues of heterogeneous catalysts and of matrices for nanomaterials confinement. |
| *Principal investigator* | M. Giovanna Vezzalini |
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| *Duration* | 3 years |
| *Assigned funding* | 100.000,00 Euro |

## Activities and results

The knowledge of the behavior of zeolites under high temperature and pressure is essential due to the impact of these thermodynamic parameters on their structure, stability and on their applications. Results of the project:

1. thermal stability and dehydration mechanism of the new Antarctic zeolites Boggsite, Tschernichite and Gottardiite.
2. elastic properties, compressibility and stability of zeolites with framework-type MFI.

1. a) The dehydration-rehydration process of Boggsite has been studied through single-crystal X-ray diffraction. Boggsite has provided an extremely rigid structure whose cell volume contraction is less than 1.4%. The dehydration process is rapid and completely reversible. The high-temperature structure is capable to hold Ca in fourfold coordination, a feature commonly reported as leading to structure collapse.

   b) Tschernichite is the natural aluminum-rich analog of zeolite beta, one of the most important acid catalysts. Tschernichite and zeolite beta have a disordered structure consisting of two polytypes with monoclinic and tetragonal symmetry, respectively. The dehydration process of the monoclinic polytype was studied by single-crystal X-ray diffraction. The variation of the unit-cell volume was less than 1.3%. At 250 °C all $H_2O$ is lost. The structural collapse occurs below 350 °C. The combination of a large frequency of silanols, associated with the stacking faults, together with the high Ca content, probably explains the relatively low temperature of the structural collapse.

   c) The thermally induced structural modifications of the natural zeolite gottardiite were studied in the temperature range 308–1203 K in a temperature-resolved X-ray powder diffraction experiment, using synchrotron radiation. Gottardiite shows a high thermal stability, as a consequence of the high Si content, and an extremely rigid structure with a substantial absence of cell volume change. The main water loss is observed in the temperature range 580–779 K. At 978 K some water molecules even remain.

   **2.** In the H*P* studies performed on zeolites, either "pore penetrating" (usually aqueous-alcohol mixtures-m.e.w.) or "non-penetrating" *P*-transmitting media (usually silicon oil-s.o.- or glycerol) are used. The penetrating media are involved in the so-called pressure-induced hydration phenomenon, characterized by the penetration of additional water molecules into the porosity. We studied, using both *P*-transmitting media, the elastic behavior of MFI zeolites with different Si/Al ratio and extraframework content: mutinaite, Na-ZSM-5, H-ZSM-5 and two silicalite samples with Si/Al ratio of 1200 and 1800. In all these phases no phase transitions are observed and the unit cell parameters of $P_{amb}$ are recovered upon decompression. In Na-ZSM-5 and H-ZSM-5 compressed in m.e.w. a strong over-hydration effect is observed with the penetration of 11 and 16 additional water molecules, respectively. Both phases show a compressibility higher in s.o. than in m.e.w. as a consequence of the penetration of water molecules which contributes to stiffen the structure. In s.o. the highest compressibility is observed in the silicalite samples, a result consistent with the lack of extraframework species, while mutinaite –with a high cation and water amount in the porosity-

resulted the less compressible phase. These results well agree with what found in other zeolite species for which a "template" effect of extraframework species is proposed.

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## Products

**A – papers in scientific magazines**

1. ZANARDI S., CRUCIANI G., ALBERTI A., GALLI E. (2004) Dehydration and rehydration process in boggsite: An in situ X-ray single-crystal study. AMERICAN MINERALOGIST, 89, 1033-1042.
2. ALBERTI A., CRUCIANI G., GALLI E., MILLINI R., ZANARDI S. (2007) In situ X-ray single-crystal study on the dehydration mechanism in the monoclinic polytype of tschernichite, the mineral analog of zeolite beta. JOURNAL OF PHYSICAL CHEMISTRY C, 111, 4503-4511.
3. ORI S., VEZZALINI G., GALLI E. (2009) Thermal induced structural modifications of the high silica zeolite Gottardiite: An in-situ XRPD study. Microporous Mesoporous Materials, 126, 171-181.
4. ARLETTI R., VEZZALINI G., DI RENZO F., DMITRIEV V., QUARTIERI S. (2010) Elastic behaviour of MFI-type zeolites: 1- Pressure induced over-hydration of Na-ZSM-5. Microporous Mesoporous Materials (inviato per la stampa)
5. MONTAGNA G., VEZZALINI G., ARLETTI R., DI RENZO F. AND QUARTIERI S. (2010) Elastic behaviour of MFI-type zeolites: II – Pressure-induced over-hydration of H-ZSM-5. Microporous Mesoporous Materials (inviato per la stampa)

**B – book chapters**

**C - proceedings of international conferences**

1. ZANARDI, S., CRUCIANI, G., ALBERTI, A., GALLI, E., VEZZALINI, G. (2004) Dehydration and rehydration process of zeolites boggsite and tschernichite from Antartica: a comparison. 32th International Geological Congress, Florence, Italy, August 20-28, 2004.
2. MONTAGNA G., ARLETTI R., VEZZALINI G., QUARTIERI S. (2008) HP-induced deformation effects in MFI-type zeolites. Oxide 2008, 6-11/07, Como, Oxide, Novelties and Prespectives, 2008, pag. 212.
3. QUARTIERI S., MONTAGNA G., ARLETTI R., VEZZALINI G. (2010) Elastic behaviour and HP-induced phase transitions in MFI-type zeolites. Meeting of the International Mineralogical Association, Budapest, August 2010.
4. MONTAGNA G., VEZZALINI G., QUARTIERI S., ARLETTI R., DI RENZO F. (2010) HP-induced deformations and phase transitions in MFI-type zeolites. International Zeolite Conference IZC2010, Sorrento, July 2010.

**D – proceedings of national meetings and conferences**

1. PARODI I., MARTUCCI A. (2006) The thermal behaviour of two polytypes of tschernichite: an "in situ" time resolved synchrotron powder diffraction study. AIZ Day and AIZ Workshop 2006.
2. PARODI I., MARTUCCI A., ALBERTI A., CRUCIANI G. (2007) Structural modifications induced by heating in tschernichite: an "in situ" single crystal and powder diffraction study. Geoitalia 2007.
3. MONTAGNA G., ARLETTI R., VEZZALINI G., QUARTIERI S. (2009) Different deformation effects at HP in MFI-type zeolites with unlike extraframework content, FIST 2009, 09-11/09/2009 Rimini.

**E – thematic maps**

**F – patents, prototypes and data bases**

**G – exhibits, organization of conferences, editing and similar**

**H - formation (PhD thesis, research fellowships, etc.)**

1. Cristina Betti - research fellowship. Title: Caratterizzazione strutturale di silicati porosi e di nanomateriali in essi confinati.
2. Rossella Arletti - research fellowship. Title: Host-guest interactions and P-induced phase transitions in nanoporous materials.
3. Silvia Ori- PhD thesis title: Structural modifications of zeolites at non ambient conditions.
4. Gabriele Montagna- PhD thesis title: Structural studies of synthetic alumino-boro-silicates with framework type ANA: possible traps for radioactive waste.

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## Research units

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