

Investigation of the silica network structure on micro- and nanocrystalline and amorphous samples

PHD THESES

Viktória Kovács Kis

Scientific supervisor: Dr István Dódy, assoc. prof.

PhD School of Earth Sciences, Leader: Dr Péter Márton, prof.

Geology and Geophysics Program, Leader: Dr Miklós Monostori, prof.



Eötvös Loránd University, Department of Mineralogy

Budapest, 2004.

1. Introduction and goals of the thesis

Oxygen and silicon are the two most common elements in the earth's crust, and their compound, SiO₂ or silica is a significant rock forming phase in crystalline and also in amorphous form. The common feature of the microcrystalline silica modifications is the abundance of structural faults such as dislocations, twin boundaries, stacking faults, grain boundaries and holes. Periodic stacking faults (twin boundaries) result polytypes (tridymite/cristobalite system) or new mineral species (quartz/moganite system). In moganite the d(101) thick lamellae of right and left handed quartz alternate periodically, and the lamellae are related by the Brazilian twin law. Individual crystallites of moganite are known from very few localities, but it is common in microcrystalline SiO₂ varieties. The amount of the structural faults in micro- and nanocrystalline materials is relatively high with respect to the faultless volume, which causes a considerable change in the material properties. The study of the nanostructures has become a hot topic of scientific investigation in the last decade.

From the geological point of view, it is useful to know the nano- and submicron structure of silica when reconstructing hydrothermal processes (Rodgers & Cressey 2001) and it provides new information about the metamorphic (Furuichi et al. 2003) and diagenetic transformation as well (Huang 2003). The structure of volcanic glasses reflects the melt structure: its study is essential for geophysics and volcanology, but archaeometry also makes use of it.

The goal of the present work was to examine the submicron structure of the silica framework in micro- and nanocrystalline, and amorphous geological samples. I studied the quartz-moganite structural relation in chert and chalcedony. Analyzing the product of the spherulitic devitrification of an obsidian, the cristobalite-tridymite structure type was investigated. I discussed the possibility of the insertion of tridymite/cristobalite type layers into smectite by studying the structure of chloropal. Finally I compared the short and intermediate range order of the three-dimensional silica network in pumice and obsidian.

2. Experimental methods

For my investigations I looked for samples from diverse geological environment with well known background. Some of my samples (Szalánc obsidian, Gönc chloropal, Tokaj pumice and Gyöngyössolymos chalcedony) form part of mineralogical/petrographical museum collections. The chert samples (Ördög-orom, Budapest, Hungary, Mátyáshegy Formation) the Bükkalja pumice sample (Harsány, Hungary, Galgavölgy Rhyolite Tuff Formation) and the Lipari obsidian were collected during field work.

During my work I used transmission electron microscopy. The real structure of micro(nano)crystalline varieties was studied by selected area electron diffraction and high resolution image analysis. The amorphous structure (volcanic glasses) was studied by electron diffraction as well. The diffraction patterns were recorded with Imaging Plates, whose high dynamic range (5-6 orders of magnitude) significantly facilitated the quantitative evaluation.

The phase composition of the samples was determined with X-ray powder diffraction, and the micromorphology was studied with scanning electron microscopy. The chemical composition was measured by a transmission electron microscope equipped with an energy dispersive spectrometer.

3. New scientific results

Regarding the submicron structure of the silica framework the following new observations were made based on the study of micro- and nanocrystalline silica and volcanic glasses with high silica content:

1. I described moganite from Hungary for the first time, it was found in the chert nodules of the carbonate rocks at Ördög-orom (Budapest). I showed that moganite, the quartz-moganite association and the {101} planar faults in quartz are more widespread than it was thought before: they are common components in equigranular chert and they also occur in obsidian. Their formation is not related to texture and non-equilibrium spiral growth, neither to the evaporitic origin. Beyond the results of Gíslason et al. (1997) I

demonstrated that samples younger than 100 Ma can also contain significant amounts of moganite.

2. I detected a difference between the degree of crystallinity of the white and dark chert nodules from the Mátyáshegy Formation. I stated that the $\{101\}$ planar faults in quartz and the moganite content is concentrated in the less crystalline silica. More generally I concluded that the frequency of moganite and the non-periodic plane faults in silica increases with the decreasing grain (domain) size, their occurrence is a specific feature of the micro(nano)crystalline state.
3. I detected two unknown quartz based superstructures from the dark chert nodules of the Mátyáshegy Formation. The discrepant symmetry from quartz and moganite is implied by the $2d(101)_{\text{quartz}}$ (6.68 Å) periodicity along $[101]^*$ and $[-111]^*$ of quartz in $[-1-21]$ projection and the $5d(032)_{\text{quartz}}$ (6.25 Å) periodicity parallel to $[032]^*$ of quartz in $[-1-23]$ projection. My observations may serve as the basis for a new quartz-based structure model.
4. I showed that chert consists of detached, ordered, 10-100 nm sized domains of quartz and moganite connected by coherent grain boundaries. Domains of moganite and quartz with randomly spaced $\{101\}$ plane faults are also separated. Based on this observation I pointed out that the electron diffraction patterns showing $\{101\}$ planar faults cannot be obviously evaluated as moganite.
5. Studying the products of the spherulitic devitrification of obsidian by electron diffraction I detected for the first time the coexistence of α - and β -modifications, ABCB tridymite interstratification and twinning in cristobalite.
6. With my coauthors I showed that chloropal is formed by the intimate intergrowth of ca. 10 nm sized domains of smectite and silica which can be modelled based on the idea of Edelman and Favejee (1940). If the tetrahedral layers are shifted by a $1/6 \mathbf{b}$ vector, a tridymite- or cristobalite-like layer forms between the octahedral layers of smectite. This arrangement makes possible the intercalation of further layers of tetrahedra into the structure and explains the oriented intergrowth of smectite and

tridymite/cristobalite. Between the silica layers twin planes can form, which manifests in the structural disorder parallel to the *c*-axis of chloropal.

7. I applied for the first time quantitative electron diffraction to study the structure of glasses of geological origin. I showed that by electron diffraction not only the primer precipitates but also the glassy matrix can be examined. My measurements support that the network structure of high silica containing volcanic glasses consists of corner-sharing Si(Al)O₄ tetrahedra. I demonstrated unambiguously that the bond distances above 3 Å measured by X-ray or neutron scattering carry information about the amorphous component (as well). I showed that the glassy matrix is composed of domains of higher and lower degrees of order. This observation proves the existence of the ordered and intracrystalline domains postulated by the modern crystallite theory of glass structure. The domain size is about 8-10 Å.

8. I showed that the structure of obsidian and pumice is different. Obsidian contains quartz crystals with {101} plane faults and slightly oriented, poorly crystalline quartz polycrystal in which crystallites are rotated around the [-1-21] axis. In pumice cristobalite polycrystal and tridymite/cristobalite type domains are present. Based on the ring diffraction patterns I concluded that these domains, which are fragments of the SiO₂ layer, form randomly oriented two-dimensional plates in the amorphous matrix. The first- and second-neighbour Si-Si(Al) distances measured in the amorphous matrix suggest that the quartz type and tridymite/cristobalite type arrangement develops already in the amorphous state. Randomly mixing silica units of obsidian can be derived from the spirals of tetrahedral chains that build up the quartz structure, while those of pumice are fragments of the tridymite/cristobalite structure. Thus, the structure of obsidian is more dense and compact, while the structure of pumice is more spacious and open.

4. Conclusions

At low pressure silica crystallizes in two configurations. Both configurations include two structures: at lower temperature the more compact quartz and moganite structure while at

higher temperature the spacious tridymite and cristobalite structure forms.

Recently the importance of moganite occurrences has grown from the petrogenetic and archaeometric points of view. Moganite content has been used for the profiling of hydrothermal silica sinters, and for the relative aging of agates samples. The moganite content of silica is basically defined by the crystallinity and the domain size. In case of impeded grain growth the relative amount of moganite can increase. Dissolution and recrystallization also influence the moganite content of the silica. These points must be taken into account when petrogenetic conclusions are drawn.

Low moganite content is hardly detected by X-ray diffraction. Electron diffraction is suitable for local examination of small amounts of moganite. When evaluating electron diffraction patterns showing diffuse scattering, special care must be taken because the {101} planar faults in quartz do not obviously mean moganite content.

Tridymite and cristobalite are built up of infinite layers of SiO₂. β-tridymite and β-cristobalite are hexagonal and cubic close packed, respectively. The continuous transition between them occurs through the insertion of twin planes. In chloropal, the SiO₂ layers are connected to the octahedral layers of smectite or to further layers of silica. Thus chloropal is composed of nanosized domains of smectite and silica. Between the SiO₂ layers, just like in cristobalite, stacking faults may form.

By electron diffraction, the quartz-like and the tridymite/cristobalite-like configuration can be distinguished in the amorphous structure as well. In pumice, the glass structure is a random mixture of the fragments of the tridymite/cristobalite type SiO₂ layer: two-dimensional plates consisting of 6-10 tetrahedra are mingled with smaller, tridymite/cristobalite-like units. The obsidian glass is built up by fragments of the spiral chains of quartz, which results shorter Si-Si distances and the absence of the two-dimensional units.

It is known that the structure of the aluminosilicate melt depends on the temperature and the structure of the quenched glass reflects the temperature at which it was frozen (Zotov et al. 1995). The study of the structure of obsidian and pumice shows that the glass structure is also significantly influenced by the volatile content at the time of quenching. If degassing occurs before the quench, the volatile-poor melt forms a compact glass structure built of quartz type units, i.e., obsidian. If a volatile-rich melt is frozen, a more spacious glass structure, pumice forms.

If the volatile content of the obsidian exceeds the mean (e.g. Lipari obsidian), the

dominant atomic distances imply the simultaneous occurrence of the two arrangements. In such cases the quartz-like and tridymite/cristobalite-like units may appear in the same rock as well. The intermediate structure, i.e., the higher volatile content of the Lipari obsidian, can be explained with a multi-phased or longer degassing process.

5. Publications

Papers:

Kovács Kis, V. & Dódonny, I. (2003): The mineralogical and crystal structural study of the chert. *Földtani Közlöny* **133/3**. 309-323. (in Hung.)

Kovács Kis, V. & Dódonny, I. (1999): Structural disorder in natural cubic HgS. *Acta Min. Petr.* **XL**. 3-10. (*)¹

Kovács Kis, V. & Dódonny, I. (2004): Mineralogical study of fibrous microcrystalline silica: chalcedony from Gyöngyössolymos, Northern Hungary. *Acta Min. Petr.* (accepted for publication)

Kovács Kis, V., Horvat, M. & Dódonny, I. (2004): Microstructures in two K-feldspar megacrysts from the Papuk Mountain, Croatia. *Geol. Croatica* (*) (accepted for publication)

Conference abstracts:

Dódonny, I., **Kovács Kis, V.** & Buseck, P.R. (2004): Microstructure of chert as shown by TEM. 22nd European Crystallographical Meeting, ECM22, Budapest. Hungary. *Acta Cryst.* **A60**. s195.

Kovács Kis, V., Dódonny, I. & Lábár, J.L. (2004): Electron diffraction study of natural rock glasses. 36th International School of Crystallography. 9-20 June, 2004 Erice, Italy.

Horvat, M., **Kovács Kis, V.** & Dódonny, I. (2002): Crystallization path of K-feldspar megacrysts from Mt. Papuk, Croatia. 17th CBGA Conference, Bratislava, Slovakia. *Geol. Carpath.* **53**. 189-190. (*)

Dódonny, I., Németh, T. & **Kovács Kis, V.** (2001): Crystal-chemical study of smectite-tridymite/cristobalite association in chloropal. Mid-European Clay Conference '01, Stará Lesná, Slovakia. Book of Abstracts. Stará Lesná, 33.

¹ publications marked with an asterisk (*) are mainly related to this work by the experimental method.

Kovács Kis, V. & Dódonny, I. (2000): What do we call chert? A mineralogical case study from Ördögörom, Budapest, Hungary. Minerals of the Carpathians, Miskolc. *Acta Min. Petr.* **XLI**. Suppl. 2000. p. 65.

Kovács Kis, V. & Dódonny, I. (1999): Structural disorder in natural cubic HgS. MinWien, Vienna, Austria. Berichte der Deutschen Mineralogischen Gesellschaft, *Beih. z. Eur. J. Mineral.* **11**. 135. (*)

Other lectures:

Kovács Kis, V. (2002): Investigating rock glasses. Questions and problems. (Petrological and Geochemical Seminar, ELTE, Budapest) (in Hung.)

Kovács Kis, V. & Dódonny, I (2000): Microstructure of non-fibrous microcrystalline silica. (invited lecture at 7*M Research Group, Arizona State University, US)

Kovács Kis, V. (2000): What do we call chert? A mineralogical case study from Ördögörom, Budapest, Hungary. (Young Scientist's Meeting, Debrecen) (in Hung.)

Kovács Kis, V. (2000): Silica minerals in chert. (Hungarian Technical and Scientific Association of Transylvania, Cluj-Napoca, Romania) (in Hung.)