MINERALOGICAL MAGAZINE, SEPTEMBER 1980, VOL. 43, PP. 879-83

# Incorporation of impurities in tridymites from a used silica brick

H. SCHNEIDER, K. WOHLLEBEN, AND A. MAJDIC

Forschungsinstitut der Feuerfest-Industrie, An der Elisabethkirche 27, 5300 Bonn 1, Germany (FRG)

SUMMARY. The incorporation of impurities in tridymites taken from a used silica brick have been studied by means of a high-resolution microprobe, X-ray fluorescence, X-ray diffractometry, and optical microscopy. The bulk impurity content of the brick changes strongly from the hot zone (4.7 wt%) to the colder part of the brick (7.6 wt%), indicating material transport along the temperature gradient. The transport medium for migration processes is probably a melt occurring in narrow veins between large tridymite crystals at high temperatures. The average impurity contents of homogeneous tridymite single crystals are 0.49 wt% in the hot zone of the brick and 0.81 wt% in the cold zone. $Al_2O_3$, $TiO_2$, and $Na_2O$ are main impurity constituents; the tridymites do not contain significant amounts of $Fe_2O_3$ or CaO. The *a* parameters of tridymites decrease by about 0.26% from 4.9837 Å to 4.9709 Å from the hot zone to the cold zone of the brick and the *c* dimension shows a smaller decrease (0.11%) from 8.2023 Å to 8.1933 Å.

THE structure of hexagonal high tridymite was first analysed by Gibbs (1927), who found the structure to be composed of six-membered rings of $SiO_4$ tetrahedra, stacked so that channels are formed along the *c* axis. Low tridymite has essentially the same structure as high tridymite. It was found that the $SiO_4$ tetrahedra sharing common corners in the Zweier-Einfach chains (single chains with a periodicity of two tetrahedra) form quasi-planar sheets of six-membered tetrahedral rings. At room temperature the symmetry is monoclinic or triclinic (Dollase and Baur, 1976; Kato and Nukui, 1976; Konnert and Appleman, 1975). An intermediate orthorhombic high-temperature phase of tridymite occurs at 220 °C (Dollase, 1967). The temperature of the displacive low-high transformation varies strongly from one tridymite specimen to another. This variation may reflect different stacking disordering of the six-membered tetrahedra sheets.

Fenner's (1913) classic paper on the stability relations of silica minerals had served as the basis for the discussion of $SiO_2$ polymorphism for a long time. High tridymite was considered to be thermodynamically stable between 870 and 1470 °C. Flörke (1955) attacked this concept and contributed some important theses to the 'tridymite problem'. Though they have been disputed by Hill and Roy (1958) these theses are now widely accepted. The most important points are:

1. It is not possible to synthesize pure two-layer ($h$ = hexagonal) tridymite. Natural and synthetic tridymite crystals always contain domains with three-layer ($k$ = cubic) cristobalite-type components. Therefore tridymite can be considered as being formed in any case from cristobalite nuclei.
2. Due to its $Si_2O_7$-group cis-arrangement, tridymite is less stable than cristobalite at any temperature. It is only formed when impurities are present.

Many attempts have been made to determine whether impurities substitute for $Si^{4+}$ ions or whether they are incorporated additively into the tridymite structure (Flörke, 1956; Rockett, 1963). There is strong evidence for additive cation incorporation, since the channels, as in other silicate structures, are wide enough (Briedl, unpublished) to enable the incorporation even of cations with relatively large ionic radii.

Previous studies on the incorporation of impurities in tridymites from industrially used silica bricks were carried out by Konopicky and Patzak (1962) and by Patzak and Konopicky (1962). These authors suggested that large quantities of impurities, especially Ca and Al, were incorporated into the tridymite structure. They believed that higher ion incorporation was related to zones of increased density in the silica bricks.

In order to get more information on the mineralogical processes in silica bricks, especially on mode and degree of impurity-ion incorporation, we reinvestigated this problem with X-ray diffraction methods and by different methods of chemical analysis. The problem seemed to us important not only from a crystallochemical point of view but also for technical purposes, since silica bricks are important refractory materials in glass tanks, coke ovens, and other high-temperature aggregates.

## *Experimental*

*Sample material.* All the samples come from a used, completely tridymitized silica brick (brick no. 4). The brick was taken from a boro-silicate glass tank and was cut into slices perpendicular to the temperature gradient. The thickness of these slices ranged between 22 and 30.5 mm, where zone 4/1 was taken from the hot zone of the brick and 4/5 from the cold zone.

*Microscopic studies.* In order to get information on the mineralogical composition and on the structure of the material, thin sections and polished sections of zones 4/1, 4/2, 4/3, and 4/5 were investigated with a polarizing microscope.

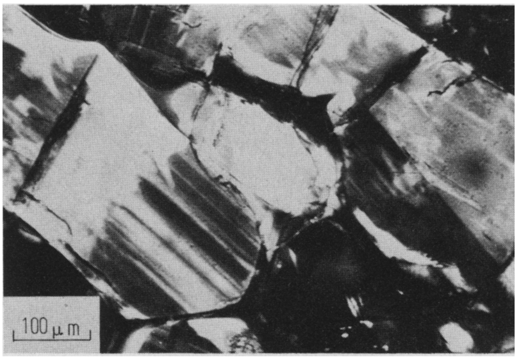
*X-ray diffractometry.* X-ray diffractograms were taken from fine-grained tridymite powders. X-ray runs were used for phase identification and for the determination of lattice parameters. Since the intensities of the X-ray reflections of tridymite rapidly decrease and simultaneously the widths of the diffraction peaks strongly increase with the diffraction angle ($2\theta$), only the strong and sharp 100 and 002* reflections were used for lattice parameter calculations. In order to obtain a maximum accuracy these reflections were scanned with low goniometer speed (1/4 and 1/8° $2\theta$/min.); chart speed was 5 and 10 mm/min. respectively. The X-ray runs were repeated six times. Pure quartz and corundum powders were used as internal standards (quartz: 100, $2\theta$ 20.88°; corundum: 012, $2\theta$ 25.58°). The error of the measurement was of the order of 0.001° $2\theta$.

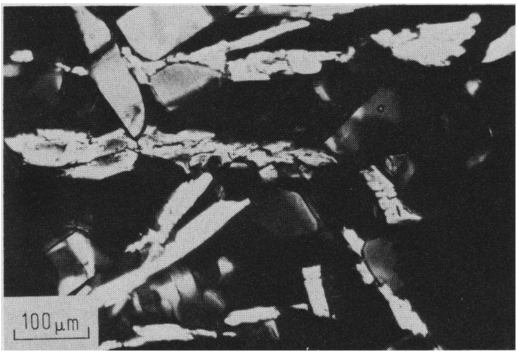
*Chemical analyses.* Bulk chemical analyses of the samples were performed with an X-ray fluorescence spectrometer. Point analyses and scanning photographs were carried out with a computer-controlled electron probe microanalyser. The resolution of adjacent analysis points was about 1–2 $\mu$m. The accuracy of analysis is estimated to be ±1% relative.

## *Results*

*Microscopic studies.* Microscopic studies or thin sections of silica brick zones 4/1, 4/2, 4/3, and 4/5 yielded some important interrelationships between the temperature gradient in the brick and the structure and mineralogical composition of the material.

Zone 4/1 is characterized by relatively large rounded tridymite crystals, frequently with intense and complex twinning (fig. 1). This type of tridymite crystal arrangement has been called 'paving structure' (Konopicky *et al.*, 1968). Zone 4/5 has a highly inhomogeneous structure, with tridymite crystals of strongly different grain sizes (fig. 2). Some tridymites show typical skeletal growth. Regions of fine-grained, elongated crystallites which show intensive intergrowth occur between larger tridymite single crystals. Many tridymites exhibit intense twinning, and typical wedge-shaped specimens are abundant. The development of tridymite crystals in zones 4/2 and 4/3 lies between those of zones 4/1 and 4/5.





FIGS. 1 and 2. FIG. 1 (*top*). Photomicrograph of silica brick zone 4/1 ('hot' zone). Crossed nicols. FIG. 2 (*bottom*). Photomicrograph of silica brick zone 4/5 ('cold' zone). Crossed nicols.

Along the temperature profile in the brick from zone 4/1 to zone 4/5 impurities are enriched considerably. Elongated colourless crystals of pseudo-wollastonite occur frequently between tridymite grains, often showing skeletal structure. Rutile is seldom found in the samples; it has a light brown colour and appears in the thin sections as small spherical grains. The amount of glass phase decreases with the temperature drop in the brick. It appears as thin yellow-brown veins between large tridymite crystals.

---

* The indices refer to a hexagonal unit cell.

TABLE I. *Lattice parameters of tridymites*

| Zone of the brick | *a* [Å] | *c* [Å] | V [Å$^3$] |
|---|---|---|---|
| (a) untreated | | | |
| 4/1 | 4.9837 | 8.2023 | 176.43 |
| 4/2 | 4.9764 | 8.1962 | 175.78 |
| 4/3 | 4.9754 | 8.1990 | 175.77 |
| 4/5 | 4.9709 | 8.1933 | 175.33 |
| (b) treated with $H_3PO_4$ | | | |
| 4/5 | 4.9758 | 8.2018 | 175.66 |

All calculations refer to a haxagonal unit cell of tridymite.

The silica brick is characterized by a high open porosity. The shape of the pores varies widely, from spherical to more elongated forms with strongly changing dimensions. The pores always have rounded contours. The pore volume varies from 9.23% at the hot side of the brick (zone 4/1), through 11.5% (zone 4/2) and 11.8% (zone 4/3), to 12.9% at the colder side (zone 4/5), involving a volume increase of about 40%. This is in contrast to results reported by Konopicky *et al.* (1968). The increase in porosity along the temperature gradient in the brick is accompanied by a slight bulk density decrease from 2.06 g/cm$^3$ (zone 4/1) to 1.99 g/cm$^3$ (zone 4/5), i.e. 3.4% (the density of pure tridymite is about 2.27 g/cm$^3$, Tröger, 1971). This is reasonable, taking into account that the heavy elements are more enriched in the colder zones than in the hot zones of the brick.

*Lattice parameters.* The lattice parameters of the tridymites from different zones of the silica brick are given in Table I. Though the measurement error is relatively large, some trends can clearly be observed. The *a* parameter decreases from the hot zone to the cold zone of the brick by about 0.26%, and the *c* dimension by 0.11%. The unit cell volume decreases from 176.43 to 175.33 Å$^3$. Treatment of sample 4/5 with hot phosphoric acid ($H_3PO_4$) makes the lattice of the 4/5 sample expand slightly.

*Chemical composition.* Table II gives bulk analyses of each zone of the brick. The untreated samples contain impurities ranging from 4.74 wt% (sample 4/1) to 7.58 wt% (sample 4/5). The removal of $Al_2O_3$, $TiO_2$, $Fe_2O_3$, CaO, and MgO from the hot zones and the addition of $Na_2O$ and $SiO_2$ into these zones can be observed. Similar results were reported by Konopicky *et al.* (1968). Phosphoric acid treatment, carried out on samples 4/3 and 4/5, showed that most of the impurities of the brick are leached during this procedure. Only $Al_2O_3$, $TiO_2$, and $Fe_2O_3$ are retained in larger quantities. This indicates that most of the impurities are contained in cristalline or glass phases occurring in channels between tridymite crystals. Investigations carried out with the electron microprobe suggest that tridymite does not incorporate as much impurities as was believed in the past (e.g. Patzak and Konopicky, 1962). Average analyses of 40 homogeneous tridymite single crystals from zones 4/1, 4/3, and 4/5 yielded impurity contents of 0.49, 0.73, and 0.81 wt% respectively (Table III). $Al_2O_3$, $TiO_2$, and $Na_2O$ are main impurities. The tridymites do not contain significant amounts of $Fe_2O_3$ or CaO (Table III, 25 analysis points). Point analyses of impurity phases occurring between homogeneous tridymite single crystals are given in Table IV. The analyses yielded inclusions of three chemically different types of chemical composition. The first group can clearly be assigned to pseudowollastonite, whereas the second and third groups may be associated with glass and/or crystalline phases not yet identified.

TABLE II. *Bulk chemical analyses of the silica brick*

| | 4/1 | | 4/2 | | 4/3 | | 4/5 | |
|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b |
| $SiO_2$ | 95.3 | — | 94.9 | — | 94.9 | 99.1 | 92.4 | 99.0 |
| $Al_2O_3$ | 0.66 | — | 0.79 | — | 0.70 | 0.40 | 0.83 | 0.43 |
| $TiO_2$ | 0.65 | — | 0.62 | — | 0.71 | 0.19 | 0.96 | 0.22 |
| $Fe_2O_3$ | 0.42 | — | 0.42 | — | 0.20 | 0.10 | 0.50 | 0.10 |
| CaO | 1.73 | — | 1.95 | — | 2.66 | 0.07 | 3.63 | 0.03 |
| MgO | 0.05 | — | 0.06 | — | 0.08 | — | 0.14 | — |
| $Na_2O$ | 1.00 | — | 1.00 | — | 0.50 | — | 0.50 | — |
| $K_2O$ | 0.11 | — | 0.10 | — | 0.10 | — | 0.10 | — |

a = untreated.
b = treated with phosphoric acid.

All analyses were performed with an X-ray fluorescence spectrometer.

TABLE III. *Electron microprobe analyses of tridymite from zones 4/1, 4/3, and 4/5*

| | 4/1 | 4/3 | 4/5 |
|---|---|---|---|
| $SiO_2$ | 99.5 | 99.3 | 99.2 |
| $Al_2O_3$ | 0.20 | 0.31 | 0.31 |
| $TiO_2$ | 0.14 | 0.22 | 0.23 |
| $Fe_2O_3$ | 0.02 | 0.04 | 0.07 |
| CaO | 0.008 | 0.01 | 0.02 |
| MgO | 0.007 | 0.004 | — |
| $Na_2O$ | 0.13 | 0.18 | 0.17 |
| $K_2O$ | 0.01 | 0.02 | 0.02 |
| $Cr_2O_3$ | 0.009 | 0.007 | 0.005 |
| $Mn_2O_3$ | 0.01 | 0.01 | 0.02 |

All analyses were performed with an electron microprobe analyser. Each analysis is the mean of fourteen (4/1 and 4/3) or twelve (4/5) point analyses.

## *Discussion*

The bulk chemical analyses show that the silica brick contains up to 8 wt % impurity oxides. There is strong evidence from this investigation, contradicting earlier suggestions of Patzak and Konopicky (1962), that only minor amounts of these impurity ions can be incorporated into the tridymite lattice. The major part is precipitated as pseudo-wollastonite, rutile, and a glass phase. In this context, it would be most profitable to reanalyse the high-impurity tridymites described by Lukesh and Buerger (1942), Buerger (1954), and Mason (1953) with a high-resolution microprobe. This would help to clarify whether tridymite is able to incorporate substantial amounts of impurities.

The amount of impurities in the silica brick clearly increases along the temperature gradient. At the same time, the amount of $SiO_2$ and alkali oxide increases from the colder parts to the hot zone of the brick (Tables II and III, see also Konopicky *et al.*, 1968), enabling the growth of large tridymite grains. One possible explanation is a countercurrent migration of material along the temperature gradient and strong sintering in the hot zone of the brick. The transport medium for migration processes may be melts occurring in narrow veins between large tridymite crystals at high temperatures. At room temperature these areas are present as a glass phase. Another explanation supposes a concentration of impurities in a low-viscosity liquid at the hot side of the brick and a subsequent separation of the liquid from the brick. Though there is more evidence for the first hypothesis, there may be a complex transport mechanism including both processes.

TABLE IV. *Electron microprobe analyses of inclusions from zones 4/1, 4/3, and 4/5*

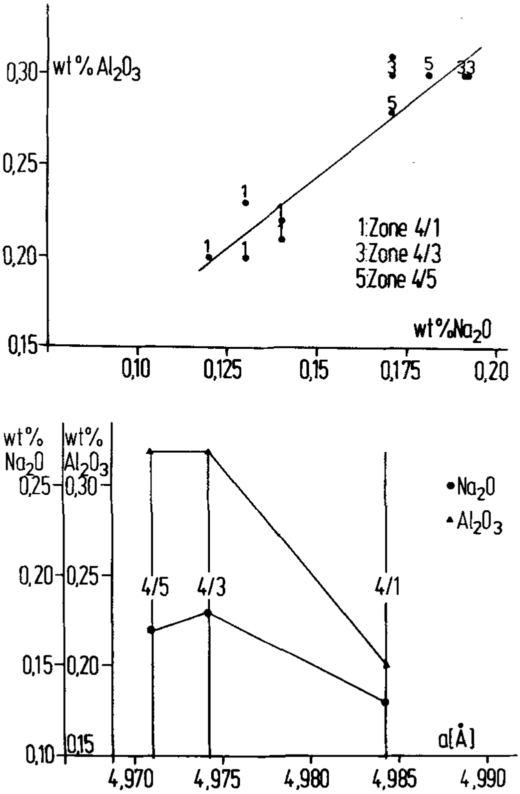
| | 4/1 | 4/3 | 4/5 |
|---|---|---|---|
| $SiO_2$ | 52.4 | 71.3 | 68.1 |
| $Al_2O_3$ | 0.03 | 3.3 | 3.2 |
| $TiO_2$ | 0.06 | 7.6 | 4.7 |
| $Fe_2O_3$ | 0.05 | 4.0 | 2.77 |
| CaO | 47.4 | 9.4 | 17.7 |
| MgO | 0.01 | 0.97 | 0.62 |
| $Na_2O$ | 0.05 | 1.97 | 2.22 |
| $K_2O$ | 0.02 | 1.11 | 0.65 |
| $Cr_2O_3$ | — | 0.06 | 0.08 |
| $Mn_2O_3$ | — | 0.21 | 0.08 |

Each analysis is the mean of at least eight point analyses.

The large number of microprobe point analyses proves that only $Al_2O_3$, $TiO_2$, and $Na_2O$ are enriched in the tridymite structure in important quantities. In contrast to findings of Patzak and Konopicky (1962), the amount of CaO in homogeneous single crystals is negligible.

According to the widely accepted theory of Flörke (1966, 1967) tridymite does not crystallize from pure $SiO_2$, but needs foreign cations for its stabilization. The reason for that is probably the unfavourable cis-configuration of $Si_2O_7$-groups in tridymite (e.g. Flörke, 1967). The concentration of the impurity cations (especially $Na^+$) is normally very low, i.e. 1 atom for 10 to 50 unit cells. According to Flörke the cations occupy indefinite positions within the wide structural channels in tridymite running parallel to the *c* axis. Charge equalization is achieved by electron disordering. Relationships are certainly different for tridymites from used silica bricks. These tridymites contain relatively large amounts of alkali, with $Na_2O$ in the order of 0.2 wt% (Table III). These high concentrations of $Na^+$ cannot be compensated by electron disordering. In this case, electric neutrality can be obtained by substitution of tetrahedral coordinated Si by Al atoms. The linear relationship between $Na_2O$ and $Al_2O_3$ content seems to support this hypothesis (fig. 3).

The incorporation of small impurity ions with high electric field strength into the structure channels causes a contraction of the tridymite structure (Schneider *et al.*, 1979). The reciprocal action of channel constituents with the tridymite lattice is stronger in the plane of the six-membered rings of tetrahedra lying perpendicular to the *c* axis than in the direction of the structure channels parallel to that axis. The lattice contraction may be reinforced by $Si^{4+}$ to $Al^{3+}$ substitution in tetrahedral sites. Lattice parameter determinations support



FIGS. 3 and 4. FIG. 3 (*top*). The relationship between the average contents of $Na_2O$ and $Al_2O_3$ incorporated in tridymite. FIG. 4 (*bottom*). The relationship between $Na_2O$ and $Al_2O_3$ contents of tridymite and the *a* lattice parameter.

these considerations. They show increasing lattice contraction with increasing $Na^+$ and $Al^{3+}$ incorporation (fig. 4), the contraction parallel to *a* being twice that parallel to *c*. The treatment of the tridymite samples with phosphoric acid makes the structure expand (Table I; see also Patzak and Konopicky, 1962). This is reasonable, since $H_3PO_4$ treatment dissolves the weakly bound $Na^+$ channel constituents which are responsible for lattice contraction. The $Al^{3+}$ and $Ti^{4+}$ ions are much more strongly bound in the tridymite structure and are less affected by the solution process (Table II).

The present studies do not take into account the influence of lattice disordering on the lattice spacings. Patzak and Konopicky (1972) give a reciprocal relationship between the degree of structural disordering and the lattice spacings of tridymite. Unfortunately, the actual chemical composition of these tridymites is not known. Furthermore, Patzak and Konopicky's definition of structural disorder in tridymite does not seem to be without problems. We plan to reinvestigate the interrelationship between impurity content, lattice disordering, and lattice spacings of tridymite with detailed X-ray single crystal and microprobe studies on crystals from different temperature zones in silica bricks.

*Acknowledgements.* We are indebted to Professor O. W. Flörke for critical reading of the manuscript and to Dr G. Oehlschlegel (both University of Bochum, Germany) for some suggestions.

## REFERENCES

Buerger (M. J.), 1954. *Am. Mineral.* **39,** 600–14.
Dollase (W. A.), 1967. *Acta Cryst.* **23,** 617–23.
——and Baur (W. H.), 1976. *Am. Mineral.* **61,** 971–8.
Fenner (C. N.), 1913. *Am. J. Sci.* **36,** 331–84.
Flörke (O. W.), 1955. *Ber. DKG,* **32,** 369–81.
——1956. *Naturwiss.* **43,** 419–20.
——1966. *Krist. u. Techn.* **1,** 405–10.
——1967. *Fortschr. Miner.* **44,** 181–230.
Gibbs (R. E.), 1927. *Proc. R. Soc. London,* **A 113,** 351–68.
Hill (V. G.) and Roy (R.), 1958. *Trans. Brit. Ceram. Soc.* **57,** 496–510.
Kato (K.) and Nakui (A.), 1976. *Acta Cryst.* **B 32,** 2486–91.
Konnert (J. H.) and Appleman (D. E.), 1975. *Geol. Soc. Am. Abstracts with Programs,* **7,** 1151.
Konopicky (K.) and Patzak (J.), 1962. *Sprechsaal,* **95,** 279–85.
——Lepère (K. E.), Routschka (G.), and Thoenes (H. W.), (1968). *Tonind. Ztg.* **92,** 41–50.
Lukesh (J.) and Buerger (M. J.), 1942. *Am. Mineral.* **27,** 143–4.
Mason (B.), 1953. Ibid. **38,** 866–7.
Patzak (J.) and Konopicky (K.), 1962. *Ber. DKG,* **39,** 168–74.
————1972. *Forschungsbericht Land NRW Nr. 2275,* Westdeutscher Verlag Köln und Opladen.
Rockett (T. J.), 1963. Ph.D. Thesis, Ohio State Univ., Columbus, Ohio.
Schneider (H.), Flörke (O. W.), and Majdic (A.), 1979. *Proc. Brit. Ceram. Soc., Basis Science Section 'Mineralogy of Ceramics',* **28,** 267–79.
Tröger (W. E.), 1971. *Optische Bestimmung der gesteinsbildenden Minerale.* Teil 1. Bestimmungstabellen. Schweizerbart, Stuttgart, p. 30.

[*Manuscript received 31 December 1979; revised 24 March 1980*]