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THERMAL EXPANSION OF TRIDYMITE

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The thermal expansion of two tridymites was measured up to 1350°*C with a mechanical dilatometer and a high-temperature X-ray diffractometer. From 20 to about* 800°*C the tridymites show strong anisotropic lattice expansions (* $\Delta a/a \geq 1.4\%$, $\Delta c/c \sim 1.0\%$*). The anisotropy of thermal expansion along the a- and c-axes is attributed to the cis-configuration of* Si_2O_7*-groups in the c-direction, which may cause pre-stressing in that direction. Above about* 800°*C the lattice contracts. Between the temperature of maximum expansion and an arbitrarily chosen end-point at* 1350°*C contractions of about 0.1% (* $\Delta c/c$ *) and* $>0.1\%$ *(* $\Delta a/a$ *) are observed. The lattice contraction is explained by preferred vibration of the Si and O atoms towards the centres of the tetrahedral rings and not to lattice site interchanges of impurities.*

INTRODUCTION

Tridymite, a polymorph of SiO_2, transforms between room temperature and 500°C into four different structural states. The displacive character of the transformations indicates close structural relationships between these tridymite polymorphs. Stacking disorder causes differences in the individual transformation temperatures as well as marked deviations in the structural displacive transformations. A remark by the late Professor F. Laves on feldspars may also be applied to tridymites: "Each feldspar (tridymite) is different, and if isn't so, it will not be a feldspar (tridymite)".

Tridymite is known from different sources: it occurs in meteorites and in terrestrial rocks, particularly volcanic rocks, and is also a common crystalline phase in certain refractories. It is of dominant technical importance as the main constituent of silica bricks, which when used for a long time in coke ovens, glass tanks and the like, consist essentially of tridymite. Furnaces built of silica bricks frequently show contraction at temperatures above 1000°C. This effect, called "negative expansion", is a reversible phenomenon. The aim of our investigation was to get information regarding the cause of this contraction.

TRIDYMITE SPECIMENS

The two tridymite samples studied came from two different silica bricks. Sample T4/5 was taken from the "cold" and sample T2 from the "hot" face of the respective bricks. Both samples contained tridymite as the only crystalline phase and some traces of glass. Their chemical composition is given in Table 1. Sample T4/5 has a higher content of impurities, particularly sodium and titanium.

TABLE 1. CHEMICAL COMPOSITION OF THE TRIDYMITES.

	T2	T4/5
Al_2O_3	1.0	0.83
SiO_2	95.4	93.42
TiO_2	0.31	0.96
Fe_2O_3	0.30	0.50
CaO	3.1	3.63
MgO	0.09	0.14
Na_2O	0.04	0.50
K_2O	0.02	0.10

The powder X-ray diffraction patterns of both tridymites differed markedly in the relative intensities of their reflections. According to PATZAK and KONOPICKY [1] and based on the work of FLÖRKE [2] this reflects different states of structural order. The number of structural faults is much higher in tridymite T4/5 than in T2.

EXPANSION MEASUREMENTS

Dilatometry

The measurements were carried out on small cylinders (approximately 50 x 7.5mm dia.) drilled from the original bricks. Expansion curves were recorded on a NETSCH 402 E dilatometer over the temperature range 20 to 1500°C; heating rate 2°C/min (DIN 51045). This heating rate is too high to give good resolution of the dilatometric effects between 20 and 300°C caused by the displacive transformations. However, the latter effects are outside the intended scope of this paper and will be presented elsewhere.

High-temperature X-ray measurements

A SEIFERT GSD high-temperature diffractometer apparatus (cf. DIERCKS[3]) was used. The ground samples (grain size ≤20 μm) were spread on a sample holder of sintered alumina (DEGUSSIT A123) from an aqueous suspension. The final sample thickness was approximately 0.15mm. An acetone-shellac mixture suggested by PATZAK and KONOPICKY [1] was not used; the sample might become contaminated with carbon which could influence the expansion behaviour (cf. ACKERMANN and SORRELL [4]). Sample temperatures were measured with a calibrated Pt-Rh-thermocouple and by a calibrated bolometer. The accuracy of the temperature measurements was ± 15°C at 1000°C.

Fine-grained corundum powder was used as the internal standard for runs up to 1300°C, because of its well-determined expansion characteristics [5,6]. For runs up to high temperatures a Pt(90)Rh(10) foil, between the sample and the sample holder, served as the internal standard and also prevented any reaction between the tridymite and α-alumina. The following reflections were used for the calculation of the cell parameters and their expansion:

Tridymite:	100 and 002*
Corundum:	012
Pt-Rh foil:	111

Ni-filtered Cu radiation was used. The measurements were carried out in a helium atmosphere to suppress the relatively strong absorption of Cu radiation in air. The X-ray diffraction patterns were recorded with a scan speed of 1/24 °2θ/min, and a chart speed of 10 mm/min. The error of measurement was of the order of 0.001°2θ. Between room temperature and 600°C the rate of heating was 5°C/min. At higher temperatures the heating rate was reduced to 2 or 1 °C/min. The highest operating temperature was 1350°C. The temperature of the sample was kept constant with an optical two-step controller. The temperature was held constant whilst the peaks, from which the cell parameters were determined, were scanned. These peaks were scanned at least twice before being measured.

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* Throughout the paper the indices given for tridymite refer to the high-temperature hexagonal cell.

RESULTS

Dilatometry

Because of the technical importance of silica bricks many dilatometer data have already been published [1,2,7,8,9]. Our own date for samples T2 and T4/5 are shown in figure 1. The curves show a steep and continuous rise between 20 and 800 to 1000°C. Above about 1000°C contraction is observed. Repeated heating and cooling show this effect to be reversible. However, there are some differences in absolute values which are attributed to irreversible microstructural effects. Both tridymites gave a maximum linear expansion of about 1.2%. Assuming $\Delta V/V \triangleq 3\,\Delta L/L$, both samples show a maximum volume expansion of about 3.6%. The volume contraction between the temperature of maximum expansion and the temperature of the end of the runs, 1400°C, is about 0.25%. In our opinion the differences in the dilatometer curves of the two tridymites are due to differences in the crystal structures of the samples as well as to different microstructures of the silica bricks from which they originate.

High-temperature X-ray measurements

Region of expansion

At low temperatures the expansion of the c-axis is almost linear and shows a flattened maximum; at about 600°C for T4/5 and 800°C for T2. Maximum expansion values are similar for both samples: 1.1% for T4/5 and 0.95% for T2 (see below). For the a-axis the situation is more complex. It expands strongly up to 250°C, contracts slightly between 250 and 350°C, and expands again above 350°C, reaching a maximum at about 750°C for T4/5 and at 900°C for T2 (Figs. 2a and 2b). The expansion of the a-axis is higher for the structurally-less-ordered and chemically more impure sample, T4/5 (~1.9%), than for sample T2 (~1.4%). The cell volumes, calculated from the lattice parameters are shown in Figure 4. Maximum volume expansions are 4.96% for T4/5 and 3.6% for T2.

The maximum linear expansion measured by the dilatometer was obviously smaller than the maximum expansion values determined with the X-ray method. This is due to the fact that the dilatometer specimens were polycrystalline and, therefore, the dilatometer result was an average over all crystallographic directions. In addition dilatometer measurements may be affected by the microstructure, which in turn may be influenced by fabric effects. Even the small amount of glass present is expected to cause smaller dilatometer values.

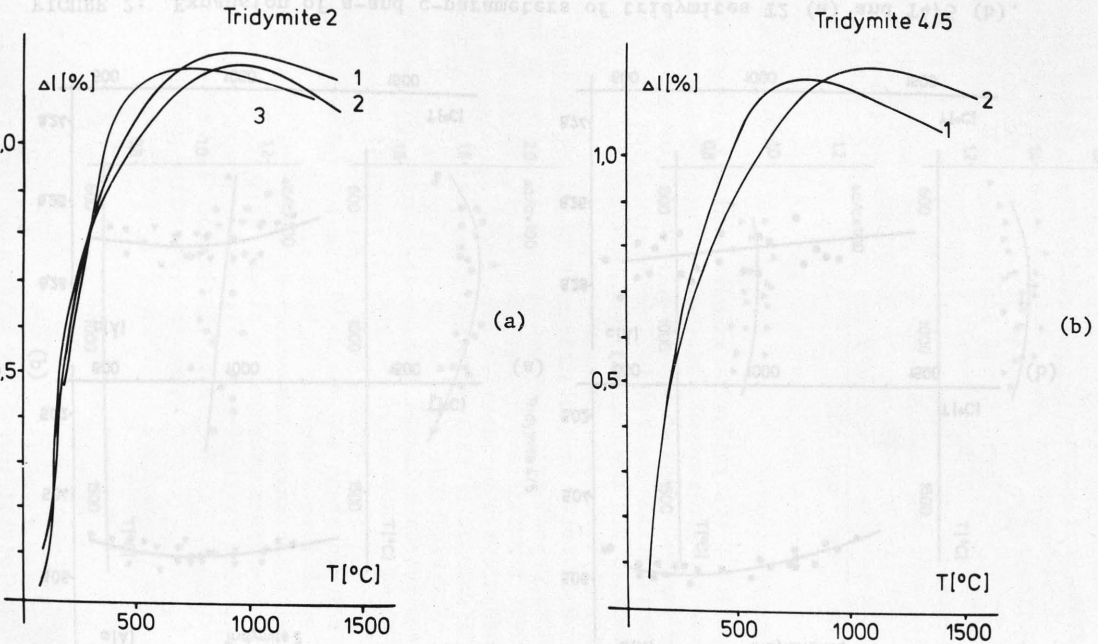


FIGURE 1: Dilatometer expansion curves of tridymites T2 (a) and T4/5 (b). Curves 1,2 and 3 are the thermal expansion after consecutive annealing procedures.

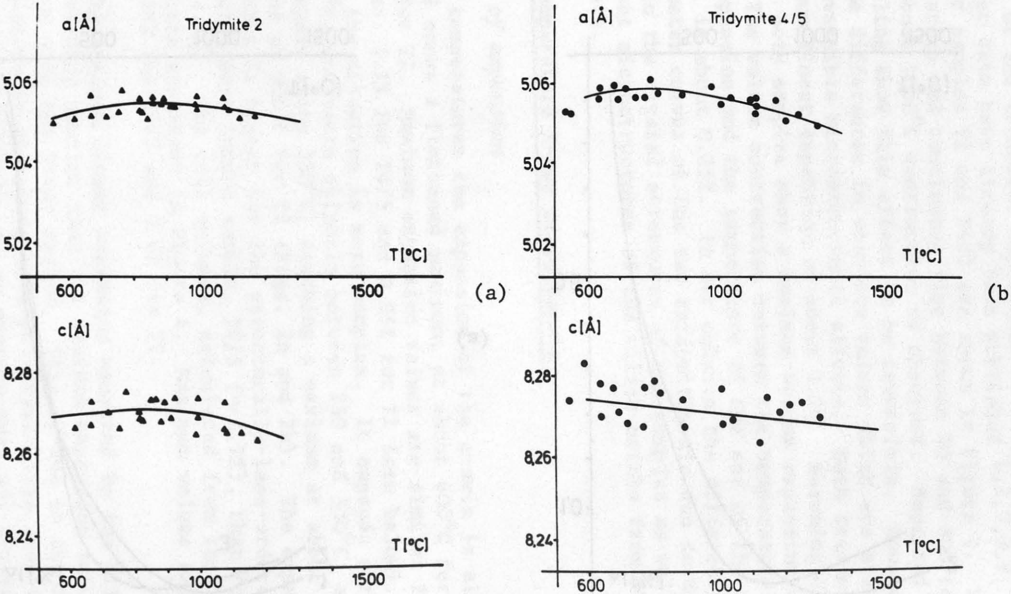


FIGURE 2: Expansion of a-and c-parameters of tridymites T2 (a) and T4/5 (b).

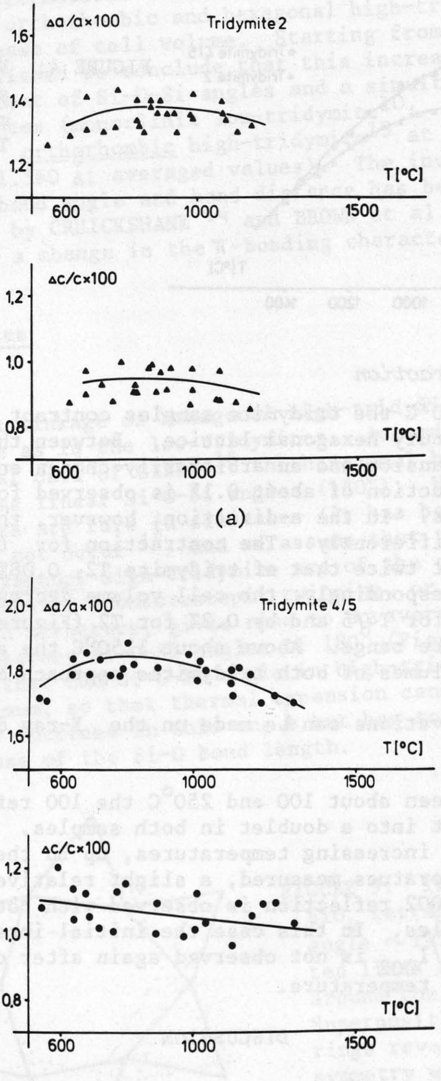


FIGURE 3: Percentage expansions Δ a/a and Δ c/c of tridymites T2 (a) and T4/5 (b).

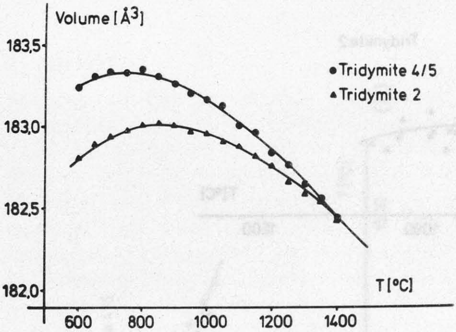


FIGURE 4: Volume expansion of tridymites T4/5 and T2.

Region of contraction

Above about 800°C the tridymite samples contract along a and c in the now truly hexagonal lattice. Between the temperature of maximum expansion and an arbitrarily-chosen end-point at 1350°C a contraction of about 0.1% is observed for the c-axis of both samples. In the a-direction, however, the two samples behave quite differently. The contraction for tridymite T4/5, 0.15%, is about twice that of tridymite T2, 0.08% (Figures 3a and 3b). Correspondingly, the cell volume decreases by approximately 0.45% for T4/5 and by 0.2% for T2 (Figure 4) for the same temperature range. Above about 1250°C the absolute values of the cell volumes of both tridymites approach one another.

Two observations can be made on the X-ray diffraction patterns:

(i) Between about 100 and 250°C the 100 reflection is split into a doublet in both samples.
(ii) With increasing temperatures, up to the highest temperatues measured, a slight relative increase of the 002 reflection is observed with both tridymite samples. In this case the initial intensity ratio I_{100}/I_{002} is not observed again after cooling to room temperature.

DISCUSSION

Low-tridymites

Details of the structures of low tridymites have recently been published[10, 11, 12]. It was found that the SiO_4 tetrahedra are shared with common corners in UD-Zweier-Einfach-chains, forming quasi-planar Zweier-Einfach-sheets of six-membered tetrahedral rings.

The transformations from monoclinic or triclinic low-tridymites to orthorhombic and hexagonal high-tridymites involve an increase of cell volume. Starting from the structural data published we conclude that this increase is effected by an enlargement of Si-O-Si angles and a simultaneous decrease of Si-O distances (monoclinic low-tridymite[10]: Si-O-Si 149.8°, Si-O 1.601 Å; orthorhombic high-tridymite[13] at 220°C: Si-O-Si 171.7°, Si-O 1.560 Å; averaged values). The inverse relationship between bond angle and bond distance has been discussed for silicates by CRUICKSHANK [14] and BROWN et al. [15], and was attributed to a change in the π-bonding character of the Si-O bond.

High-tridymites

Expansion

The framework linkage of hexagonal high-tridymite is principally the same as in the low-tridymites. According to the very old structural data of GIBBS [16] the hexagonal high-tridymite structure has linear Si-O-Si angles (180°). However, linear Si-O-Si angles are rare in silicates (it has been suggested that they do not occur [17]) and we assume that the Si-O-Si angles in hexagonal high-tridymite are of the order of 150° However, intensive submicroscopic twinning, or a submicroscopic domain structure, gives rise to an average X-ray structure with apparent Si-O-Si angles of 180° (Figure 5). It is our opinion that the Si-O-Si angle in high-tridymite is opened to a maximum, so that thermal expansion cannot be attributed to a further increase in this angle but has to be attributed to an increase of the Si-O bond length.

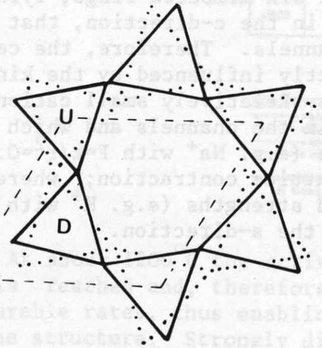


FIGURE 5: Two UD-6-rings of SiO_4 tetrahedra; Si-O-Si angle ~155°. Full and dotted lines are rotated by 60° around the trigonal axis. Superposition of the two rings reveals pseudohexagonal symmetry with apparent Si-O-Si angles of 180°.

The anisotropy of the thermal expansion in the a- and c-directions is due to the cis-configuration of those Si$_2$O$_7$-groups in tridymite which have their trigonal axes parallel to c (FLÖRKE [18]). This unfavourable configuration causes a distortion of the SiO$_4$ tetrahedra in the c-direction into elongated trigonal pyramids (Figure 6). This primary structural prestressing of the SiO$_4$-groups is assumed to hinder thermal expansion along c. In contrast, the expansion of cubic high-cristobalite is isotropic [19]. This is not unreasonable since cristobalite shows the favourable transconfiguration of its Si$_2$O$_7$-groups, whose trigonal axes point into the four equivalent ⟨III⟩ —directions (FLÖRKE [18]), and consequently do not cause prestressing.

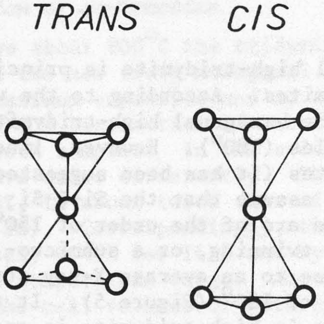


FIGURE 6: Si$_2$O$_7$-groups in transconfiguration (cristobalite) and cis-configuration (tridymite); both idealized. The height difference between trans- and cis-configuration is exaggerated 10-fold.

The anisotropy of expansion of tridymite may be accentuated by the incorporation of impurities. In the tetrahedral framework of tridymite the electric force field of the cations is stronger in the place of the six-membered rings, lying perpendicular to the c-axis, than in the c-direction, that is the direction of the structural channels. Therefore, the cell volume of tridymite could be directly influenced by the kind and amount of channel constituents. Relatively small cations, occupying interstitial sites in the channels and which have relatively high field strengths (e.g. Na$^+$ with $F=z/r^2=0.17$) could be expected to cause a lattice contraction; whereas larger cations with lower field strengths (e.g. K$^+$ with F=0.13) may even cause an expansion in the a-direction.

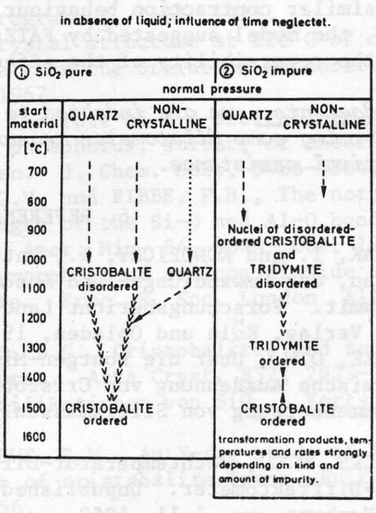
Another intrinsic parameter causing variation in the lattice expansion of tridymites is the concentration of stacking faults. These defects (FLÖRKE[20]) cause an increased thermal expansion due to an increase in the configurational trans-orientation with increasing proportions of cristobalitic stacking sequences.

Shrinkage

The temperature-induced increase of the Si-O bond length is limited. Above a critical temperature range the thermal motion of the Si and O atoms in the six-membered rings gives rise, more and more, to vibration components towards the centres of the rings. At the same time the Si-O-Si angles decrease on average. Above about 800°C we assume the latter effect to be stronger than the increase of bond length, leading to a contraction of the lattice (see also ACKERMANN and SORRELL[4]).

Table 2

Transformation kinetics of pure (<0.02%) and impure (>0.02%) silica in absence of liquid; influence of time neglectet.



At about 1200° C the activation energy for Si-O bond breaking is reached and, therefore, Si-O bonds start to break in measurable rates, thus enabling a reconstructive rearrangement of the structure. Strongly disordered tridymite becomes more ordered and with increasing temperature (still well below

1470°C, the so-called transition temperature of tridymite into cristobalite) more and and more cristobalitic stacking sequencies are formed (see Table 2, SiO_2 impure). The irreversible change of the X-ray intensity ratio I_{100}/I_{002} is attributed to this effect.

We do not agree with PATZAK and KONOPICKY[1] that the volume contraction is due to a change in the occupation of the interstitial lattice sites by "impurities", as has been shown for the stuffed derivative of quartz, β-eucryptite[21], and has been suggested for cordierite by one of us (H.S.). Tridymite contains few impurities (cf. FLÖRKE and LANGER[22]) in its structure, even if it is formed in an impurity-rich environment. The majority of the impurities measured by chemical analysis are inclusions and not incorporated into the structure. Our rejection of the theory of PATZAK and KONOPICKY[1] is supported by the results of ACKERMANN and SORRELL[4], who found a similar contraction behaviour with pure quartz. Furthermore, the model suggested by PATZAK and KONOPICKY does not explain the reversibility of the effect.

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