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Tridymite Polymorphs and Polytypes

by *Mechthild Wennemer* and *Alan Bruce Thompson*

Abstract

Relations among the monoclinic (MC and MX-1) and pseudo-orthorhombic (PO) tridymites are discussed in terms of their structures, when known, differential thermal investigations of the transitions relating them and structural observations at elevated pressure. The progressive structural changes of MC-tridymites with increasing temperature can be explained in terms of rearrangement of stacking sequences of layers of SiO_4-tetrahedra. These changes are also consistent with the ambient temperature phase transition at about 5 ± 1.5 kbar of MC to PO-10, described by NUKUI et al. (1980). However this interpretation is complicated by the observation by HOFFMANN et al. (1983) that MC may be transformed to MX-1 by grinding, which then transforms to a PO type with increasing temperature. Possible pressure-temperature relations for the three types MC, MX-1 and PO are suggested on the basis of available data.

Keywords: tridymite, cristobalite, phase transitions, stacking sequences, polymorphs, polytypes.

INTRODUCTION

Several distinct types of tridymite are observed at ambient conditions. On the basis of x-ray data these types can be classified into a) monoclinic (MC, MX-1 [NUKUI et al., 1980b, p. 368]) and b) pseudo-orthorhombic (PO-n, n = 1.5, 2, 5, 6, 10 [HOFFMANN, 1967], n = 1 [NUKUI et al., 1980b], n = 12 [SHAHID and GLASSER, 1970]). The MC-structure is considered to be the low temperature polymorph of meteoritic and most of the synthetic and industrial tridymites. Despite previous classification (KONNERT and APPLEMAN, 1978, p. 391), it appears that the synthetic and meteoritic tridymite can belong to either group, and even terrestrial material is not always orthorhombic (KAWAI, 1978).

A common structural feature of the two SiO_2 modifications, cristobalite and tridymite, is their construction of layers consisting of six-membered rings of

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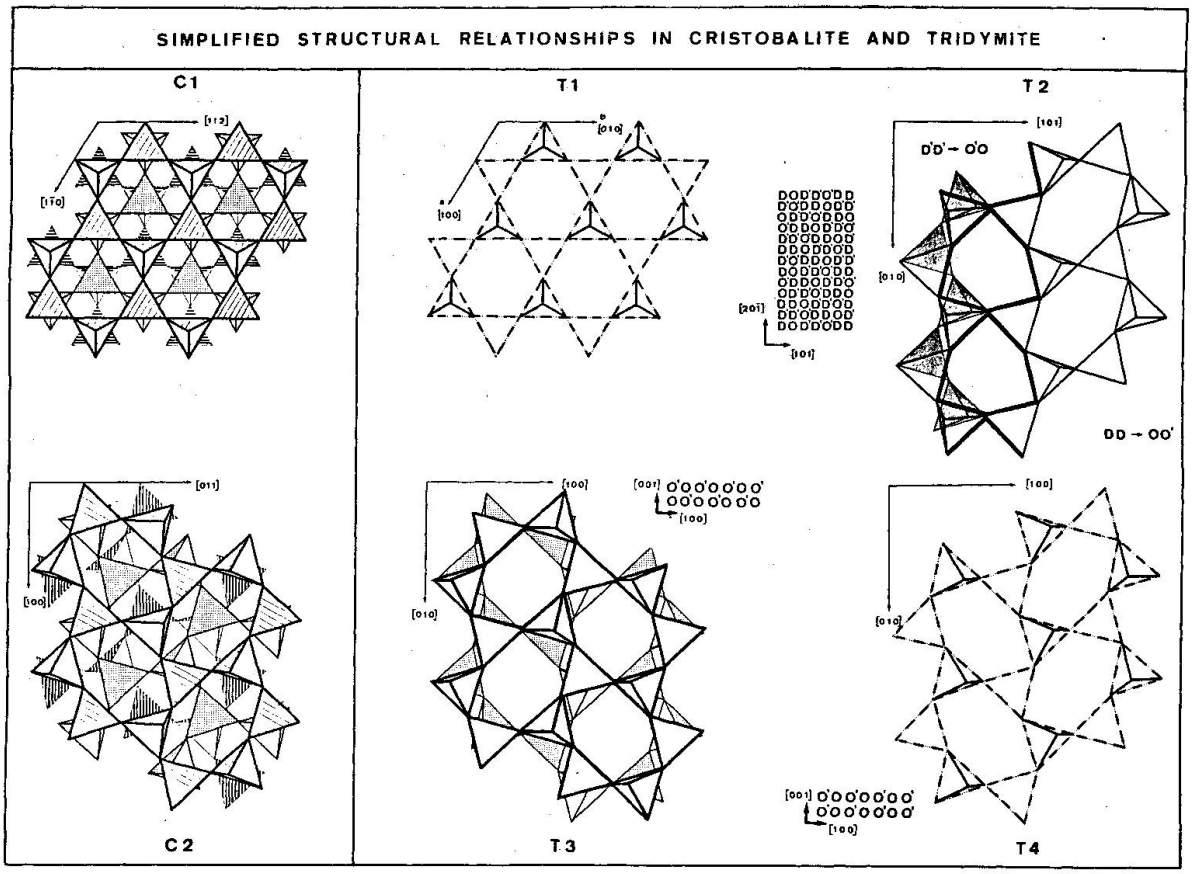

Fig. 1 Stacking sequences of layers of linked SiO_4-tetrahedra in cristobalite (C1, C2) and tridymite (T1, T2, T3, T4).
C1 – shows three successive layers in idealized β-cristobalite (constructed from the data of WYCKOFF, 1925, p. 199).
C2 – shows three successive layers in α-cristobalite (constructed from the data of DOLLASE, 1964, Table 2).
T1 – shows two successive layers in idealized high tridymite (modified from GIBBS, 1927, Figure 10).
T2 – shows a part of one layer (marked in Figure 2) of the MC-tridymite structure of DOLLASE and BAUR (1976, Figure 2) together with the suggested tetrahedral displacement of one chain (NUKUI et al., 1980, Figure 4) by which D-rings may be transformed to O-rings. The stacking sequence of the 12-layer structure of MC-tridymite from DOLLASE and BAUR (1976, Figure 3) is shown at the left and is the same as that shown in Figure 2.
T3 – shows two layers of the possible PO-10(N) type (NUKUI et al., 1980) resulting from the tetrahedral displacement of two successive layers of O above O'.
T4 – shows two layers of another part of the possible PO-10(N) type with O above O and O' above O'.

SiO_4-tetrahedra (see Figure 1). Two different types of rings can be distinguished, so-called O-rings (with oval shape) and D-rings (with ditrigonal shape) showing a distinct deviation from the ideal hexagon, commonly used to depict the high-temperature structures of each of the two modifications. The two SiO_2-modifications, cristobalite and tridymite, differ from each other in both the combination of ring types (O or D) in individual layers and the stacking sequence of the successive layers. The monoclinic MC-tridymite has one-third O-rings and two-thirds D-rings in each layer (KATO and NUKUI, 1976, DOLLASE and BAUR, 1976). A terrestrial tridymite, whose structure has been refined by KONNERT and APPLEMAN (1978), is said to consist of only O-type rings

as does α-cristobalite. The structure of the PO-type tridymite has not yet been solved. Appendix 1 summarises structural data on tridymite from the literature.

Because many of the authors of the vast literature on SiO_2 modifications (see Appendix 1) consider that their results are at variance with those of other workers, we think it appropriate to ask first, why tridymite forms in at least two different structural types (monoclinic and orthorhombic) each with several members (MC, MX-1, PO-n) at ambient conditions and, second, are these structure types real polymorphs of tridymite related by structural transitions that have not yet been recognised, or polytypes related by different stacking sequences?

The close relationship between the structures of tridymite and cristobalite has many consequences for their modes of formation, twinning relations and intergrowths, and hence for their transition behaviour. The possible ring and layer sequences of the linked SiO_4-tetrahedra and the known influence of chemical impurities, which seem to be an essential part of the tridymite structure (FLOERKE, 1956, HOLMQUIST, 1958), are apparently key factors in understanding the relation between these modifications of SiO_2.

Stacking Sequences in Tridymite and Cristobalite

Quartz, cristobalite, and tridymite are distinct *polymorphs* of SiO_2, because of the nature of the transitions relating them, although cristobalite and tridymite differ mainly in the sequence of the SiO_4-tetrahedra layers. Complications to the structure of tridymite come from the existence of *polytypes.* Stacking faults within the samples are not wholly random, but occur with a definite periodicity thus giving multiples of $\underline{c}$ for the unit cell constant perpendicular to the tetrahedral layers. As a rearrangement of the stacking sequence could not occur by a simple change in tetrahedra orientation during a transition, the x-ray-reflections indicate that these periodic stacking faults are preserved above the transition. Up to now, multiples of $\underline{c}$ with $\underline{n}$ = 1, 1.5, 2, 4, 5, 6, 10 and 12 have been identified. On the basis of the known tridymite and cristobalite structures, n = 1.5 can be related to the three layer sequence in cristobalite, and n = 4, 6 and 12 to MC-tridymite. HOFFMANN and LAVES (1964) and HOFFMANN (1967) suggested that the sequences n = 2, 5, 10 which indicate PO-tridymite, should be called *polytropes* of tridymite. They considered the occurrence of polytropes to be due to periodic displacive distortions (perhaps of chains of linked SiO_4-tetrahedra) which disappear reversibly during the transitions of tridymite. As the MC-structure was still unknown at that time, these authors included n = 6 in this group. The large c-axis period in the terrestrial Fl-tridymite is, according to KONNERT and APPLEMAN (1978), due to the construction of ten crystallographically different layers and not caused by periodic displacive distortions, and thus Fl cannot be regarded as a polytrope.

GENERAL ASPECTS OF RINGS AND LAYERS WITH SiO_2 STACKING SEQUENCES

At high temperatures, both cristobalite (PEACOR, 1973) and tridymite (DOLLASE, 1967) consist of only D-type rings (Figure 1). In the ideal case the shape of these rings would be a perfect hexagon. However, this would mean that the Si–O–Si bond angle must be 180 degrees which is not the case here (TAYLOR, 1972, BAUR, 1977, BAUR, 1980, FLOERKE, 1967 p. 192, MISCHKE, 1971, p. 31, KIHARA, 1980, p. 98). Thus, slight deviation from the hexagonal symmetry always leads to D-type rings.

The layer sequence in idealized cristobalite can be considered as cubic close packing: that is ABCABC, etc. parallel to [111] in the cubic crystal (FLOERKE, 1955, p. 371). In idealized tridymite the layer stacking refers to hexagonal close packing: that is AC'AC'AC', etc. parallel to [001], where C' indicates that the original C layer has been rotated by 180 degrees (FLOERKE, 1967, p. 192). In both structures the sequence may be disturbed thus producing three layer units, that is cristobalite structure units in tridymite and vice versa. Following FLOERKE (1967, p. 197), crystals with predominant AC'AC'-units are called ordered tridymite whereas increasing amounts of ABC-units produce disordered tridymite. At an intermediate state, when equal numbers of two- and three-layer units exist, it is not possible to distinguish between tridymite and cristobalite. Decreasing AC'AC'-units lead to disordered cristobalite until finally the ideal ABC-layer sequence is characteristic of well ordered cristobalite. In the AC'-sequences of idealized tridymite, Si_2O_7-groups are formed parallel to the hexagonal axes which are called "unfavourable" by FLOERKE (1965) and "cis" by NUKUI et al. (1980b, p. 364) because these groups, formed by two SiO_4 tetrahedra connected by a common oxygen-atom, possess mirror-plane symmetry causing the layers in tridymite to be 0.05 Å thicker than in cristobalite. Within the layers, the Si_2O_7-groups are related by inversion symmetry. According to FLOERKE (1956, p. 419 and 1967, p. 196), the existence of these "unfavourable" Si_2O_7-groups is the reason for the incorporation of impurities (as charge balance) to form or to stabilize the tridymite structure and by influencing the location of these impurities an explanation for the anisotropy of expansion of tridymite (SCHNEIDER, et al., 1979, p. 276).

RING AND LAYER SEQUENCES AS A FUNCTION OF TEMPERATURE AT ONE ATMOSPHERE

With decreasing temperature β-cristobalite, containing large D-rings, becomes unstable and at about 543 K (FLOERKE, 1957, p. 346, DOLLASE, 1964) transforms to low or α-cristobalite with only O-rings (Figure 1, C1 to C2).

For MC-tridymite, we find a stepwise series of transformations relating the different structures. These are illustrated in Figure 2 on the basis of single-crys-

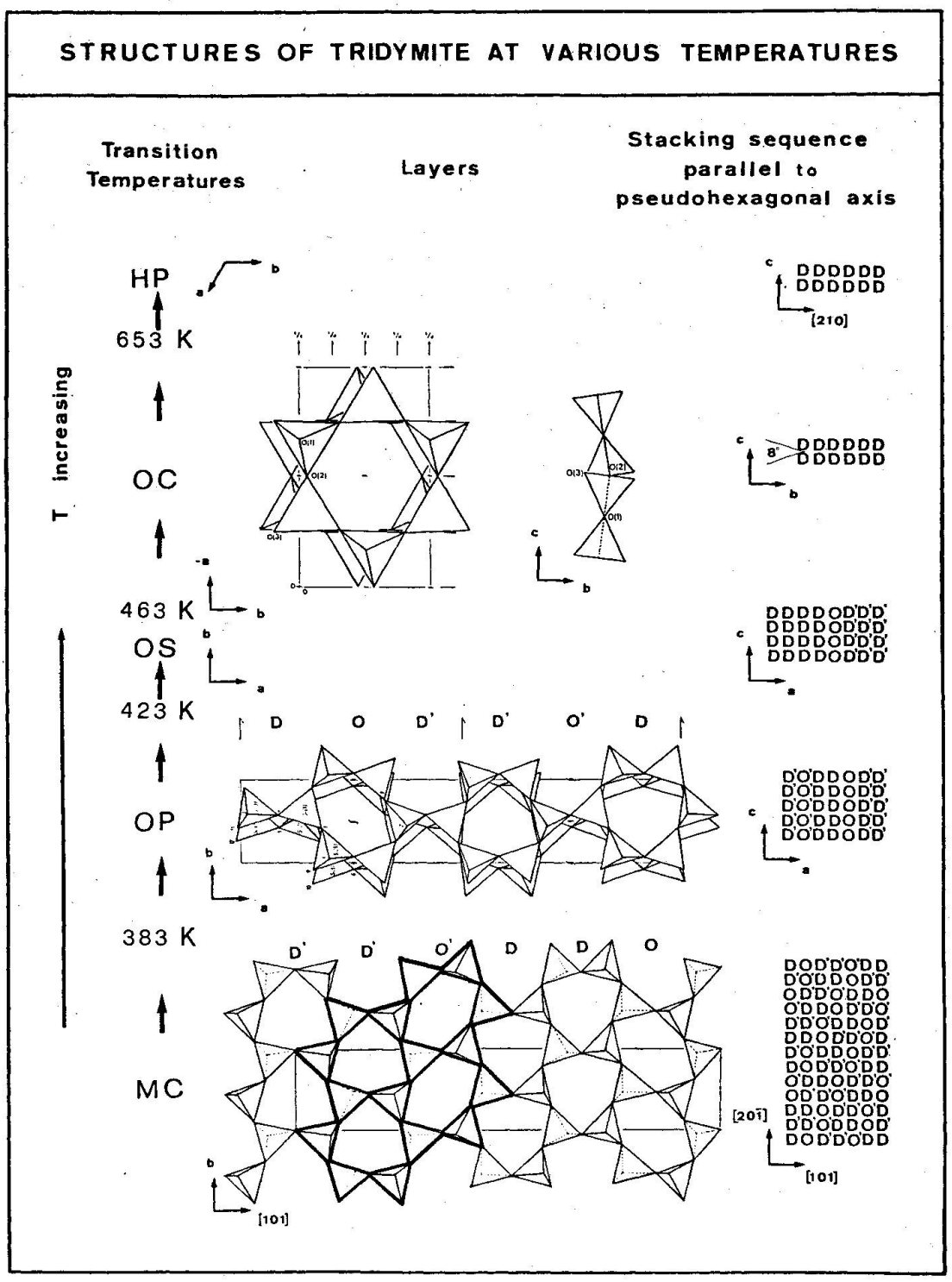

Fig. 2 Structures and stacking sequences of the various forms resulting from the heating of MC-tridymite. The transition temperatures and polymorph nomenclature are from NUKUI et al. (1978, Figure 9). Sources of structural information are:
MC - DOLLASE and BAUR (1976, Figure 3)
OP - KIHARA (1977, Figure 3)
OC - DOLLASE (1967, Figure 2 and 3)
The stacking sequences at the right are constructed so as to be consistent with the nomenclature for MC of DOLLASE and BAUR (1976, Figure 3).

tal structure refinements of each form and using the nomenclature of NUKUI et al. (1978). With decreasing temperature from the hexagonal high-temperature form (HP, containing only D-rings) several forms occur which contain both D- and O-rings (OS, OP and MC). The stacking sequences parallel to the hexagonal axes are shown schematically in Figure 2.

The transition from HP and OC at 653 K causes a deviation of the tetrahedra from their exactly perpendicular orientation to the hexagonal c-axes of about 8°, without destroying the large D-rings.

At temperature lower than 463 K, an intermediate type occurs, called OS, which after SATO (1964c, p. 224) could be interpreted as a domain-structure consisting of parts of both OP and OC. OS is a superstructure with the a-axes increasing from 65 to 95 Å as the temperature is decreased from 463 K to 423 K. Below 423 K the OP-structure is observed. Hence one third of the rings must change their shape to become O-rings. Still the same type of rings stack on top of one another in successive layers, thus forming channels of either D- or O-rings parallel to the pseudo-hexagonal axes.

At 383 K the OP-structure transforms to the MC-structure. Although the ring arrangement within layers remains the same, the layer to layer stacking sequence is changed placing different types of rings above each other thus creating an orthorhombic supercell with a 12 layer repeat.

Phase Transitions and the Related Structural Rearrangement in Synthetic Tridymites

There is good correspondence among the inversion temperatures observed in the one-atmosphere x-ray single crystal study at elevated temperature reported by NUKUI et al. (1978), the measurements of the instantaneous coefficient of linear thermal-expansion reported by AUSTIN (1954, Figure 1) and the differential scanning calorimetric (DSC) investigation by THOMPSON and WENNEMER (1979, Figure 1). All three studies used synthetic tridymites prepared by similar methods.

There appear to be three distinct reasons for the variety of tridymite transformations:

1. The shape (and hence the volume) of the 6-membered D- or O-rings of SiO_4-tetrahedra.
2. The "unfavourable" (cis) orientation of Si_2O_7-groups.
3. The intergrowth with three-layer units of cristobalite.

If the reported structures of the high-temperature forms of the MC-tridymite family are correct, then the structural rearrangements that have to take place with decreasing temperature, can be described as follows.

In the HP-structure the existence of these large D-type rings is favoured by high temperature as in β-cristobalite (Figure 1, C1) and in β-quartz. The connec-

tion between the layers in tridymite is due to the unfavourably oriented Si_2O_7-groups and, consequently, the negative "excess charge" caused by the mirror plane arrangement of the oxygen atoms is concentrated in only one direction. But as the rings are large, these groups are separated from each other as far as is possible. The existence of these Si_2O_7-groups has a destabilizing effect on the ideal HP-structure and thus leads with decreasing temperature to the HP-OC transformation at 653 K. The large D-rings, however, are still stable and remain more or less unchanged, but through the tilting of the tetrahedra by about 8° relative to the direction of the c-axis, a more favourable distribution of the Si_2O_7-groups is achieved, that is, they are no longer oriented exactly parallel to the pseudohexagonal axes. There are two possible reasons why this HP-OC transformation cannot be seen in the thermal expansion (AUSTIN, 1954, Figure 1) or the DSC traces (THOMPSON and WENNEMER, 1979, Figure 1). Either the structural change, and hence the energy required for it, is so small that it cannot be detected, or there is no transition point but a transition interval (between 483 and 577 K for thermal expansion). The second interpretation is more probable because of the observation made by MISCHKE (1971, p. 20) and KIHARA (1978, p. 243) that the intensity of a significant x-ray reflexion, 221, gradually faded into the background and did not disappear suddenly at one temperature.

With decreasing temperature (Figure 2) the large D-rings become more unstable and in cristobalite collapse at 535 K to form the smaller O-rings of the α-form. That means that all the tetrahedra of the β-cristobalite structure have to change their orientation at the same time. A large peak is observed in the DSC-measurements on cristobalite at 535 K (THOMPSON and WENNEMER, 1979, Figure 2), which suggests that a large amount of energy is required to simultaneously reorient the tetrahedra.

In the case of tridymite, although at lower temperature the D-rings are less stable, a collapse of the bigger D-rings would lead to a closer approach of the "unfavourable" Si_2O_7-groups. Therefore, the next transformation to OP is a compromise between both effects. Here only one third of the D-rings become O-rings, while the rest of them seem to be stabilized by the repulsive force of the unfavourable Si_2O_7-groups. As only one third of the rings need to change (i.e. only part of the tetrahedra have to reorient), this DSC-peak is quite small compared to the cristobalite transformation.

Between OP and OC, the occurrence of a dynamic superstructure, OS, has been observed by NUKUI et al. (1978, p. 1255), DOLLASE (1967, p. 617) and SATO (1964, 3). SATO interprets this intermediate phase as a domain structure, consisting of parts of both forms, OP and OC. The formation of this phase could be described as follows: to transform OP to OC with *increasing* temperature means that all the O-rings in OP have to become D-rings. It is not possible to build up a layer by combination of both D and D' without any O-rings. Therefore the

D-rings must have the same orientation. If the nucleation of the OC-structure starts at several points within the OP-structure at the same time, it is not likely that all the D-rings of the whole crystal will find the same orientation right from the beginning. Thus a domain-structure would be formed, consisting of regions with oppositely oriented D-rings, connected by single strips of remaining O-rings. The D-rings in the OC-structure are more nearly hexagonal and thus with increasing temperature the difference between D and D' becomes smaller, making it possible for the remaining O-rings to also become D-rings. A further indication to the domain-structure of OS tridymite comes from the interpretation of the α-β-quartz transformation by PUTNIS and MCCONNELL (1980, p. 93), who on the basis of transmission electron micrographs envisaged submicroscopic domains oscillating between the two forms, and from the single crystal x-ray structure refinement of high temperature OS tridymite by NUKUI et al. (1979, p. 329).

A further decrease in temperature (Figure 2) from the OP-tridymite causes the structure to rearrange the "unfavourable" Si_2O_7-groups once more. By destroying the previous D- and O-channels through the formation of a new stacking sequence, only one third of the layer-connecting Si_2O_7-groups could still be called "unfavourable" while two thirds could change their orientation so as to be approximately inversion symmetric. The formation of the MC-structure from OP is indicated by a large peak in both heat capacity and thermal expansion measurements with temperature. To build up the new stacking sequence nearly all of the tetrahedra have to move, and in correspondence to the α-β-cristobalite transition, a large amount of energy will be required.

So far, two of the three given factors that are presumed to control the transition behaviour of tridymite have been discussed, leaving the problem of the intergrowth with cristobalite three layer-units. The total amount, the continuity of three layer-units and their distribution in the crystal could give an explanation for the changes in transition behaviour, observed in tridymite samples of increasing disorder.

In well ordered tridymite samples, only two transitions can be seen by DSC-measurements: MC-OP (at 388 K) and probably OP-(OS)-OC (432 K). With increasing amounts of cristobalite units a third DSC-peak appears with increasing intensity, so that now for example in TR-IV (WENNEMER and THOMPSON, 1984, Figure 2) there are three transitions which may be correlated to MC-OP, OP-OC, and α-β-cristobalite. What happens in the structure could be interpreted as follows: in a sample like TR-IV, there are layers with the tridymite MC-structure interrupted by layers with α-cristobalite structure. When the temperature is raised, the MC-layers will transform to OP at the MC-OP-transition. As the total amount of pure tridymite is diminished by the amount of cristobalite in the sample, fewer tetrahedra have to be moved and consequently the DSC-peak is smaller. The cristobalite structure units keep their O-rings, while the

tridymite blocks consist of $^2/_3$ of the channels with D-shape and $^1/_3$ with O-shape. So the total structure could be expressed by OP-tridymite plus α-cristobalite. With increasing temperature the next transition is reached, causing the OP-parts of the sample to transform to OC (where all tridymite rings become D-shaped) while the α-cristobalite still consists of O-rings. This would lead to a misfit of the rings in neighbouring layers. The result could be some interlayer strain perhaps causing more O-rings in α-cristobalite to change their shape to D-rings, although the transition temperature for pure cristobalite is not yet reached. So the third broad peak could be ascribed to the α-β-transition of interstratified cristobalite layers (FLOERKE, 1957, p. 344, FLOERKE and MÜLLER-VONMOOS, 1971, p. 201). This could also explain why, with increasing amount of cristobalite in the sample, this DSC-peak is shifted to higher temperatures and increases its sharpness and intensity. The thicker the blocks of cristobalite, the weaker is the "seed"-effect of the neighbouring tridymite layers and the more the temperature of the third peak is raised until finally this is the only transition peak that occurs. A similar effect (an increase of the transition temperature with increasing degree of order) has been observed in disordered and ordered cristobalite (FLOERKE, 1957, p. 344) and may be the explanation for the temperature and intensity changes in the heat capacity data (THOMPSON and WENNEMER, 1979, Figure 3, and WENNEMER and THOMPSON, 1984, Figure 2).

Low Temperature Transitions in Synthetic Tridymite

OBSERVATIONS AT ONE ATMOSPHERE PRESSURE

WENNEMER and THOMPSON (1984) have interpreted their differential thermal measurements on synthetic tridymites in terms of previously reported x-ray structural refinements. In addition, HOFFMANN et al. (1983) reported that MC-tridymite can be partially converted to MX-1 tridymite by grinding and that between 323 and 368 K, MX-1 transforms to a PO-type. These observations are of significance for attempts to interpret studies made at elevated pressure.

OBSERVATIONS AT ELEVATED PRESSURES

In addition to the x-ray, DSC and DTA-studies made at elevated temperature at one atmosphere, there are several studies made at both elevated pressure and temperature and one elevated pressure single crystal x-ray diffraction study at room temperature. In this latter study NUKUI et al. (1980a) observed that synthetic MC-type tridymite transformed at 5 ± 1.5 kbar to a PO-10 type, pseudo-orthorhombic with 10 layer repeat along $\underline{c}$ ($\underline{a}$ = 17.07, $\underline{b}$ = 9.81, $\underline{c}$ = 81.26 Å) as

refined at 7 kbar. These authors note (p. 1254) that the PO-10 type could represent the coexistence of PO-2 and PO-5 types. Similar high pressure experiments on a natural pseudo-orthorhombic PO-5 tridymite ($\underline{a}$ = 17.21, $\underline{b}$ = 9.93, $\underline{c}$ = 40.91 Å) did not show any significant changes in reflections to 30 kbar. In a personal communication to NUKUI et al. (1980a, p. 1285), APPLEMAN reported that PO-10 and PO-5 tridymite are invariably related by submicroscopic twinning. NUKUI et al. (1980a, p. 1285) proposed a tetrahedron displacement-mechanism (T2 in our Figure 1) by which the low pressure MC-tridymite, containing $^1/_3$ O-rings and $^2/_3$ D-rings, could be related to the suggested structure of high pressure PO-10 tridymite. This is proposed to contain only O-rings, because PO-10 has a smaller molar volume than that of the MC-type, which is in accordance with a volume difference between D- and O-rings (NUKUI et al. 1980a, p. 1284). NUKUI and NAKAZAWA (1980b, p. 375) suggested that this transition could have a very steep and positive dP/dT.

P-T Diagram for Tridymite

Figure 3 a, c and d give different versions of phase diagrams for tridymite on the basis of literature data, the information from a Tridymite Workshop in Bochum in January 1983, and the results of the new measurements reported by WENNEMER and THOMPSON (1984).

Perhaps the principal problem lies with the existence of several forms at room-temperature one-atmosphere. A phase diagram for only MC-tridymite, neglecting the occurrence of MX-1 and as well the different PO-types at one atmosphere, is given in Figure 3 a. From the DTA-studies presented by WENNEMER and THOMPSON (1984, Figure 2), it must be concluded that if the transition between PO-10 (N refers to NUKUI et al., 1980a) and MC passes through a region near 5 ± 1.5 kbar and 298 K (NUKUI and NAKAZAWA, 1980b, Figure 6) and has a positive dP/dT, then either it occurs below 150 K at one atmosphere or cannot be detected betwen 150 and 298 K by DTA-methods. Alternatively, this metastable boundary may not be visible at any temperature at one atmosphere. In Figure 3 b, the DTA-scan on T-1sa from WENNEMER and THOMPSON (1984, Figure 2) is reproduced to demonstrate the correspondence of its transitions to those expected for MC-tridymite. Nevertheless, the 336 K peak clearly reveals that the T-1sa DTA-sample contains a mixture of at least two phase, MC and MX-1.

Figure 3 c considers MX-1 tridymite as the only room-temperature phase. MX-1 can be formed from MC by an increase in pressure (grinding), and MC itself, according to NUKUI et al. (1980, Figure 8 a) transforms to a PO-type at room-temperature and high pressure. Hence a negative dP/dT is suggested for the MX-1 to PO (HOFFMANN and co-workers, 1983) phase-boundary, although

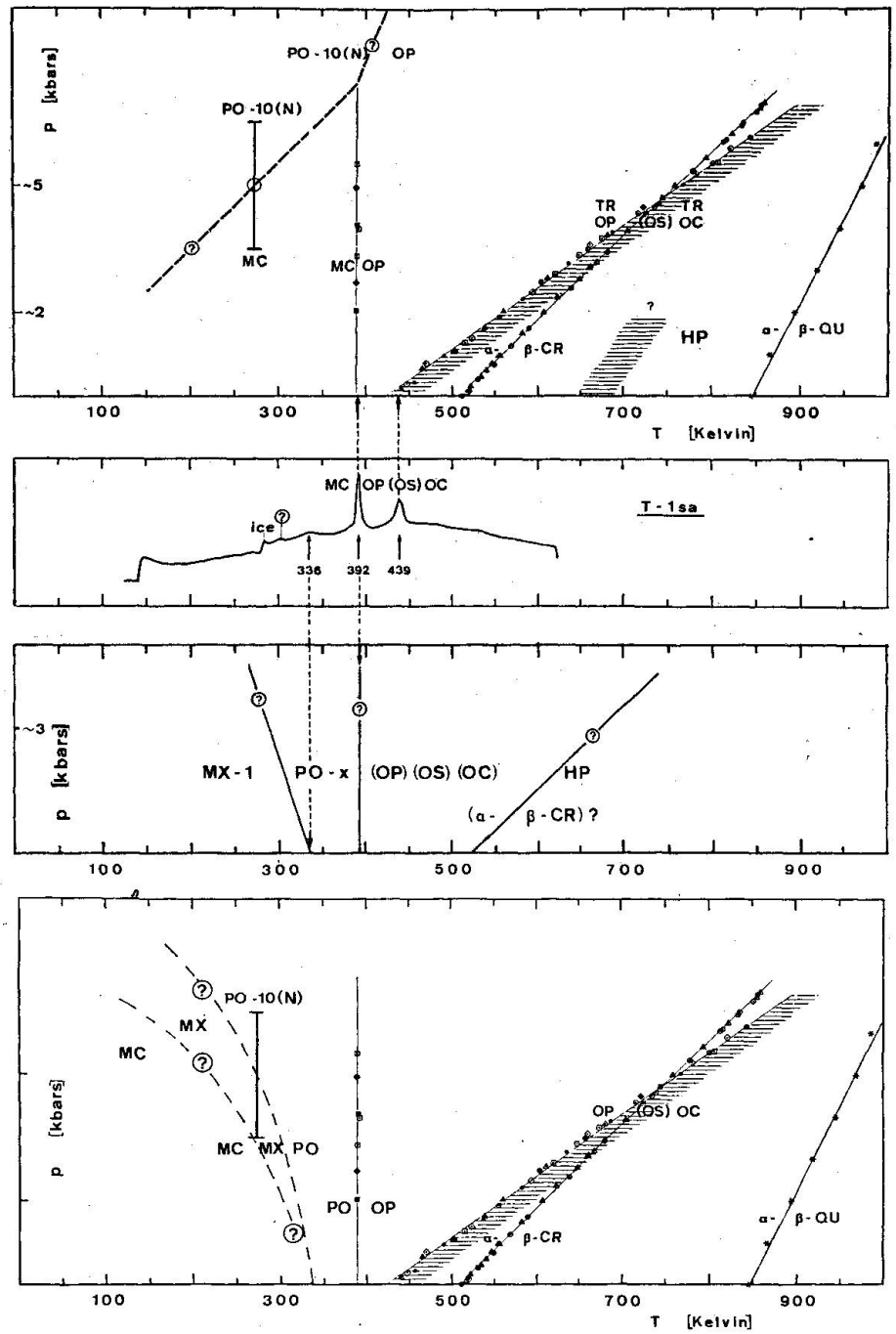

Fig. 3 Suggested P-T diagram for tridymite. Transition curves of α-β-cristobalite and α-β-quartz are shown for comparison. Sources for transitional information are:

α-β-cristobalite:	COHEN and KLEMENT (1975, Figure 1)
α-β-quartz:	COHEN and KLEMENT (1976, Table 1)
PO-(OS)-OC-tridymite:	COHEN and KLEMENT (1980, Figure 1)
MC-OP-tridymite:	COHEN and KLEMENT (1980, Figure 1)
MC-PO-10(N)-tridymite:	NUKUI et al. (1980, p. 1284)
MX-1-PO-X:	HOFFMANN and coworkers (1983)
PO-X-(OP)(OS)(OC):	NUKUI et al. (1980, p. 368)

a) MC is assumed to be the only low temperature / 1 atm phase
b) Trace of the DTA-curve for T-1sa
c) MX-1 is assumed to be the only low temperature/1atm phase
d) Several low temperature forms (MC, MX-1, PO) coexist at low temperature / 1 atm

Table 1 Structural data of cristobalites and tridymites from the literature

designation	n(1)	crystal system, space group	cell constants [Å], [°]	orientations and dimensions(2) layer [uvw]	m	[Å]	stacking [uvw]	m	[Å]	specimen-type, stability	references
α	3	tetragonal $P4_12_1$ or $P4_32_1$	a= 4.978 c= 6.948	011 100	2 2	17.09 9.96	$02\bar{1}$	2/3	8.09	cristobalite low-temperature	DOLLASE (1964)
β	3	cubic Fd3m	a= 7.1315	$1\underline{1}2$ 110	1 1	17.47 10.09	001	2/3	8.23	cristobalite high-temperature	WRIGHT and LEADBETTER (1975)
PO-12	12	orthorhombic	a= 4.97 b= 51.3 c= 97.8	010 100	1/3 2	17.10 9.94	001	1/2	8.15	synthetic K_2WO_4	SHAHID and GLASER (1970)
PO-10	10	orthorhombic	a= 9.91 b= 17.18 c= 81.57	010 100	1 1	17.18 9.91	001	1/10	8.16	terrestrial Plumas County	BUERGER and LUKESH (1942)
PO-10	10	orthorhombic	a= 9.94 b= 17.17 c= 81.60	010 100	1 1	17.17 9.94	001	1/10	8.16	terrestrial	GARDNER and APPLEMAN (1974)
"PO-10"	10	triclinic	a= 9.932 b= 17.216 c= 81.864 α= β= γ= 90	010 100	1 1	17.22 9.93	001	1/10	8.19	terrestrial Plumas County	KONNERT and APPLEMAN (1978)
PO-10	10	orthorhombic	a= 17.07 b= 9.81 c= 81.26	100 010	1 1	17.07 9.81	001	1/10	8.13	synth., hydroth. > 5 kbar	NUKUI et al. (1980)
PO-6	6	orthorhombic	a= 30.05 b= 52.08 c= 49.56	010 100	1/3 1/3	17.36 10.02	001	1/6	8.26	meteoritic Sideroph. Grimma	GOETZ (1962)

desig-nation	n[1]	crystal system, space group	cell constants [Å], [°]	orientations and dimensions[2] layer [uvw]	layer m	layer [Å]	stacking [uvw]	stacking m	stacking [Å]	specimen-type, stability	references
PO-6	6	orthorhombic	a= 5.01 b= 25.7 c= 48.6	010 100	2/3 2	17.13 10.02	001	5/3	8.10	terrestrial	SHAHID and GLASER (1970)
PO-5	5	orthorhombic	a= 9.91 b= 17.18 c= 40.78	010 100	1 1	17.18 9.91	001	1/5	8.16	terrestrial San Cristobal	LUKESH and BUERGER (1942)
PO-5 (M)	5	orthorhombic $C222_1$	a= 9.940 b= 17.21 c= 40.92	010 100	1 1	17.21 9.94	001	1/5	8.18	synthetic	SATO (1963)
PO-5	5	pseudoorthorh. $C222_1$	a= 17.21 b= 9.93 c= 40.91	100 010	1 1	17.21 9.93	001	1/5	8.18	terrestrial Kumamoto, Japan	NUKUI et al. (1980)
PO-2	2	orthorhombic	a= 9.96 b= 17.18 c= 16.29	010 100	1 1	17.18 9.96	001	1/2	8.15	terrestrial Gereszes, Hungary	GOETZ (1962)
PO-1	1	orthorhombic $C222_1$	a= 8.660 b= 4.999 c= 8.205	100 010	2 2	17.32 10.00	001	1	8.21	lunar Apollo 12	APPLEMAN and NISSEN (1971)
MX-1 (S_1)	1	monoclinic	a= 10.04 b= 17.28 c= 8.20 β= 91.50	010 100	1 1	17.28 10.04	001	1	8.20	synth., industr. < 60° - 75°C	SATO (1964)
MX-1 (T-1sa)	1	monoclinic	a= 5.007 b= 8.600 c= 8.218 β= 91.50	010 100	2 2/3	17.20 10.01	001	1	8.22	synthetic Na_2WO_4-flux	FLOERKE and LANGER (1972)
MX-1	2	monoclinic	a= 15.0256 b= 8.6006 c= 16.4343 β= 91.496	010 100	2 2/3	17.20 10.02	001	1/2	8.22	synthetic	HOFFMANN (priv. comm. 1983)

Table 1 (continued)

designation	n(1)	crystal system, space group	cell constants [Å], [°]	orientations and dimensions(2) layer [uvw]	layer m	layer [Å]	stacking [uvw]	stacking m	stacking [Å]	specimen-type stability	references
MC	6	monoclinic	a= 18.524 b= 5.0032 c= 23.810 β= 105.82	101 010	2/3 2	17.25 10.01	20$\bar{1}$	1/3	8.20	meteoritic Steinbach < 107°C	DOLLASE and BAUR (1976)
"MC"	4	monoclinic Aa or A2/a	a= 25.89 b= 5.00 c= 18.59 β= 117.7	100 010	2/3 2	17.26 10.00				terrestrial Japan	KAWAI (1978)
MC	6	monoclinic C2/c or Cc	a= 18.54 b= 4.99 c= 23.83 β= 105.65	101 010	2/3 2	17.30 9.98	20$\bar{1}$	1/3	8.20	meteoritic Steinbach and industrial < 107°C	DOLLASE and BUERGER (1966)
MC	4	monoclinic C2/c or Cc	a= 18.54 b= 5.01 c= 25.79 β= 117.67	001 010	2/3 2	17.19 10.02	301	1/2	8.21	synth., from Na_2WO_4 on quartz	HOFFMANN (1967)
MC	6	monoclinic C2/c or Cc	a= 18.52 b= 4.98 c= 23.79 β= 105.6	001 010	2/3 2	17.28 9.96	20$\bar{1}$	1/3	8.19	lunar	DOLLASE, CLIFF and WETHERILL (1971)
MC	4	monoclinic Cc	a= 18.494 b= 4.991 c= 25.832 β= 117.75	001 010	2/3 2	17.22 9.98	301	1/2	8.19	synth., hydroth. Na_2CO_3	KATO and NUKUI (1976)
OP (S_2)	1	orthorhombic	a= 10.04 b= 17.28 c= 8.20	010 100	1 1	17.28 10.04	001	1	8.20	synth., industr. (60-75)° - 115°C	SATO (1964)
"OP"	1	orthorhombic $P2_12_12_1$	a= 26.171 b= 4.986 c= 8.196	100 010	2/3 2	17.45 9.97	001	1	8.20	industrial 105° - 180°C	KIHARA (1977)

designation	n(1)	crystal system, space group	cell constants [Å], [°]	orientations and dimensions(2) layer [uvw]	m	[Å]	stacking [uvw]	m	[Å]	specimen-type stability	references
OS (S_3)		orthorhombic	dynamic structure from S_2 and S_4							synth., industr. 115° - 250°C	SATO (1964)
OS	1	orthorhombic $C222_1$	a= 65-95 b= 5.02 c= 8.18	100 010	4/15 2/11 2	17.33 17.27 10.04	001	1	8.18	synth., hydroth. Na_2CO_3 150° - 190°C	NUKUI (1978)
OC	1	orthorhombic	a= 8.74 b= 5.04 c= 8.24	100 010	2 2	17.48 10.08	001	1	8.24	meteoritic Steinbach 180° - 250°C	DOLLASE (1967)
HP	1	hexagonal $P6_3/mmc$	a= 5.05 c= 8.28	210 010	4 2	17.50 10.10	001	1	8.28	synth., hydroth. Na_2CO_3 > 380°C	NUKUI (1978)
HP	1	hexagonal $P6_3/mmc$	a= 5.03 c= 8.22	210 010	4 2	17.42 10.06	001	1	8.22	> 168°C	GIBBS (1927)
HP (S_4)	1	hexagonal	a= 5.046 c= 8.236	210 010	4 2	17.48 10.09	001	1	8.24	synth., hydroth. > 250°C	SATO (1964)
HP	1	hexagonal	a= 5.0519 c= 8.2689	210 010	4 2	17.50 10.10	001	1	8.27	synth., from Na_2WO_4 on quartz > 500°C	MISCHKE (1971)
"HP"	1	orthorhombic pseudohexag.	a= 8.75 b= 5.052 c= 8.27	100 010	2 2	17.50 10.14	001	1	8.27	industrial 420°C	KIHARA (1981)

Notes: (1) n=periodicity of stacking sequence based on the 2-layer stacking in HP (n = 1)

(2) orientation (in terms of respective crystal system) of three mutually orthogonal vectors in- and perpendicular to the layers of six-membered rings of SiO_4-tetrahedra. Vector dimensions refere to a stacking of 2 layers, each consisting of 2 times 4-rings.

m=factor, relating the length of the [uvw]-direction in the crystal cell to the length of the corresponding orthogonal vector.

the structural relationship between the various PO-types is not yet clear. To indicate the possibility of an interpretation of the 525 K transition reported for MX-1 (= S1) tridymite of SATO (1964), as being due to cristobalite, the same dP/dT as was found for the α-β-cristobalite transformation has been assigned to the (OP)(OS)(OC) versus HP boundary.

Finally, Figure 3d shows one possible combination of all the information available, taking into account the co-existence of several low-temperature forms. According to the observation that an increase in pressure transforms MC to MX-1, MX-1 has to be regarded as being (more)-metastable at one atmosphere with its real "stability" field at higher pressures. The reverse transformation of MX-1 to MC at slightly increased temperature further indicates the MX-1 is metastable at one atmosphere with respect to MC.

Suggestions for Future Work on Tridymite

It has been suggested by FLOERKE (1966, p. 405) that *all* tridymite growth starts from cristobalite nuclei. Thus, in addition to the tridymite data, the α-β-cristobalite phase boundary has been incorporated in Figures 3a and d. Under appropriate temperature (-pressure) conditions and presence of suitable impurities, the stacking sequence of the layers of six-membered rings of SiO_4-tetrahedra changes from cubic (ABCABCA... in cristobalite) to hexagonal (AC'AC'AC'... in tridymite). In view of the fact that MC-tridymite consists of $^2/_3$ D and $^1/_3$ O-rings and provided that all rings in the F1-tridymite (terrestrial) of KONNERT and APPLEMAN (1978) are really oval, it can be suggested that these forms represent growth on different cristobalite polymorph substrates, α-(only O-rings) and β-(only D-rings), respectively (see Figure 1). This implies that MC and F1-tridymite must have (a) different formation histories and (b) something of a memory. To further clarify the transitions among the tridymite polymorphs it is necessary to know about the crystal structure of MX-1 and PO, to understand their relationships to MC. Complete crystal structure refinements of these forms at temperature ranges covering the possible transitions shown in Figure 3 are also necessary. Likewise, complete crystal structure refinements at high pressures are needed to understand the possible relations among the PO-10 types, and in particular to determine whether to PO-10 (N) type found by NUKUI et al. (1980a) at high pressures has the same structure as the PO-10 type stable at room-temperature.

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