

Polymorphism of silica

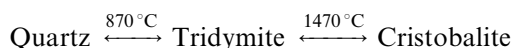
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A study of the stability relations of pure silica phases is described. It is shown that although cristobalite can be produced from pure quartz by heating it is not possible to produce tridymite in this fashion; a flux or mineralizer is required for tridymite formation and even in this case cristobalite is produced before any tridymite is observed. Thus it is concluded that the stability relations for the silica minerals proposed by Fenner are incorrect and that tridymite is not a stable phase in the pure silica system.

1. Introduction

Silica has three distinct crystalline forms at atmospheric pressure: quartz, cristobalite and tridymite. The stability ranges of these forms have been subject to many investigations but one of the earliest, and probably still most frequently quoted, is that of Fenner [1]. Using Na_2WO_4 as a flux, which he assumed would act as a catalyst, Fenner determined the following stability relations for quartz, cristobalite and tridymite:



In addition to questions, engendered by Fenner's use of a flux, about the temperatures at which the reconstructive transformations occur in the silica system, doubts have been raised as to whether tridymite is a stable phase in the pure silica system. In particular it has been suggested that the more open structure of tridymite, which can readily accommodate atoms such as sodium or potassium, actually requires the presence of such impurities for stability (see, for example, [2–7]).

In this paper we describe a study of the reconstructive transformations of the silica polymorphs in the pure silica system; the transformations were carried out by the application of heat alone and by heating in the presence of a flux. Particular attention is paid to whether tridymite forms and thus whether the stability relationships proposed by Fenner are correct or whether alternative relationships are required to describe the silica system.

2. Background

The basic structural unit of all the silica polymorphs is a tetrahedron composed of four oxygen atoms with a silicon atom at the centre. The tetrahedra are linked at the corners with each oxygen atom being common to two tetrahedra resulting in continuous structures in which every silicon atom is linked through an oxygen atom. In the high temperature forms of cristobalite

and tridymite, the oxygen atoms are arranged in the manner of cubic and hexagonal close packing, respectively, although these are open structures, hence the low densities (around 2.3 g cm^{-3}) of cristobalite and tridymite. In quartz, on the other hand, the tetrahedra are more closely packed in a spiral formation leading to a higher density (2.65 g cm^{-3}). Cristobalite and tridymite are polytypes with cristobalite being represented by a three layer stacking sequence ABCABC... whereas tridymite has a two layer stacking sequence AC'AC'..., where C' is related to C by a rotation of 180° . The fundamental units of these layers are 6-membered puckered rings of corner-sharing tetrahedra pointing alternatively up and down [8]. Quartz, cristobalite and tridymite all have high and low temperature forms. Thus as well as the reconstructive transformations between the three polymorphs they all undergo displacive transformations between these low and high temperature forms on heating and cooling. The low temperature forms are simply distorted versions of the high temperature forms in which the Si–O–Si bond angle decreases, while the silicon atoms remain in tetrahedral sites with respect to the oxygen atoms.

If cristobalite is formed at high temperatures then the idealized three layer structure is produced; however, two layer stacking sequences may occur in addition to the three layer structure in cristobalite produced at lower temperatures which results in disorder in the structure. The phase produced may be referred to as disordered cristobalite, C_D , or disordered tridymite, T_D , depending on which of the stacking sequences is most prevalent [9].

The structure of tridymite depends on the origin of the samples [10]. Varying degrees of stacking disorder can occur, resulting in line broadening, differing reflection profiles, peak shifts and changes in intensity of X-ray diffraction (XRD) peaks [11]. Coexistence and intergrowth of tridymite and cristobalite in the same crystal is also possible [12, 13].

Because cristobalite and tridymite have more open structures than quartz there are voids in the structure which are large enough to accommodate atoms such

as sodium, potassium or calcium [3]. These atoms may help to stabilize the structure and some authors have suggested that tridymite cannot exist without these stabilizing atoms. For example Buerger and co-worker [2, 3] stated that naturally occurring tridymite is not a pure form of silica and that its chemical formula is $\text{NaCaAl}_3\text{Si}_{15}\text{O}_{36}$.

Flörke [4] (and in a paper reviewed by Eitel [5]) suggested that tridymite only became stable in the presence of foreign ions such as Na^+ , Ca^{2+} and Al^{3+} . This conclusion was based on structural considerations; electrolytic removal of impurities in synthetic tridymite produced quartz below 1050°C and cristobalite above 1050°C ; and the fact that tridymite had never been prepared in the absence of mineralizers.

Alternatively, Hill and Roy [14] have suggested that there are two forms of tridymite; the metastable form (tridymite-M) only being able to convert to the stable form (tridymite-S) via cristobalite. Hill and Roy reported successful preparation of both of these forms of tridymite, as well as a third, less well characterized unstable phase called tridymite-U. However, a small amount of water (< 3 mol %) may have been present to stabilize the tridymite structure.

In a thermodynamic analysis of the possible transformations of the silica minerals, Holmquist [6] agreed with Flörke that the mineral tridymite is not a stable phase of pure silica at one atmosphere but belongs in the binary and multicomponent systems. Holmquist repeated Flörke's electrolysis experiment at 1350°C and found that after 12 h electrolysis with 200 V d.c., the anode section of the sample was completely converted to cristobalite, whilst the cathode section contained tridymite and some cristobalite. Holmquist assumed that the hydrothermal preparation of tridymite was due to the presence of the hydroxonium ion, H_3O^+ ; hydroxonium ions can replace Na^+ ions in soda-silica glasses [15].

In a later study Holmquist [7] found experimentally that without the presence of an alkali oxide no tridymite was formed. In addition, even in the presence of an alkali oxide, quartz converted directly to tridymite only in a very narrow temperature range; at temperatures above $898 \pm 5^\circ\text{C}$ cristobalite formed first as an intermediate phase. Flörke and Schneider [9] found that under solid state conditions, tridymite never nucleated directly from quartz but always from cristobalite nuclei.

From the published literature it would seem that tridymite may not be a stable phase in the pure silica system. All reported incidences of its preparation are in the presence of some impurity, be it alkali ions from a mineralizer or hydroxonium ions from water; it has therefore been suggested that such impurities are necessary to stabilize the tridymite structure. In spite of these reports, the reaction sequence and even the temperatures of conversion of the polymorphs given by Fenner are still frequently quoted in books and the scientific literature (see, for example, [16–18]). It seems to be timely, therefore, to re-investigate the high temperature conversion of quartz.

TABLE I Impurity levels in Iota quartz (data provided by suppliers)

Element	Maximum amount (p.p.m)	Typical amount (p.p.m)
Al	25	20
Li	2.0	1.0
Na	2.0	1.0
Fe	2.0	0.9
K	2.0	0.9
Ca	2.0	0.7
Cu	0.1	< 0.08
Cr	0.01	< 0.01

3. Experimental details

Iota quartz (Unimin Corporation, USA), which is a very pure form of quartz with a maximum of 35 p.p.m. impurities (see Table I) was used throughout the study described in this paper.

3.1. Firing of pure quartz samples

50–100 g of unground Iota quartz contained in an alumina crucible was heated at 5°C min^{-1} to a given soaking temperature between 1100 and 1600°C . The soak temperature was maintained for a prescribed time ranging between 1 and 50 h, except in the 1100°C case where a dwell time of 350 h was used, after which the sample was furnace cooled at 3°C min^{-1} to room temperature. Some preliminary experiments indicated the importance of controlled cooling: samples simply cooled at the natural rate of the furnace were found to contain much less cristobalite than samples fired at the same temperature but cooled at a controlled rate. At temperatures below 500°C the cooling rate will have been slower than that specified, as in this temperature range the natural cooling rate of the furnace, which determines the maximum cooling rate obtainable, was slower than 3°C min^{-1} . The temperature of the furnace was checked using a Pt/Pt:Rh 13% thermocouple connected to a microcomputer thermometer (Jenco Electronics Ltd., model 700H). The furnace temperature was found to be always within 6°C of the programmed temperature over the 15 cm range in the centre of the furnace within which all the samples were fired.

3.2. Firing of pure quartz samples in the presence of a mineralizer

Samples were prepared using 0.10, 0.25, 0.50 and 1.00 wt % sodium carbonate as a mineralizer. The appropriate weight per cent of the mineralizer was accurately weighed and finely ground with a small amount of unground Iota quartz before being thoroughly mixed with the remaining Iota quartz necessary to make the sample up to the required weight (normally 50 g). The prepared samples were placed in alumina crucibles and heated at 5°C min^{-1} up to a given soaking temperature between 1100 and 1600°C . The soak temperature was maintained for a prescribed time ranging between 1 and 50 h, after

which they were furnace cooled at $3\text{ }^{\circ}\text{C min}^{-1}$ to room temperature. In the same fashion a limited set of samples was prepared with 0.50 and 1.00 wt % potassium carbonate as a mineralizer.

3.3. Characterization techniques

The products from all firings were examined by powder X-ray diffraction (XRD) using a Philips PW1050 diffractometer with CuK_{α} radiation. The majority of the data was collected using an IBM compatible PC running the Sietronics SIE122D XRD package but some early data was collected via a chart recorder. In the latter case only peak heights have been recorded whereas in the former peak area data were also obtained. Samples were prepared by placing 2 g of the fired sample in a mechanical pestle and mortar and grinding for 20 min. To minimize any orientation effects XRD plates were back-filled with the ground powder and they were scanned at $0.25^{\circ} 2\theta \text{ min}^{-1}$.

The amounts of quartz and cristobalite present in the fired samples were estimated using a direct comparison technique similar to that described by Chaklader [19] and described more fully below. This method may be used for samples which only contain polymorphs of one phase as the mass absorption coefficient will be identical for each polymorph and thus the peak areas for a given polymorph will be identical for each polymorph and thus the peak areas for a given polymorph will be proportional to the amount of this polymorph that is present. Although the addition of a mineralizer to some of the samples will alter the mass absorption coefficient slightly, the error introduced by assuming it to be the same for all samples is $< 1\%$, even for a sample containing 5% mineralizer (which is not considered here).

The direct comparison technique depends on having reference materials of known purity; for quartz unfired Iota quartz was used as a standard and the 0.3340 nm peak in the sample was compared with the same peak in the standard. Two different standard cristobalites were examined: the DIN standard reference material and the US standard reference material (supplied by Dr P. Watkins of Hepworth Minerals). The US standard material was found to give considerably higher peak intensities than the DIN standard material and was therefore used as the cristobalite standard. A sample of this cristobalite was run with every set of XRD samples, so that the XRD data were always normalized by data collected under the same conditions at the same time thus minimizing the effect of any variations in the equipment set-up over time. The weight percentage of cristobalite in the fired samples was calculated by comparison of the peak height and peak area of the 0.2841 nm peak in the sample with that of the same peak in the US standard. Despite attempts to obtain a pure sample of tridymite to use as a standard material from sources thought likely to have such a sample, the authors have only managed to obtain one sample from the Natural History Museum, London, which was too small for quantitative XRD. Quantitative determinations of the amount of tridymite present in a given sample were therefore not

possible and the height of the (4 0 2) peak at 0.3818 nm only has been recorded. This peak height has been normalized by comparison with the peak height of the 0.2841 nm peak in the cristobalite standard, run at the same time to ensure that the relative tridymite peak heights are comparable even though absolute percentages of tridymite could not be obtained.

The products were also examined by differential scanning calorimetry (DSC) using a DuPont 2000 DSC connected to a PC. In each case finely powdered samples, of mass 5.0 ± 0.2 mg, were weighed into aluminium sample pans and covered with an aluminium lid. The covered pan was compressed to form a flat disc. The samples were heated, in an atmosphere of flowing nitrogen, at a rate of $10^{\circ}\text{C min}^{-1}$ to 600°C . They were maintained at 600°C for 10 min and then cooled at the same rate.

4. Results

4.1. Pure quartz

The only crystalline phases detected in the fired samples by XRD were quartz and cristobalite; no tridymite was detected. Higher firing temperatures and longer firing times were found to result in greater conversion of quartz to cristobalite. The results are summarized in Table II. The percentage of cristobalite was calculated using both peak height and peak area. The two calculations give different results when the peaks in the fired material are broader than those in the US standard reference material. It can be seen from Table II that samples fired at 1400 and 1500°C in particular have broader cristobalite peaks than the US reference material.

In addition to quartz and cristobalite peaks some small additional peaks were seen in some samples. These corresponded to *d*-spacings of approximately 0.3215 and 0.2380 nm. These additional peaks were not observed in the unfired quartz. Although the

TABLE II Percentage of quartz and cristobalite in fired samples of unground quartz

Firing temperature ($^{\circ}\text{C}$)	Dwell time (h)	% Quartz	% Cristobalite peak	
			height	area
1100	350	118	0	0
1300	50	125	0	0
	1	84	7.6	12
1400	5	58	17.5	25
	50	6	36	48
1500	1	55	29	37
	5	36	39	47
	15	14	66	74
1600	1	1-2	77	81
	3	0	73	91
	5	0	77	89
	15	0	102	101
	50	0	88	92
1700	15	0	99	99

TABLE III Percentages of quartz, cristobalite and tridymite in samples fired at 1100 °C with sodium carbonate as a mineralizer

% Na ₂ CO ₃	Dwell time (h)	% Quartz	% Cristobalite peak		Tridymite peak height
			height	area	
0.10	1	107	1.5	1.7	0
	5	44	26	32	2
	15	24	37	49	4
	50	20	33	42	8
0.25	1	112	6.5	7	0
	5	34	31	40	6
	15	18	33	51	7
	50	9	37	44	16
0.50	1	95	8	9	0
	5	52	27	32	9
	15	9	29	44	20
	50	18	25.5	31	30
1.00	1	91	12.5	13	0.5
	5	36	25	31	18
	15	11	26	26	31
	50	5	17	42	42

TABLE IV Percentages of quartz, cristobalite and tridymite in samples fired at 1300 °C with sodium carbonate as a mineralizer

% Na ₂ CO ₃	Dwell time (h)	% Quartz	% Cristobalite peak		Tridymite peak height
			height	area	
0.5	15	< 1	40	48	30
1.0	15	0	19	23	48

intensities of these additional peaks were in all cases low they were greater in samples fired at lower temperatures. In general, samples showing these anomalous peaks had cristobalite peaks that were broader than those in the US standard reference material.

The XRD results were confirmed by the DSC results. No cristobalite inversions were observed in the samples fired at 1100 and 1300 °C and no tridymite inversions were observed in any of the samples [20].

4.2. Quartz heated in the presence of sodium carbonate

All the samples fired at 1100 °C contained some residual quartz and in some of the samples fired for very short times the calculated per cent was greater than 100, even though some cristobalite had formed (see Table III). Although this may be due in part to experimental error it is thought that it is mainly due to the crystallization of some previously glassy material in the unfired Iota quartz. In general the percentage of cristobalite formed with increasing dwell times increased for dwell times up to 15 h and thereafter decreased. The tridymite peak height showed a steady increase with dwell time for all percentages of mineralizer with a maximum amount of tridymite being formed in the sample fired for the longest time (50 h) with the highest addition (1 wt %) sodium carbonate.

In addition to the XRD peaks normally associated with quartz, cristobalite and tridymite small anomalous XRD peaks were again observed corresponding to *d*-spacings of 0.3215 and 0.2380 nm. Strictly speak-

ing there is a very small peak associated with tridymite at 0.3215 nm but the peaks observed at 0.3215 nm were anomalously large given the amounts of tridymite present. The peaks were only observed in samples where an appreciable amount of quartz had been transformed.

After firing for 15 h at 1300 °C very little quartz remained in the samples (Table IV). Although this temperature is well within the tridymite stability range determined by Fenner, both cristobalite and tridymite were present in appreciable amounts. As shown in Table V, after heating at 1400 °C little or no quartz remained even after dwell times of only 1 h. Again both cristobalite and tridymite were formed and those samples fired with greater percentages of mineralizer contained less cristobalite and more tridymite. Samples fired at 1400 °C with 0.5 and 1% mineralizer contained steadily decreasing amounts of cristobalite and increasing amounts of tridymite with increasing dwell times. However, samples fired at 1400 °C with 0.1 and 0.25% mineralizer showed the opposite trend of steadily increasing cristobalite percentages with increasing dwell time. In these cases the tridymite peak heights increased with dwell times up to 15 hours and showed a sharp decrease after firing for 50 h. All of the samples fired at 1400 °C had the additional XRD peaks described above.

The data given in Table VI show that after firing for 15 h at 1500 °C no quartz was found in any sample and that tridymite was observed in all of them. As the amount of mineralizer increased from 0.5 to 5%, there was again a reduction in the amount of cristobalite

TABLE V Percentages of quartz, cristobalite and tridymite in samples fired at 1400 °C with sodium carbonate as a mineralizer

% Na ₂ CO ₃	Dwell time (h)	% Quartz	% Cristobalite peak		Tridymite peak height
			height	area	
0.10	1	6	45	55	5
	5	< 1	54	71	7
	15	< 1	56	67	8
	50	< 1	67	78	2
0.25	1	< 3	49	–	10
	5	0	58	70	13
	15	< 1	56	66	21
	50	0	67	78	2
0.50	1	< 1	46	–	21
	5	< 1	43	–	32
	15	0	40	46	35
	50	0	37	42	39
1.00	1	< 1	30.5	–	39
	5	0	25	–	44
	15	0	24	31	50
	50	0	20	25	51

TABLE VI Percentages of quartz, cristobalite and tridymite in samples fired at 1500 °C with sodium carbonate as a mineralizer

% Na ₂ CO ₃	Dwell time (h)	% Quartz	% Cristobalite peak		Tridymite peak height
			height	area	
0.5	15	0	86	88	5
1.0	15	0	80	79	13
5.0	15	0	50	50	31

TABLE VII Percentages of quartz, cristobalite and tridymite in samples fired at 1600 °C with sodium carbonate as a mineralizer

% Na ₂ CO ₃	Dwell time (h)	% Quartz	% Cristobalite peak		Tridymite peak height
			height	area	
0.10	1	< 1	85	88	0
	5	0	88	91	0
	15	0	92	99	0
0.25	1	0	85	95	0
	5	0	89	91	0
	15	0	96	100	0
0.50	1	0	80	86	3
	5	0	83	88	1
	15	0	88	96	0
1.00	15	0	102	96	2.5

obtained and an increase in the amount of tridymite. All these samples had an additional XRD peak at around 0.2380 nm and the samples fired with 1 and 5% mineralizer also had a small additional peak at 0.2644 nm. With these samples the peak at 0.3215 nm was not anomalously large for the amounts of tridymite that were present. The additional peaks were larger for the sample fired with 5% than that fired with 1% mineralizer.

Much more cristobalite was formed at 1600 °C than at any of the other temperatures, although there was a significant shortfall in crystalline material in samples fired for shorter time periods (see Table VII). The

amounts of cristobalite measured by peak height and peak area were generally very similar. In general no tridymite was observed in these samples, although there were slight traces for samples fired with 0.5 and 1% mineralizer. No additional XRD peaks were observed in these samples.

The phases detected by DSC were consistent with those detected by XRD. In addition to the cristobalite and quartz inversions seen in the samples fired without a mineralizer, endotherms due to the tridymite inversions were also seen in many of the samples which had been found to contain tridymite by XRD [20].

TABLE VIII Percentages of quartz, cristobalite and tridymite in samples fired at various temperatures with potassium carbonate as a mineralizer

Firing temperature (°C)	% K ₂ CO ₃	Dwell time (h)	% Quartz	% Cristobalite peak		Tridymite peak height
				height	area	
1300	0.5	50	0	35	42	32
	1.0	50	0	21	25	52
1400	0.5	50	0	39	–	41
	1.0	50	0	12	–	60
1500	0.5	15	0	73	–	15
1600	0.5	15	0	90	90	0
	1.0	15	0	94	87	0.5

4.3. Quartz heated in the presence of potassium carbonate

The XRD results obtained using potassium carbonate as a mineralizer after firing Iota quartz at four temperatures between 1300 and 1600 °C are given in Table VIII. It can be seen that the percentages of cristobalite observed were very similar to those obtained with samples fired with sodium carbonate (see Tables IV–VII). The tridymite peak heights were slightly higher for the samples fired with potassium carbonate. The presence of both cristobalite and tridymite in the samples fired at 1300, 1400 and 1500 °C was confirmed by observation of the appropriate inversions using DSC.

5. Discussion

There are obviously significant differences between samples fired with and without the addition of the alkali carbonate mineralizer. As tridymite was formed only when a mineralizer was present, this study offers further support to the hypothesis that tridymite is not a stable phase in the pure silica system. In addition samples produced by firing at lower temperatures or for shorter time periods tended to have broader XRD peaks, which indicates that at least some of the cristobalite in these samples was disordered.

After firing pure quartz at 1100 °C, no transformation to either cristobalite or tridymite was observed in disagreement with Fenner's [1] assertion that quartz is converted into tridymite at temperatures above 870 °C. However, when small amounts of mineralizer were added (down to as little as 0.1 wt %) there was a reduction in quartz content, even after a dwell period of only 1 h and both cristobalite and tridymite were formed. The amount of tridymite formed increased with increasing dwell time, whereas the amount of cristobalite formed tended to be greater after 15 h than after 50 h firing (Table III). These observations suggest that not only tridymite is the stable phase at 1100 °C in the presence of >0.1 wt % sodium carbonate, but also that quartz transforms to tridymite via cristobalite. These conclusions are in agreement with the proposals of Holmquist [7].

At 1400 °C the equilibrium composition depended considerably on the amount of mineralizer used (Table V). Small amounts (0.1 and 0.25 wt %) gave only small amounts of tridymite and high cristobalite

contents. As the content of mineralizer was increased, the cristobalite content decreased and much more tridymite was observed. These results imply that for mineralizer contents of 0.5 wt % and greater tridymite is the stable phase but again it is produced via cristobalite as a transition phase.

1500 °C is within the cristobalite stability range proposed by Fenner. For small amounts of mineralizer cristobalite was the dominant phase formed, but when the amount of mineralizer was increased to 5 wt % a reduced amount of cristobalite was observed and a large amount of tridymite was formed (Table VI). The tridymite may have been formed on cooling through its stability range rather than directly by firing. The close agreement in the peak height and peak area results indicates that the cristobalite formed at 1500 °C was well ordered.

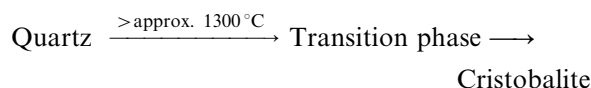
At 1600 °C almost all the crystalline material was cristobalite but small amounts of tridymite were observed in the presence of 0.5 and 1 wt % sodium carbonate. Since the amount of tridymite decreased after longer periods of firing with 0.5 wt % sodium carbonate (Table VII), cristobalite is confirmed to be the stable polymorph at 1600 °C.

Although a full study of the transformations in the presence of a potassium carbonate mineralizer was not undertaken those results that were obtained with potassium carbonate point to it having a very similar effect to sodium carbonate.

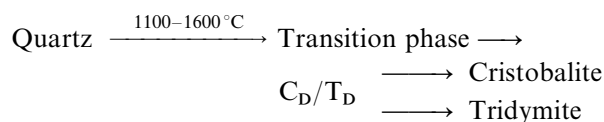
With the exception of samples fired to 1600 and 1700 °C for 15 h the total amount of crystalline material (% quartz plus % cristobalite by peak area) was less than 100%. This apparent loss of crystalline material must be due to the retention of some non-crystalline transition phase on cooling from high temperature. The conversion of quartz to cristobalite is widely believed to occur via an amorphous transition phase [21] and Chaklader and Roberts [22] have reported that it can account for up to 25 wt % of the silica present. The shortfall in crystalline material was generally greater for samples fired at lower temperatures, which may be a kinetic effect caused by the lower rates of reaction at lower temperatures, or it may indicate greater stability of the non-crystalline phase at lower temperatures.

Marians and Hobbs [23] have made a topological study of the structure of silica polymorphs. They

describe the silica polymorphs in terms of local clusters which are irreducible descriptions of the environment around an individual SiO₄ tetrahedron. The local cluster for quartz contains 63 silica tetrahedra, cristobalite 29 and tridymite 27. Based on these local clusters Marians and Hobbs have shown that for the conversion of quartz to cristobalite roughly one third of all the bonds must be broken and reformed. Marians and Hobbs have also noted that the interchange of just one pair of bonds in quartz is stable against recrystallization and that therefore any subsequent bond breaking, unless it happens to involve the original bonds, will tend to drive quartz further from the crystalline state. Therefore the transformation of quartz to cristobalite via a disordered state would be more likely than a direct transformation of quartz to cristobalite. Hence for pure silica the stability relationship is:



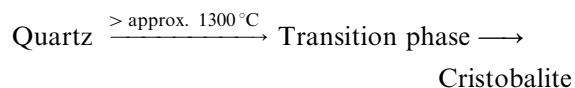
Although Marians and Hobbs only considered the transformation of quartz to cristobalite and also assumed that tridymite is a polymorph of pure silica, it is clear from the size of the local clusters that converting quartz to tridymite will actually be slightly more difficult than converting quartz to cristobalite (more bonds will have to be broken and reformed). It should, however, be less difficult to convert cristobalite to tridymite as fewer bonds have to be broken and reformed and thus more restricted atomic movements are required [16]. The fact that tridymite does not then form in the pure silica system indicates that alkalis are required to stabilize the tridymite structure. As the cristobalite and tridymite structures are relatively closely related it would not be surprising that the cristobalite first formed in the presence of an alkali was actually relatively disordered and contained a number of tridymite stacking faults, presumably in regions of high alkali concentration. This disordered cristobalite/tridymite structure then converts to true cristobalite or tridymite depending on the temperature and alkali concentration. This is summed up in the following stability relationships:



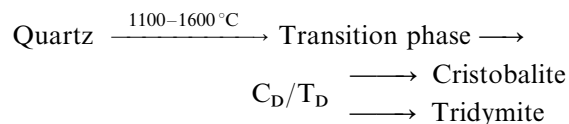
6. Conclusions

The results obtained in this study confirm the belief that tridymite is not a stable phase in the pure silica system, since no tridymite was detected in any sample prepared by firing very pure, Iota quartz to temperatures between 1100 and 1700°C, inclusively. Cristobalite formation only occurred for firing temperatures of 1400°C and above with a more rapid transformation at higher temperatures. The cristobalite formed at 1400 and 1500°C was disordered. Transformation, therefore, seems to occur via a non-crystalline tran-

sition phase. Thus the stability relation for the pure silica system should be written:



If either sodium carbonate or potassium carbonate is used as a mineralizer then tridymite can be formed and the stability relations become:



Thus the stability relations proposed by Fenner [1] require modification. In particular they do not apply to the pure silica system as tridymite is not a stable phase in this system.

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