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Characterisation of fired silicas

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Abstract

The products produced by firing a very pure quartz and a commercial purity quartz, with and without a mineral additive, to temperatures between 1100°C and 1700°C have been studied by DSC. The temperature at which the cristobalite α–β inversion occurred and the degree of hysteresis observed on heating and cooling were both dependent on the sample history. The highest inversion temperature and greatest degree of hysteresis on heating and cooling were obtained with pure quartz samples heated at 1600°C or 1700°C. Products produced by firing finely ground pure quartz had a lower inversion temperature and less hysteresis than coarse grained samples. If a mineral additive was present tridymite inversions were also observed. Firing of the commercial purity quartz at a given temperature led to cristobalites with lower inversion temperatures and less hysteresis. The variations in inversion temperature and hysteresis are probably related to the degree of order in the cristobalite structure with the most highly ordered material having the highest inversion temperature and greatest degree of hysteresis. © 1998 Elsevier Science B.V.

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1. Introduction

Three distinct crystalline forms of silica are recognised at atmospheric pressure: quartz, cristobalite and tridymite. All three of the silica polymorphs also have high and low temperature forms; the low temperature forms are simply distorted versions of the high temperature forms. Silica polymorphs therefore undergo reversible displacive transformations between their high and low temperature forms as well as reconstructive transformations from one polymorph to another.

Although tridymite is often assumed to be a polymorph of pure silica (see, for example, [1–4]) a number of authors have suggested that impurities, such as sodium and potassium [5–9] or even hydroxonium ions [10], are required to stabilise the relatively open structure of tridymite. Using X-ray diffraction (XRD) to study the products produced on firing pure quartz, with and without a mineral additive, we have concluded that tridymite is not a stable form in the pure silica system [11]. We have also concluded that the stability relations for the pure silica system should be written as

$$\textbf{Quartz} \xrightarrow{>\text{approx.}1300^\circ\text{C}} \textbf{Transition phase} \longrightarrow \textbf{Cristobalite.}$$

The transition phase was shown to be amorphous. If, however, either sodium or potassium ions are present, then tridymite can be formed and the stability relations become:

$$\text{Quartz} \xrightarrow{1100\text{–}1600^\circ\text{C}} \text{Transition phase} \longrightarrow \mathrm{C_D}/\mathrm{T_D} \begin{array}{l} \longrightarrow \text{Cristobalite} \\ \longrightarrow \text{Tridymite} \end{array} .$$

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where C_D and T_D are disordered cristobalite and disordered tridymite, respectively [11]. Well ordered cristobalite has a three layer stacking sequence ABCABC... whereas tridymite has a two layer stacking sequence; AC′AC′...; C′ is related to C by a rotation of 180°. The fundamental units of the layers are six-membered puckered rings of corner-sharing SiO_4 tetrahedra that point alternatively up and down [12]. Disordered forms of cristobalite may contain two layer stacking sequences rather than the three layer sequence and are referred to as disordered cristobalite or disordered tridymite depending on which of the stacking sequences is most prevalent [13]. Co-existence and intergrowth of tridymite and cristobalite in the same crystal is also possible [14,15].

Firing of quartz may, therefore, lead to the production of either ordered or disordered cristobalite and, if a suitable alkali ion is present, tridymite. We have previously shown that the temperatures at which the displacive transformations between high and low temperature forms of cristobalite occur are affected by the firing history, and therefore by implication the degree of crystalline order in the sample being examined [16]. In this paper we describe in detail the effects of firing history on the displacive transformations in cristobalites and tridymites obtained by firing (a) pure quartz and (b) a commercial purity quartz, with and without addition of a mineral additive. We also consider the effect of particle size on the observed displacive transformation temperatures.

2. Experimental

Two principal sources of quartz were used in the work described in this paper: Iota quartz (Unimin Corporation, USA) and a commercial quartz supplied by Specialist Refractory Services. Iota quartz is a very pure form of quartz with a maximum of 35 ppm impurities (see Table 1). Some additional experiments have been undertaken using Loch Aline sand, which has a maximum of 500 ppm impurities. The impurity levels in the commercial quartz are given in Table 2.

In order to assess the effect of particle size on the reconstructive transformations, Iota quartz was hand ground in an agate mortar and pestle to achieve six different mean particle sizes: 163, 113, 69, 58, 49 and 32 μm. The mean particle size was measured using a Coulter LS130 particle size analyser. To eliminate, as far as possible, any differences in the reaction rate that might arise from differences in particle size distribution between the Iota quartz and commercial quartz the latter quartz was separated into various size fractions and then the sample reassembled with an appropriate amount of each particle size to match the size distribution of the Iota quartz, which had previously been classified by sieving (see Table 3).

All three types of quartz studied were fired, with or without a mineral additive, at a range of temperatures.

Table 1
Impurity levels in Iota quartz (data provided by suppliers)

Element	Maximum amount/(ppm)	Typical amount/(ppm)
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

Table 2
Typical impurity content of the as supplied commercial quartz (data provided by suppliers)

Oxide	Maximum amount/(%)	Typical amount /(%)
Al_2O_3	0.90	0.65
K_2O	0.55	0.35
TiO_2	0.10	0.07
Na_2O	0.10	0.04
Fe_2O_3	0.035	0.029
Cr_2O_3	0.0007	0.0005
Loss on ignition	0.25	0.20

Table 3
Particle size distribution of Iota quartz (data obtained by sieving)

Size range/(μm)	Percentage passing sieve size (%)
>250	22.2
150–250	57.2
75–150	19.2
53–75	0.3
<53	1.1

If no mineral additive was present 50–100 g of quartz was placed in an alumina crucible and heated at 5°C min^{-1} to a soak temperature between 1100°C and 1700°C. The ground Iota quartz samples were only fired to soaking temperatures of either 1500°C or 1600°C. The soak temperature was maintained for a prescribed time ranging between 1 and 50 h, except in the 1100°C case when a dwell time of 350 h was used, after which the sample was furnace cooled at 3°C min^{-1} to room temperature; preliminary experiments indicated that samples simply cooled at the natural rate of the furnace contained less cristobalite than samples fired at the same temperature but cooled at the controlled rate. At temperatures below 500°C the cooling rate was slower than that specified, because in this temperature range the natural cooling rate of the furnace, which determines the maximum cooling rate obtainable, was less 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, 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.

Samples were also prepared using 0.10, 0.25, 0.50 and 1.00 wt.% sodium carbonate as a mineral additive. The appropriate weight percent of the mineral additive was accurately weighed and finely ground with a small amount of the quartz sample before being thoroughly mixed with the remaining quartz necessary to make the sample 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 soak temperature between 1100°C and 1600°C. Again the soak temperature was maintained for a prescribed time ranging between 1 and 50 h, after which they were furnace cooled at 3°C min^{-1} to room temperature.

After firing, the products were assessed using differential scanning calorimetry (DSC) and XRD. The DSC studies were undertaken using a DuPont 2000 DSC connected to a PC. In each case finely powdered samples, of mass 5.0±0.2 mg, were weighed in aluminium sample pans and covered with an aluminium lid. The covered pan was compressed to form a flat disc. The samples were heated, into an atmosphere of flowing nitrogen, at a rate of 0°C min^{-1} to 600°C. They were maintained at 600°C for 10 min and then cooled at the same rate. The XRD studies were carried out using a Philips PW1050 diffractometer with CuK$_\alpha$ radiation. 2 g of the fired material was ground for 20 min in a mechanical pestle and mortar. The XRD plates were back-filled with the ground powder and scanned at 0.25°2θ min^{-1}.

As all the samples investigated here only contained polymorphs of silica, the mass absorption coefficients of all the XRD samples could be assumed to be the same; the mass absorption coefficient is not affected by whether the silica is present as quartz or cristobalite. Although mineral additives and impurities will alter the mass absorption coefficient slightly, the error introduced, even if 5% of the mineral additive were present, is <1%. Therefore, a direct comparison technique was used to estimate the amounts of quartz and cristobalite that were present in each sample. Unfired Iota quartz was used as the quartz standard and the 0.3340 nm peak in the sample was compared with the same peak in the standard. The US standard cristobalite was used as the cristobalite standard; the 0.2841 nm peak in the sample was compared with the same peak in the standard. Fuller details of the XRD measurements and detailed results of the measurements have been reported elsewhere [11].

3. Results and discussion

3.1. High purity quartz fired without a mineral additive

No tridymite inversions were detected in any of the samples of pure Iota quartz fired without a mineral additive. No cristobalite inversions were observed in samples fired at 1100°C and 1300°C. These results are consistent with those obtained by XRD [11]. Similarly when Loch Aline sand was fired without a mineral additive no tridymite inversions were detected in any sample and no cristobalite was produced when the firing temperature was 1300°C or less. The quartz inversion temperature varied very little from one sample to another and occurred at 572±1°C on heating. The cristobalite inversion temperature however varied with firing temperature, dwell time and the particle size of the initial quartz. Some samples had more than one maximum to the cristobalite inversion peak. The appearance of the endotherms due to the

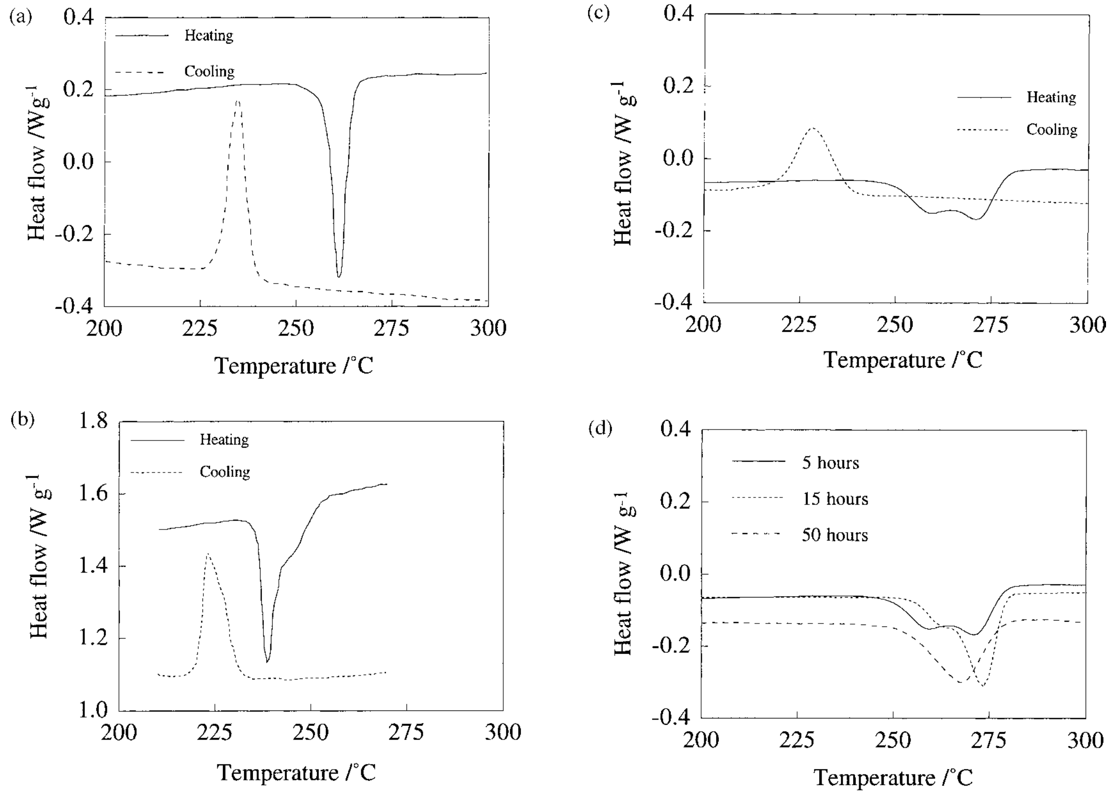

Fig. 1. DSC traces for samples of cristobalite prepared from pure Iota quartz (a) ground to a mean particle size of 163 μm and fired at 1600°C for 15 h; (b) ground to a mean particle size of 69 μm and fired at 1600°C for 15 h; (c) as supplied and fired at 1600°C for 5 h; (d) as supplied and fired at 1600°C for 5, 15 and 50 h.

cristobalite α–β inversion can be seen in Fig. 1. A single peak (Fig. 1(a)); or a single peak with a shoulder on one side (Fig. 1(b)) or a double peak (Fig. 1(c)) were all observed. The shoulder was sometimes observed on the high temperature side of the main peak as in Fig. 1(b), or on the low temperature side as in Fig. 1(d) (sample heated for 15 h).

The detailed nature of the cristobalite inversion depended on both the firing temperature and duration. The effects of firing duration at 1600°C are shown in Fig. 1(d). After only 5 h firing at 1600°C a double peaked cristobalite inversion was observed whereas after 15 h firing at 1600°C a single peaked inversion with a shoulder on the low temperature side was observed. An increase in the firing time to 50 h led to a single peaked cristobalite inversion. It should be noted that although all the peaks appear to be broad this is in part a reflection of the expanded temperature scale used in these figures.

Fig. 1(a) and (b) also show the effect of grinding the Iota quartz on the α–β inversion of the resulting cristobalite. Smaller particle sizes lead to cristobalites with lower inversion temperatures, a smaller degree of hysteresis and broader inversion peaks. In addition XRD showed that there was a greater shortfall in crystalline material when the Iota quartz was ground before firing (see Table 4). This result supports Chaklader's suggestion [17], that the amorphous intermediate phase is more readily formed when a fine starting material is used and that there is an increased sintering of the amorphous phase with fine particles which reduces the rate of conversion of the amorphous phase to cristobalite.

Cristobalites formed from pure quartz at high temperatures (1600°C and 1700°C) have the highest inversion temperatures on heating and the greatest hysteresis (see Fig. 2(a)). The correlation between the degree of hysteresis and the inversion temperature

Table 4
Percentage shortfall in crystalline material from quantitative XRD in Iota quartz samples fired for 15 h

Mean quartz particle size/(μm)	Firing temperature	
	1500°C	1600°C
	Percentage of non-crystalline phases	
163	23	13
113	23	6
69	25	—
58	22	12
49	28	10
32	26	16
Unground	12	0

on heating can be seen for all the Iota quartz samples studied and is summarised in Fig. 2(b). In addition the cristobalites with the highest inversion temperatures on heating tended to have narrower XRD peaks [11]. This indicates that cristobalite samples with the highest inversion temperatures are the most highly ordered: displacive transformations are co-operative phenomena and hence the most highly ordered structures are the most stable and require the greatest driving force to produce the transformation. Highly ordered cristobalites therefore have to be heated to higher temperatures before the α–β inversion occurs. They also have to be cooled to a greater extent before the reverse transformation occurs and hence have the largest hysteresis. Therefore, highly ordered cristobalites can be produced by heating pure quartz at 1600–1700°C; cristobalites produced from pure quartz at lower temperatures are inevitably less highly ordered.

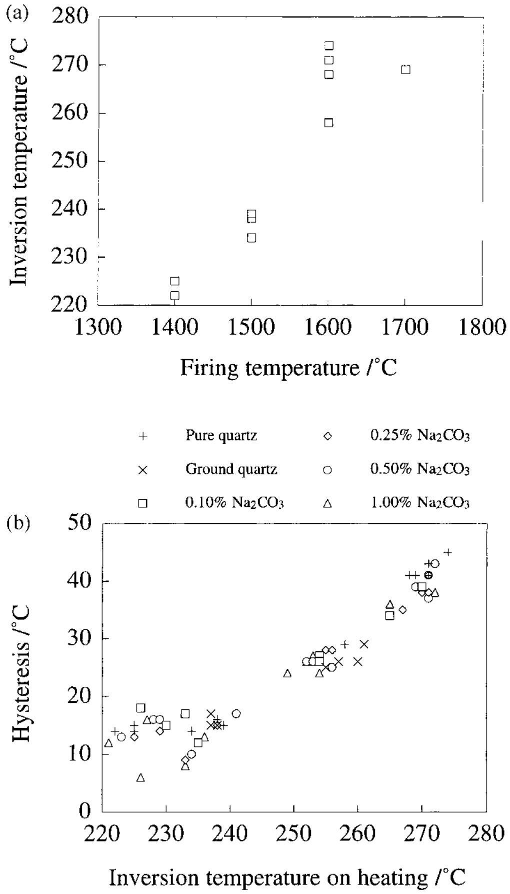

Fig. 2. (a) Cristobalite inversion temperature on heating vs. firing temperature and (b) hysteresis of the cristobalite α–β inversion vs. the inversion temperature on heating. All samples produced by firing Iota quartz.

3.2. *High purity quartz fired with a mineral additive*

The situation is more complex when cristobalites produced from pure quartz with the aid of a mineral additive are considered. In a significant number of the Iota quartz samples fired with a mineral additive, tridymite inversions were apparent as well as cristobalite and quartz inversions. The tridymite inversions were always single peaked endotherms on heating, although the endotherms could be very broad and shallow especially if the sample only contained a small amount of tridymite (Fig. 3). As before the quartz inversion was observed at 572±1°C whereas the cristobalite inversion temperature was dependent on firing time, temperature and the amount of mineral additive present [16]. Very similar results were obtained when Loch Aline sand was fired with a mineral additive.

All the Iota quartz and Loch Aline sand samples fired at 1100°C had a quartz inversion; for samples fired for 1 h with the incorporation of 0.10% and 0.25% mineral additive this was the only peak present. Samples fired for 1 h with 0.50% and 1.00% mineral additive had small, broad, fairly flat endotherms at the cristobalite α–β inversion with no sharply defined maximum (Fig. 4); 90–95% of the quartz remained unconverted in these samples. Cristobalites produced at 1100°C in the presence of 0.50% and 1.00% sodium

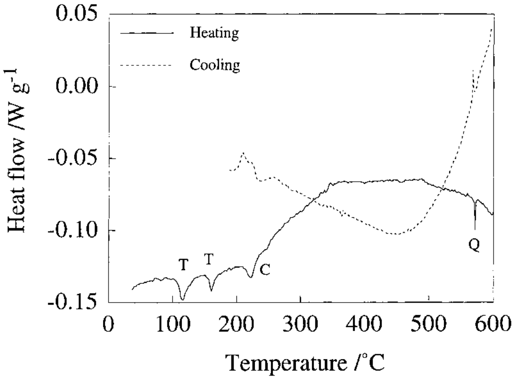

Fig. 3. DSC trace of a sample prepared from Iota quartz and 1.00 wt.% sodium carbonate fired at 1100°C for 50 h (C-cristobalite; Q-quartz and T-tridymite inversions).

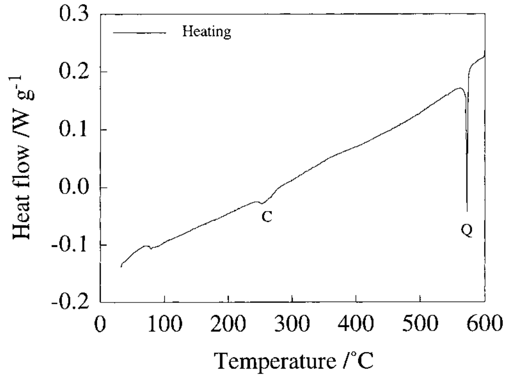

Fig. 4. DSC trace of a sample prepared from Iota quartz and 1.00 wt.% sodium carbonate fired at 1100°C for 1 h (C-cristobalite and Q-quartz inversions).

carbonate after short firing times exhibited anomalously high inversion temperatures; the inversion temperature was considerably lower in the samples fired for 5 h than those fired for 1 h. Similar results have been obtained by Grimshaw [18]. It might be expected that the cristobalite formed in the early stages of firing would be more disordered with a lower inversion temperature. As the anomalously high inversion temperatures only occurred with the larger additions of mineral additive they may be due to some hinderance of the inversion by the alkali metal ions. Endotherms at about 115°C and 160°C were observed and were attributed to tridymite inversions in samples that contained the greatest amounts of mineral additive and which had been fired for the longest periods.

The inversions observed after firing at 1300°C were very similar to those observed at 1100°C, except that an extra tridymite endotherm at around 86°C was observed in a sample fired for 15 h with 1.00% mineral additive (Fig. 5(a)). This additional endotherm was also seen when Loch Aline sand was fired at 1300°C with a mineral additive (see Fig. 5(b) and (c)). Comparing Fig. 5(a) to (c) suggests that increased amount of mineral additive lead to larger tridymite endotherms; further evidence for tridymite production being dependent on the presence of a mineral additive. A tridymite inversion at this temperature was also observed in other samples fired at 1400°C and 1500°C. The fact that the 86°C inversion only appeared when tridymite was present although all the DSC samples had been stored in the same fashion tends to rule out water as the cause of this endotherm. In the samples fired at 1300°C and 1400°C the endotherm at around 86°C only appeared when there was a relatively large endotherm at around 115°C. In the samples fired at 1500°C the endotherm at around 86°C was much larger than in any other sample and the endotherm at around 115°C was small in comparison; in some cases this latter endotherm was not observed (Fig. 6). Although a tridymite inversion at 86°C has not been explicitly reported elsewhere, Lamkin et al. [3] noted that there is a small structural change at 64°C whilst Heaney [4] notes that there are a number of low temperature terrestrial mineral tridymites with a corresponding range of transition behaviour.

Samples of Iota quartz fired at 1400°C for 1 h had fairly simple DSC traces with a single endothermic peak on heating and a single exothermic peak on cooling. Samples fired for longer times had more complicated DSC traces, most with double peaked cristobalite endotherms on heating (Fig. 7) and many also had an exotherm with a shoulder or a double peaked exotherm on cooling. A quartz inversion was only seen in the sample fired with 0.1% mineral additive for 1 h. In addition as discussed above tridymite inversions were also observed in samples fired at 1500°C.

No quartz or tridymite inversions were seen in the Iota quartz or Loch Aline sand samples that had been fired at 1600°C with a mineral additive. With the exception of the samples fired with 0.10% and 0.25% mineral additive for 1 h all the samples showed a single sharp endotherm on heating at around 270°C and a single sharp exotherm on cooling.

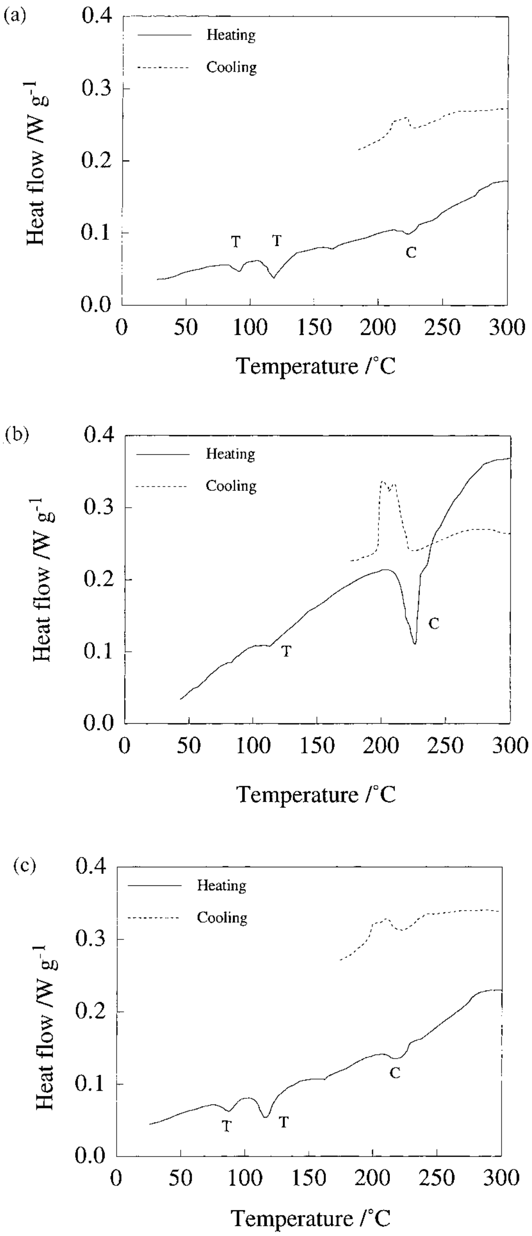

Fig. 5. DSC traces of samples fired at 1300°C for 15 h (a) Iota quartz and 1.00 wt.% sodium carbonate; (b) Loch Aline sand and 0.5 wt.% sodium carbonate; (c) Loch Aline sand and 1.5 wt.% sodium carbonate (C-cristobalite and T-tridymite inversions).

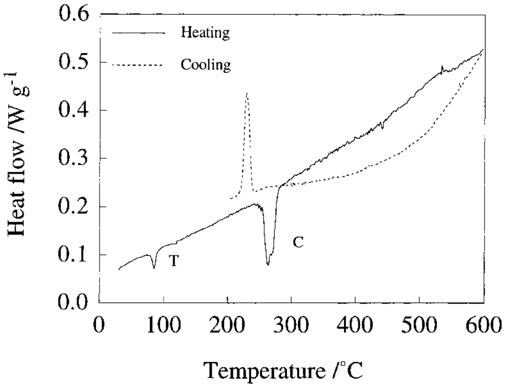

Fig. 6. DSC traces of a sample prepared from Iota quartz and 1.00 wt.% sodium carbonate fired at 1500°C for 15 h (C-cristobalite and T-tridymite inversions).

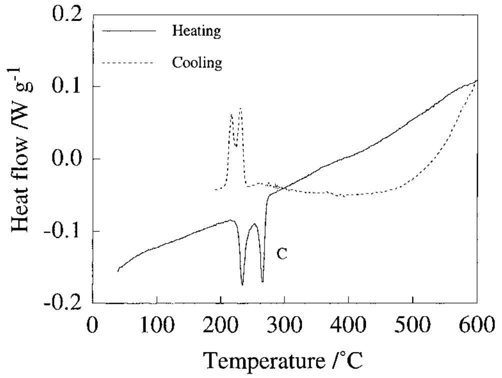

Fig. 7. DSC trace of a sample prepared from Iota quartz and 0.10 wt. % sodium carbonate fired at 1400°C for 50 h.

3.3. Commercial quartz samples

No tridymite inversions were observed in samples prepared on firing the commercial quartz without a mineral additive. This observation is supported by the XRD data with one exception; a sample fired at 1400°C for 50 h had one weak tridymite XRD peak. Cristobalite produced by firing the commercial purity quartz at 1400°C and 1500°C had similar inversion temperatures and hysteresis to those produced by firing Iota quartz to the same temperature. At 1600°C cristobalites produced from the commercial quartz had lower inversion temperatures and smaller hystereses than those produced from pure quartz.

Quantitative XRD showed that there was a more rapid reduction in the amount of quartz present as a function of both firing time and temperature with the commercial quartz compared to the Iota quartz. In addition, although more cristobalite was formed from the commercial material at the lower firing temperatures, at 1600°C more cristobalite was produced from

Table 5
Percentages of cristobalite and quartz from quantitative XRD after firing commercial quartz and Iota quartz without a sodium carbonate

Firing temperature /(°C)	Dwell time	Commercial quartz		Iota quartz	
		% Cristobalite	% Quartz	% Cristobalite	% Quartz
1400	1	21	67	12	84
1400	5	25	71	25	58
1400	50	50	<3	48	6
1500	1	54	11	37	55
1500	5	54	<1	47	36
1500	15	55	<1	74	14
1600	1	64	0	81	2
1600	3	63	0	68	14
1600	5	67	0	89	0
1600	50	65	0	83	0

the pure system. Overall for the commercial quartz there is a significant shortfall in crystalline material after firing it compared to firing the pure Iota quartz (see Table 5). The shortfall was particularly marked following firing at 1600°C. It is suggested that this is because the amorphous transition phase is more readily produced when larger amounts of impurities are present. However, the additional impurities make the transition phase more stable with respect to cristobalite and thus less cristobalite is produced. In addition, the lower cristobalite inversion temperatures indicate that the impurities in the commercial material hinder, or even prevent, the production of well-ordered cristobalites.

The sample of commercial quartz fired at 1400°C with 0.1% sodium carbonate for 1 h had a very similar DSC trace to the corresponding Iota quartz sample. However, the sample of commercial quartz fired at 1600°C with 0.1% sodium carbonate for 1 h had a significantly lower cristobalite inversion temperature (237°C compared to 273°C) and hysteresis (21°C compared to 44°C) than the corresponding Iota quartz sample.

4. Conclusions

Firing temperature, soak time and the presence of impurities all affected the quality of cristobalite produced by firing quartz. Higher inversion temperatures on heating were associated with greater degrees of hysteresis; the highest inversion temperatures were also associated with the sharpest XRD peaks. Therefore the inversion temperatures and hysteresis, as measured by DSC, provide an assessment of cristobalite quality.

Well ordered cristobalites were produced by firing pure quartz at 1600°C or 1700°C or by firing pure quartz in the presence of a mineral additive at 1500°C and 1600°C. However, in the latter case, if larger amounts (1–5%) of mineral additive were present, tridymite was also formed. Cristobalites produced from commercial quartz under equivalent conditions with or without a mineral additive had lower inversion temperatures and exhibited less hysteresis and therefore were less well-ordered.

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