Changes in Quartz During Heating and the Possible Effects on Si Production

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In Si and FeSi production, the main Si source is SiO_2, in the form of quartz. Reactions with SiO_2 generate SiO gas that further reacts with SiC to Si. During heating, quartz will transform to other SiO_2 modifications with cristobalite as the stable high-temperature phase. Transformation to cristobalite is a slow process. Its rate has been investigated for several industrial quartz sources and has been shown to vary considerably among the different quartz types. Other differences in behavior during heating between these quartz sources, such as softening temperature and volume expansion, have also been studied. The quartz-cristobalite ratio will affect the rate of reactions involving SiO_2. The industrial consequences and other implications of the observed difference between quartz types are discussed. Initial studies of industrial quartz were published by Ringdalen et al. In the current work, a new experimental method has been developed, and an investigation of several new quartz sources has confirmed the earlier observed large variation between different sources. The repeatability of the data has been studied and the effect of gas atmosphere investigated. The results from the earlier work are included as a basis for the discussion.
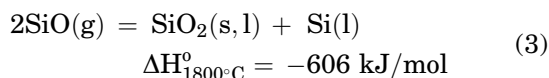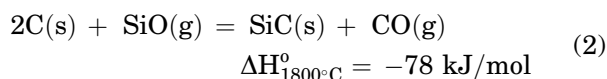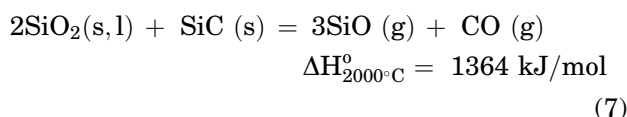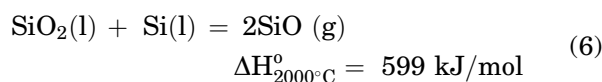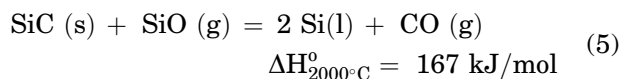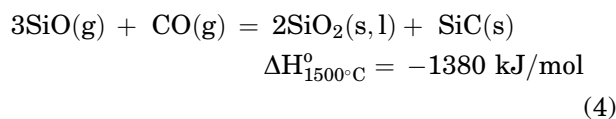
INTRODUCTION

Reactions in Silicon Production

Metallurgical silicon (Si) and ferrosilicon (FeSi) are produced in submerged arc furnaces (SAF), where the two main raw materials are quartz and carbon reductants such as coke, coal, charcoal, and wood chips. For FeSi production, iron sources are added. Energy, approximately 11–13 MWh/ton alloy for Si production, is another important input factor. The reduction of silica to Si takes place by the overall reaction 1:

$$SiO_2 + C = Si + CO \quad \Delta H^o_{2000°C} = 687 \text{ kJ/mol} \tag{1}$$
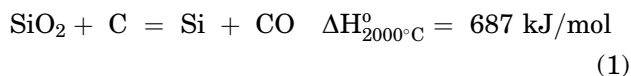
In industrial furnaces, the reactions take place in several steps as described by Schei et al.[1] The raw materials are fed to the top of the furnace where the temperature is around 1000°C to 1300°C.[2] In the upper part of the furnace, descending raw materials meet ascending SiO and CO gas. Here, carbon reacts to SiC by reaction 2, and the ascending gases react as a result of the decreasing temperature to "condensates" according to reactions 3 and 4. In the lower part of the furnace, where the temperatures reach more than 2000°C, Si is produced by reaction 5. SiO gas required for this reaction and for SiC production in the upper part of the furnace is produced from SiO_2 by reactions 6 and 7. Dominant reactions and their stability depend strongly on the partial pressures of SiO and CO.

$$2C(s) + SiO(g) = SiC(s) + CO(g)$$
$$\Delta H^o_{1800°C} = -78 \text{ kJ/mol} \tag{2}$$

$$2SiO(g) = SiO_2(s,l) + Si(l)$$
$$\Delta H^o_{1800°C} = -606 \text{ kJ/mol} \tag{3}$$

$$3SiO(g) + CO(g) = 2SiO_2(s,l) + SiC(s)$$
$$\Delta H^o_{1500°C} = -1380 \text{ kJ/mol} \tag{4}$$

$$SiC(s) + SiO(g) = 2Si(l) + CO(g)$$
$$\Delta H^o_{2000°C} = 167 \text{ kJ/mol} \tag{5}$$

$$SiO_2(l) + Si(l) = 2SiO(g)$$
$$\Delta H^o_{2000°C} = 599 \text{ kJ/mol} \tag{6}$$

$$2SiO_2(s,l) + SiC(s) = 3SiO(g) + CO(g)$$
$$\Delta H^o_{2000°C} = 1364 \text{ kJ/mol} \tag{7}$$

Reactions 6 and 7, which produce SiO from quartz and Si or SiC, are both strongly endothermic. The reaction with SiC requires nearly three times as much energy as the reaction with Si. As a result, the energy distribution in the furnace will depend on which of the two reactions that are dominating. These reactions take place at temperatures of approximately 1500°C to 2000°C. Changes in quartz during heating and high-temperature properties of SiO_2 are therefore important. SiO produced above 1811°C reacts to Si by reaction 5. This requires at 1 atm total pressure, a partial pressure of SiO of 0.67 atm. Excess SiO plus SiO produced at lower temperatures react by reaction 2 with carbon to SiC, needed for final Si production. SiO-reactivity of carbon materials was described by Myrhaug[3] to have a large effect on furnace performance. The remaining SiO will react by reactions 2 and 3 to "condensate" in the furnace or leave the furnace with the off-gas and reduce Si-yield. The amount of SiO condensate, temperature distribution in the furnaces, and Si yield is through this shifted by quartz reactivity at different temperatures toward Si and SiC.

Changes in Quartz During Heating

When quartz is heated, its structure will change to different SiO_2 polymorphs as shown in the phase diagram in Fig. 1.[4]

When heated in air at 1 atm, α-quartz is transformed to β quartz at 573°C. This transformation is fast and will be reversed during cooling. It will lead to an increase in volume of around 0.4%. According to the phase diagram, tridymite will be formed at 873°C. It is debated whether this phase change really will take place or if β quartz alternatively will be transformed directly to β cristobalite at a temperature somewhere between the temperature for
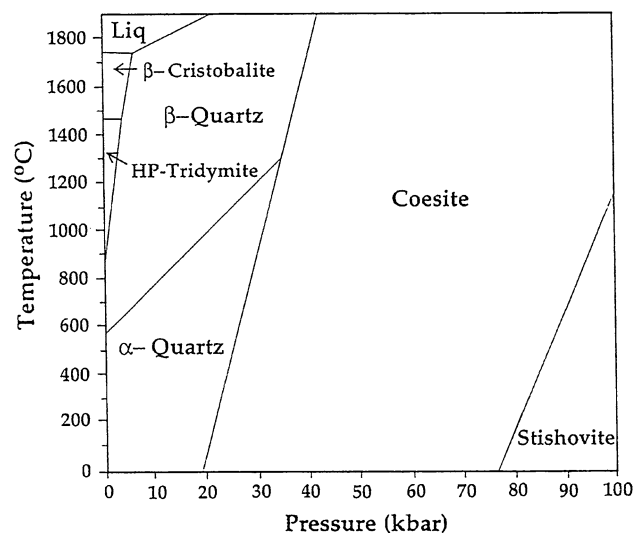

Fig. 1. SiO_2 phase diagram.[4]

tridymite formation from the phase diagram and the melting temperature for SiO_2 at 1711°C. As described by Wiik,[5] the α-quartz/β-cristobalite transformation is assumed to go through an amorphous transition phase. During this transformation, the volume will increase to approximately 17%. During cooling, β cristobalite is transformed to α-cristobalite and not back to the stable phase, α-quartz. The large increase in volume by the phase transformations will give a lower density and a higher specific surface area after heating. Cracking as a result of the volume change will contribute to the higher surface area. Wiik[5] measured that the original surface area of 0.025 m^2/g for quartz had increased to 0.50 m^2/g after the material had been heat treated, transformed to cristobalite, and cooled down. The α-quartz/β-cristobalite transformation is slow, and in Wiik's experiment the quartz was heat treated at 1400°C for 5 days in order to achieve complete transformation to cristobalite. Silica is expected to be more reactive when it has a high percentage of amorphous silica during the transition. Investigations by Andersen[6] and by Adisty[7] indicated that the effect of heating varies among different quartz sources.

Experiments by Andersen[6] and by Aasly[4] in the same sessile drop apparatus that was used in this study showed that the melting properties and volume expansion varied among different quartz sources and that volume expansion for some of the quartz sources was higher than the theoretical value of 17.4%. The investigation also indicated that cristobalite is more readily formed in inert than in a reducing atmosphere and that volume expansion increased with increasing amount of cristobalite. Because the amount of amorphous phases were not included in quantification of cristobalite in this study, the results have a lot of uncertainties and are only indicative.

Most of the above studies were performed in air. During Si production in SAF, the quartz will be heated in an atmosphere that is a mixture of CO and SiO. The effect on phase transformations of such an atmosphere is not much studied.

SiO-Producing Reactions

The rates of the two SiO-producing reactions involving silica, reaction 6 and 7, have been investigated by Andersen[8] and by Bao et al.[9] in DTA-TGA equipment from 1550°C to 1800°C with quartz as the Si source. Both reactions are slow at 1550°C. Between 1550°C and 1730°C, reaction 6 with Si is around 1.5 times faster than reaction 7 with SiC. The rate for the reaction with SiC increases most with temperature and is the dominating reaction at 1800°C. SiO production from SiO_2 and SiC had a reaction rate of 0.1 mg/min at 1550°C, while at 1730°C it was 1.3 mg/min and at 1830°C 4.1 mg/min. A conversion rate of 0.8 was reached after 56 min at 1820°C and after 112 min at 1730°C for this reaction.

The rate for the reaction between silica and carbon was found by Wiik[5] to be nearly twice as fast when cristobalite was used as the silica source instead of quartz. The difference was attributed to a higher specific surface area for cristobalite versus quartz. Similar work by Adisty[10] indicated a higher rate with use of cristobalite versus quartz for reaction with SiC (reaction 6). Although the relative importance of these reactions in the silicon furnace is not known, these results indicate that furnace performance can be affected by the rate of cristobalite formation.

EXPERIMENTAL

Materials

Quartz from 18 different sources for industrial Si production has been investigated. The name of the sources and chemical analysis of the different quartz are confidential and therefore not presented. Their purity varied from 97.6% to 99.8% SiO_2. From one source, two different samples, Qz 1 and Qz 17, were taken out and investigated separately. Comparison specimens were investigated from two quartz sources, two specimens of Qz 11 and three specimens of Qz 17. The material was first crushed down to 1–3 mm. The specimens with the desired weight were then split out from the crushed material.

Phase Transformations

The first experiments comparing the rate of cristobalite formation in different quartz types, Qz 1 to Qz 11, were done by heat treatment in a Super kanthal rapid heating furnace as described by Ringdalen.[11] Approximately 50 g quartz in the size fraction 1–3 mm was used in each experiment. The furnace was heated as fast as possible to the target
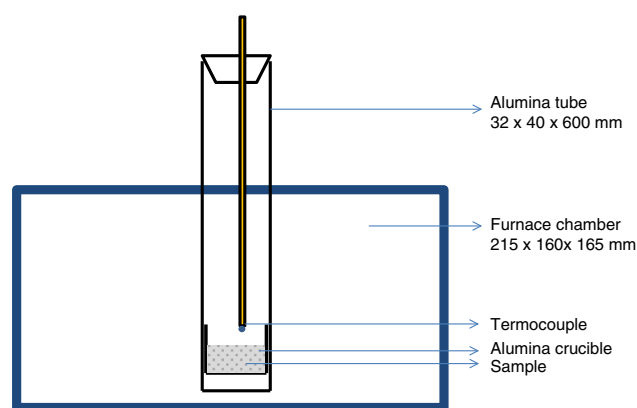

Fig. 2. Sketch of set up for test of cristobalite formation.

Alumina tube
32 x 40 x 600 mm

Furnace chamber
215 x 160x 165 mm

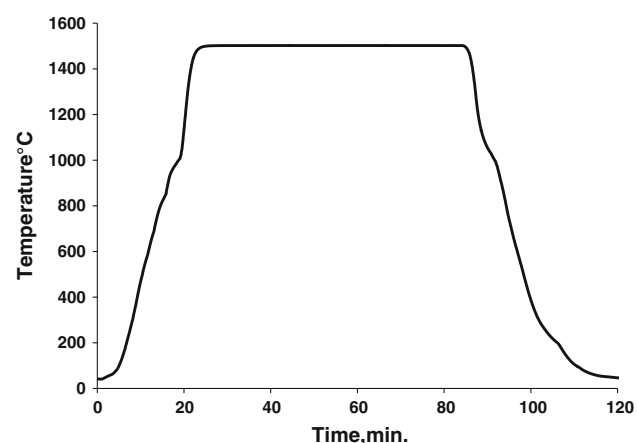Termocouple
Alumina crucible
Sample

Fig. 3. Heating profile for sample Qz17a.

temperature and held at that temperature for a predetermined time. Heating from 25°C to 1500°C took between 21 and 47 min. Samples Qz 2 and Qz 9 had the longest heating time compared with the other samples. The tests conducted for 1 h at 1500°C were all heated for 21–22 min.

To allow a more rapid heating around the interesting temperature and to have the possibility to test in different gas atmospheres, a new setup was created, as shown in Fig. 2. This setup was used in the new experiments for Qz 12–Qz 18 that continued the work presented at TMS 2014 by Ringdalen.[11] Here, 10 g material was placed in a small alumina container, which was loaded into the furnace quite rapidly. Heating from 1000°C to 1500°C took around 3–4 min, and approximately the same time was needed for cooling from 1500°C to 1000°C. The total heating time in both setups was around 25 min; however, the new setup had a shorter cooling time. The heating profile for the new method is shown in Fig. 3.

The surface area of the samples was measured by nitrogen adsorption; 1–3 mm material was used for the measurements. All samples were measured after heat treatment; the samples Qz 2 and Qz 9 were also measured before heat treatment. The

amounts of different phases in the samples were measured by quantitative XRD (Bruker D8 advance with the software DIFFRAC[PLUS]TOPAS). The amount of amorphous silica was determined by the method described by Sørensen and Vedeler.[12] The surface area and amount of different phases were measured on materials after cooling; thus, the changes that appeared during cooling were included.

The reproducibility of the results was investigated by comparing results from two different samples, Qz 1 and Qz 17, from the same quartz source and by investigating three different specimens from the same sample, Qz 17. The effect of atmosphere was studied by heat treatment both in air and in CO of samples from Qz 2 and Qz 9.

Melting Properties and Volume Expansion

The melting properties and volume expansion have been studied for Qz 1 to Qz 11. These properties were investigated in a wetting furnace described by Ringdalen and Tangstad.[2] Three samples from each quartz source were investigated. The test samples were drilled from lump quartz samples. They had a cylindrical form with a diameter of 4 mm and were ground on the two sides to achieve a flat surface. The quartz sample were placed on an ISO88 graphite substrate and heated in CO atmosphere first to 900°C in about 3 min, then with a rate of 50°C/min to 1500°C, and subsequently at 10°C/min to final melting. Images were recorded and analyzed afterward to determine the following:

- The change in volume with increasing temperature
- The temperature for softening—when the shape of the sample has lost the sharp edges
- The temperature for final melting—when the droplet is round, with no artefacts

It must be emphasized that the temperature for final melting determined here is not the same as the melting temperature. With the relatively fast heating rates used in this investigation of melting properties, the temperature for final melting is a measure for how fast the different quartz will melt.

RESULTS

Changes in Quartz During Heating

Measurements of volume expansion during heating showed up to 37% volume expansion (see Fig. 4). There were large variations between the different quartz sources. Volume expansion started for most samples around 1500°C and reached its maximum around 1800°C. The Qz 3 sample had the highest volume expansion.

Changes in quartz after heating for 6 h in air at different temperatures were investigated for samples Qz 2 and Qz 9 and are presented in Fig. 5. The phase transformation started below 1400°C, a lower
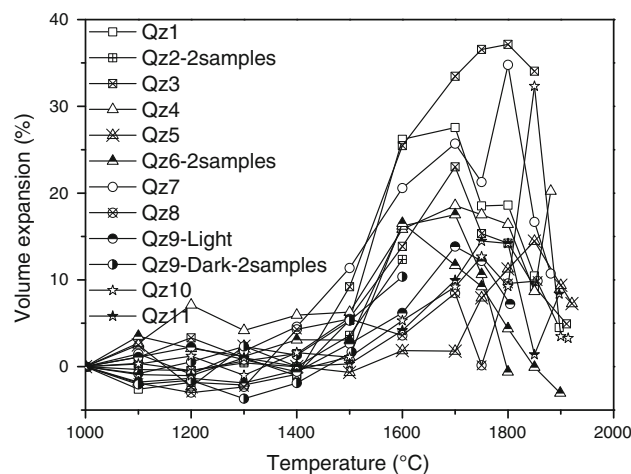

Fig. 4. Volume expansion of the investigated quartz samples.

temperature than expected from the phase diagram in Fig. 1. Both the amount of cristobalite and the specific surface area increased with increasing temperature. For Qz 2, the specific surface area was eight times higher than the original value after 6 h at 1500°C. The quartz had not completely transformed to cristobalite even after 6 h at 1600°C.

The effect of time was investigated by heating to 1500°C at different holding times, and the results are presented in Fig. 6. The transformation rate differs between the different quartz sources, with Qz 2 as the fastest and Qz 3 as the slowest. The amount of amorphous silica increased quickly at the start of the transformation and then the rate slowed down and finally decreased. The relatively low amounts of amorphous silica in most of the samples are assumed to have a relatively large uncertainty. From Qz 2 and Qz 9, peak amounts of amorphous silica seem to be at around 40% cristobalite. Qz 3 did not reach this value for cristobalite formation. The ratio between cristobalite and amorphous silica varies between the samples, and this is especially pronounced for Qz 3, which has a higher content of amorphous silica than cristobalite.

The amounts of cristobalite and amorphous silica after 1 h heating at 1500°C in all the investigated samples are shown in Fig. 7. There are large differences between the samples; the cristobalite content varies from 1% in Qz 11 to 76% in Qz 12. In Qz 3, Qz 4, Qz 6, Qz 14, and Qz 18, the content of amorphous silica was higher than the content of cristobalite, whereas the ratio was opposite for the other quartz type.

The cristobalite content and specific surface areas for the different samples are compared in Fig. 8. The three specimens of Qz 17 and the two specimens of Qz 11 are included and marked. Qz 1 and Qz 17 represent the same quartz source but are from two different samples.

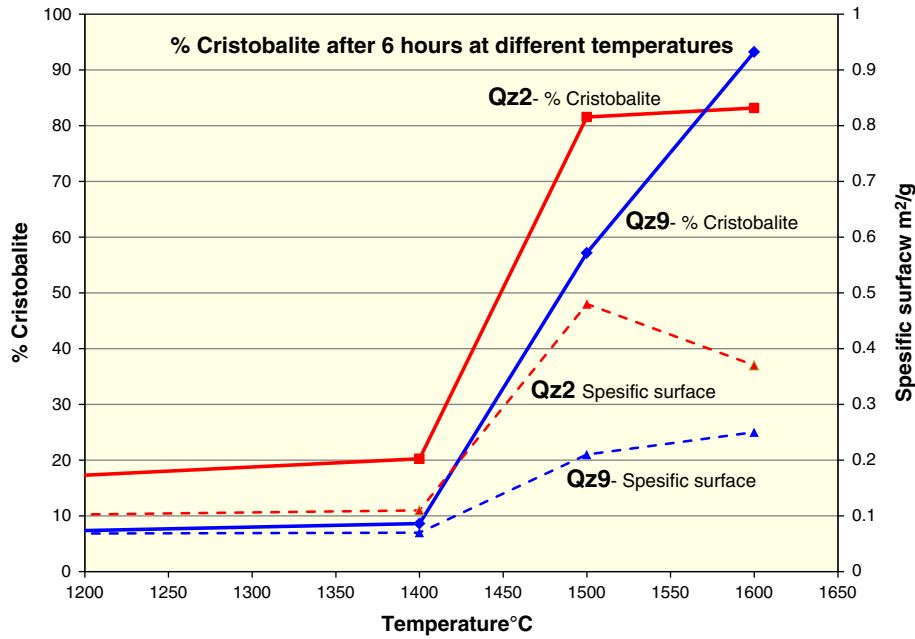The average cristobalite content in the three specimens of Qz 17 is 77%. The highest value is 9%

Fig. 5. Percentage of cristobalite and specific surface area in sample after 6 h heating in air at different temperatures.
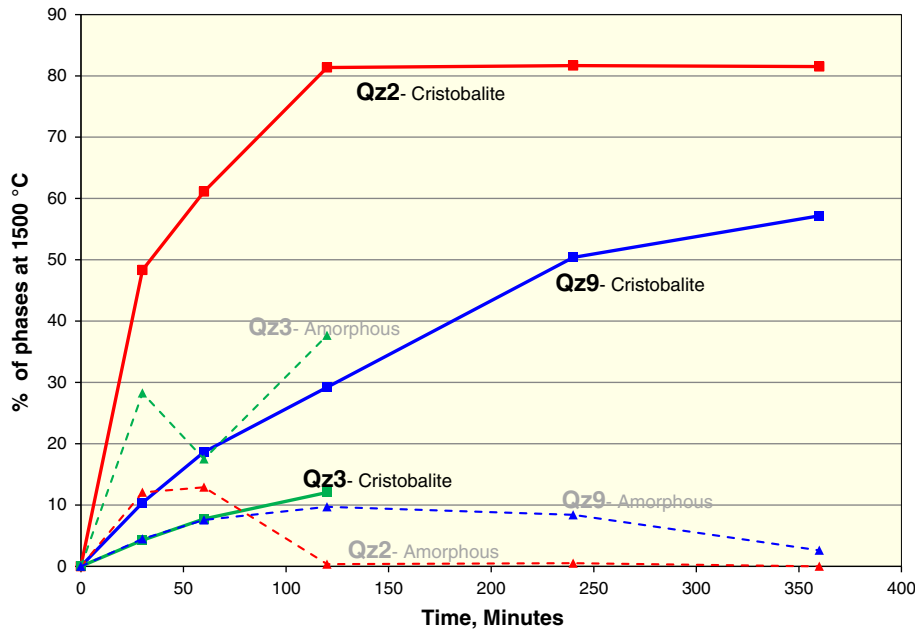

Fig. 6. Effect of time on formation of cristobalite and amorphous silica when quartz is heated in air at 1500°C.

higher than the average and the lowest is 12% lower than the average value. Given that naturally occurring raw materials are inhomogeneous and the assumed high inaccuracy in XRD quantification of mixtures with amorphous phases, a variation in this range is as expected. In the earlier investigated sample of Qz 1 from the same source, the cristobalite content was 58%, which is 25% lower than average in the new samples. The three specimens had an average specific surface area of 0.39 m^2/g with a variation from 0.38 m^2/g, 3% lower than average, to 0.42 m^2/h, 7% higher than average. In the earlier investigated samples, the specific surface was 0.47 m^2/g, which is 19% higher than the average in the new sample. The specific surface area of untreated quartz was measured to be 0.06 m^2/g. The two samples of Qz 11 contained 1% and 3.3% cristobalite and had a specific surface area of 0.01 and 0.07. These low values have a large uncertainty, but they give some confidence to the observed very low rate for phase transformation in quartz from some sources.
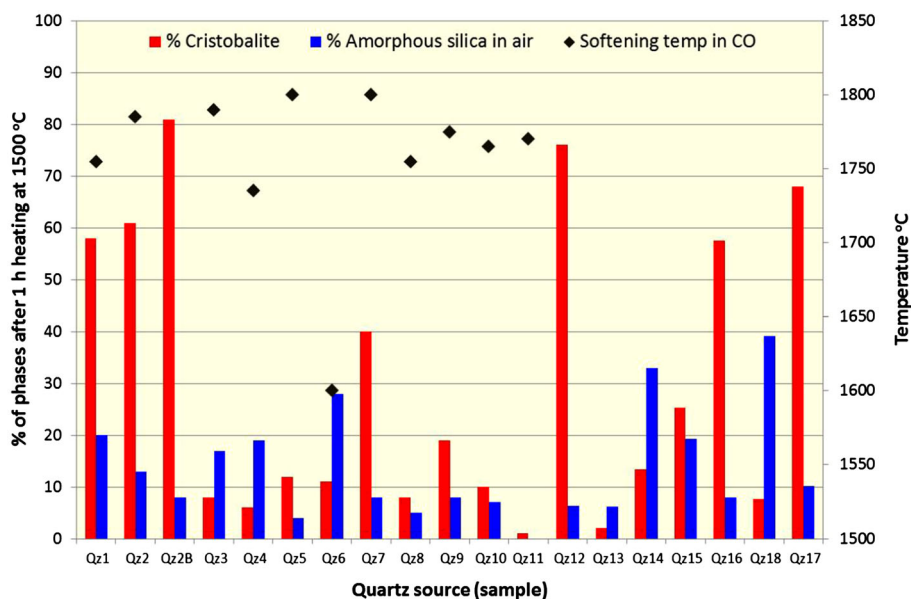
Fig. 7. Amount of cristobalite and amorphous silica in different quartz samples after heating for 1 h at 1500°C. Softening temperatures for sample Qz 1-11 are also included.
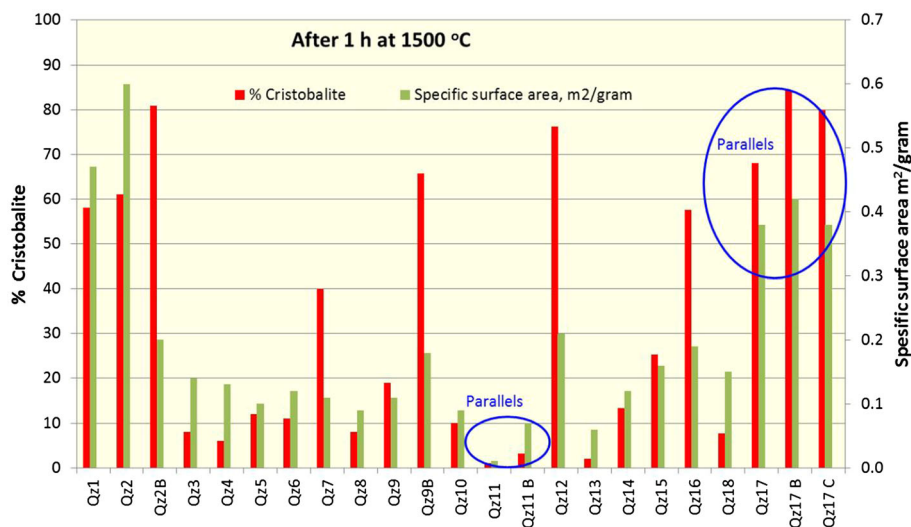

Fig. 8. Content of cristobalite and specific surface area after 1 h at 1500°C for all investigated samples. Reproducibility is illustrated by Qz 1 and Qz 17 (three specimens) that are from the same quartz source.

The effect of gas atmosphere on phase transformation was investigated in two samples, Qz 2 and Qz 9. The results presented in Fig. 9 show only a minor effect of change in atmosphere. The specific surface area was also approximately the same after heating in CO versus air, 0.20 m²/g in air and 0.34 m²/g in CO for Qz 2 and 0.18 and 0.17 m²/g, respectively, for Qz 9. During the tests, some of the samples had reacted with the alumina to other minerals, and this together with testing only two samples gives a large uncertainty, so that the results are only initial indications.

DISCUSSION

Investigations of several industrial quartz sources have identified considerable differences in how they are affected by heating. The melting properties, volume expansion, and rate of cristobalite formations vary between different quartz sources. The main questions are then what is the mechanism behind these differences, what are their industrial implications, and how should these findings affect further quartz research. This work is an initial investigation designed to determine the most
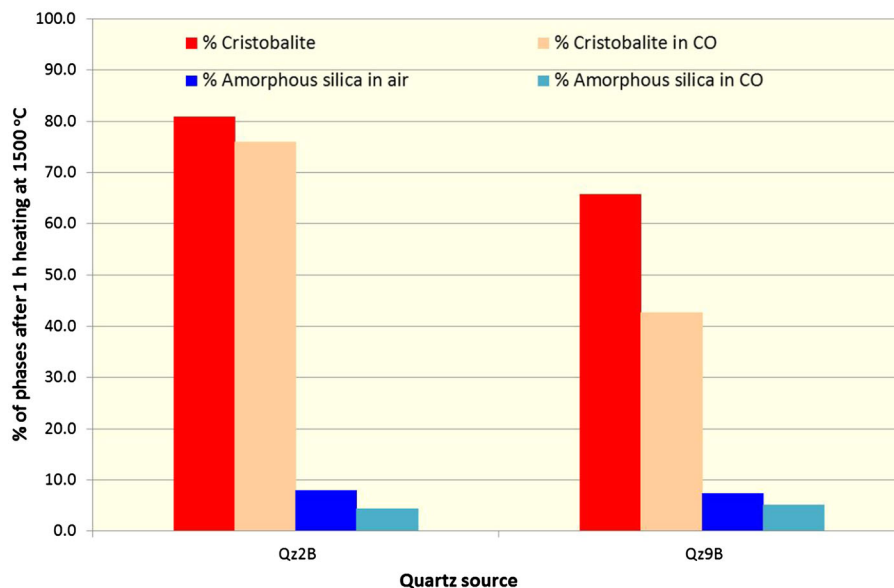
Fig. 9. Effect of gas atmosphere on cristobalite formation.

important parameters. Reproducibility and variance of the experiments are, therefore, investigated only to a limited extent and cannot be quantified. The main uncertainty for all experiments is representative sampling. Further uncertainties for cristobalite formation are related to quantitative determination of amorphous silica in the samples. The change of measurement method where the amount of material was decreased from 50 g to 10 g introduces extra uncertainty when results are compared, independent of the method used.

Heat treatment of quartz showed, as expected, that the quartz/cristobalite phase transformation is slow, and the observed differences between the quartz types indicate that it is affected by the quartz properties. Cristobalite is formed already at 1400°C, a lower temperature than expected from the phase diagram. It is not completed even after 6 h at 1600°C. The tridymite phase expected from the established phase diagram was observed only in a few samples that are believed to be contaminated. The amount of amorphous silica increases fastest in the beginning of the transformation until it stabilizes at a certain level and then decreases. The maximum amount of amorphous phase and ratio between cristobalite and amorphous silica varies between the investigated quartzes. The observed peak in amount of amorphous silica at the start of the heating supports the theory that transformation from quartz to cristobalite formation goes through an intermediate phase of amorphous silica as proposed by Aasly[4] and Wiik.[5] The rate-determining step can either be transformation from quartz to amorphous silica or from amorphous silica to cristobalite. Further investigations are needed to identify mechanism and rate-determining step.

The rate of cristobalite formation varies considerably between the different quartz types in this study.

When the rate is compared with other parameters, it is represented by the amount of cristobalite formed after the material has been held for 1 h at 1500°C. The effects of time and of temperature vary. The rate for cristobalite formation could not be correlated to other parameters as chemical composition or softening temperature. Investigations of reproducibility showed internal variation between the three investigated samples of Qz 17 and the difference in values between this sample and another sample, Qz 1, from the same source. This difference is lower than the difference between Qz 17/Qz 1 and other quartz sources. This method can therefore be used to identify differences in the rate for cristobalite formation between quartz sources. Initial studies indicate that the rate for cristobalite formation is approximately the same in air and CO, but further development of the investigation method and more tests are needed before any conclusions can be drawn. In industrial Si production, quartz is heated in a SiO/CO atmosphere. Knowledge about effect of gas atmosphere is therefore of industrial interest.

Cristobalite has a higher volume than quartz and cristobalite formation is expected to generate higher specific surface area due to both the lower density itself and cracking when the volume increases. The observed increases in volume and specific surface area are higher than expected because of the additional change of structure. Figure 10 shows a slight increase in specific surface area with an increasing amount of cristobalite for most of the investigated quartz sources. Qz 1 and Qz 17, which are from the same source, together with Qz 2 have an anomalous high specific surface area. The mechanism behind the variation in rate of cristobalite formation and the large increase in specific surface area is not known, but it is a suitable starting point and basis for further studies.
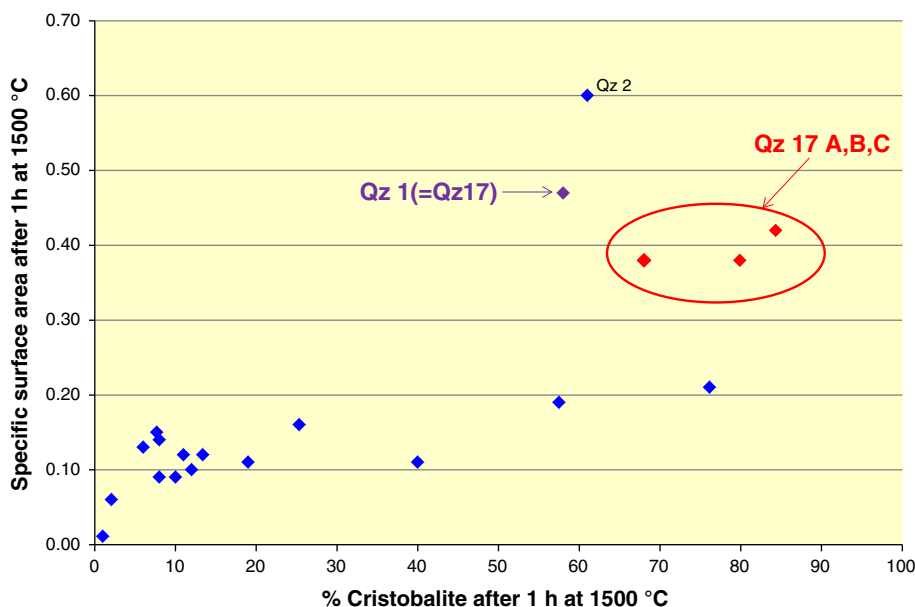
Fig. 10. Correlation between specific surface area and percentage of cristobalite.

The increase in specific surface area for materials, here with up to 6–8 times, will contribute to a higher reaction rate in reactions governed by kinetics. Wiik[6] proposed that reduction rate for reactions with SiO_2 will increase with increasing amounts of both cristobalite and amorphous silica in the SiO_2 source. The varying amounts of amorphous silica are, together with the differences in amount of cristobalite and in specific surface area, expected to give different reaction rates depending on the quartz type.

Reactions involving SiO_2 are often studied at temperatures above 1500°C. The amount of cristobalite and specific surface area will then vary with heating rate and quartz source. The results from investigations with different quartz types can therefore not be compared directly.

Reactions with SiO_2 are believed to affect furnace performance and Si yield in silicon production. The rates for reactions involving SiO_2 are expected to increase with increasing specific surface areas and with increasing amounts of cristobalite and amorphous silica. Because these parameters vary with quartz type, the choice of quartz can affect the performance in industrial furnaces. The relative importance of these properties versus other parameters of importance for furnace performance is not known, and therefore no definite correlations can be drawn.

CONCLUSION

The rates of quartz/cristobalite transformation and of amorphous silica formation vary with quartz source. This phase transformation is expected to be of importance for the rate of SiO formation from SiO_2 which is one of the main parameters governing temperature distribution in Si furnaces. The source

of quartz, the most important SiO_2 source, may thus affect the performance of furnaces for Si production.

In the investigations of reactions with SiO_2 above 1400°C, cristobalite is formed, and the specific surface area increases during heating to the reaction temperature. The amount and specific surface area varies with quartz type. Therefore in investigations of reactions with solid SiO_2, different quartz types, or different heating rates cannot be compared.

ACKNOWLEDGEMENTS

OPEN ACCESS

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