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Parameters Affecting Softening and Melting of Quartz

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Preface

This report describes the work carried out for the author's master's thesis at the Norwegian University of Science and Technology. It is the final work of a master's degree in Chemical Engineering and Biotechnology with specialization in Materials Chemistry and Energy Technology. The report is the evaluation basis for the course TMT4900, and describes the process of further developing and use of a method for investigating softening and melting of silica. All experiments carried out for this thesis were performed at the Department of Materials Science and Engineering at NTNU. The work was in cooperation with SFI Metal Production, a Center for Research-based Innovation.

First, I would like to thank my supervisors Professor II at NTNU Halvard Tveit and PhD Senior Research Scientist Eli Ringdalen at Sintef Materials and Chemistry for giving me the opportunity to continue my work with quartz and the silicon production. I am also very grateful for feedback and discussions with Eli Ringdalen regarding the experimental work and writing of this report. I would also like to thank Tine Christin Eikevik for helping me with thermocouples and Dmitry Slizovskiy for assistance with the induction furnace. Tone Anzjøn at Sintef has helped me with experiments in the wetting furnace. For that I am also very thankful. I would like to thank Odd Corneliussen, Ove Darell and Kjartan Følke for helping me with sample preparation. Siri Marie Bø's help with SEM investigations are also very appreciated. I would like to thank Marthe Erdal Kjelstadli for helpful discussions regarding quartz, and Sofie Aursjø for helping me in the laboratory.

Lastly, I would like to thank the Simanti-group for helpful feedback, inspirational trips and social happenings through the semester.

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Karin Fjeldstad Jusnes

Abstract

The aim of this work was to develop and improve a new method for investigating how different parameters affect the softening and melting of quartz. The method should give quantitative results. Quartz is the stable phase of silica at room temperature, and is used as raw material for silicon production. When silica starts to soften and melt it can react with the surroundings in a furnace. This is undesirable too high in the furnace, because it can cause a more compact charge leading to decreased gas permeability. Softening of silica can also alter the reaction rates. A deeper understanding of the softening and melting properties of silica can lead to a more thorough selection of new raw materials and efficient furnace operations. Costs and energy consumptions can be decreased.

This study has focused on the following parameters effect on softening and heating: temperature, heating rate, quartz type, holding time and particle size. The method used for the investigation was based on the stationary charge in controlled environment (S.C.I.C.E) technique. Carbon crucibles were filled with quartz and silicon carbide, and then heated in an induction furnace. Temperature control was important, and therefore several experiments were performed to establish the uncertainty. After cooling, the crucibles were cut into two halves, so each surface could be studied and the areas of softened and melted silica measured.

The new method for investigating softening and melting properties of silica was adequate. Results from the experiments show that a more impure quartz type will soften and melt at a lower temperature than a purer type. Increasing the holding time at maximum temperature also causes the softening and melting to increase. The effect of particle size was inconsistent, but at higher temperature the softening and melting will increase with decreasing particle size. Increasing the heating rate also showed some inconsistent results. At higher temperature the difference was negligible.

Sammendrag

Målet med dette arbeidet har vært å utvikle og forbedre en metode brukt til å undersøke hvordan ulike parametre påvirker mykning og smelting av silika. Metoden skulle gi kvantitative resultater. Kvarts er den stabile fasen til silika ved romtemperatur og atmosfærisk trykk. Som råstoff i produksjon av silisium brukes kvarts. Når silika begynner å mykne og smelte kan den reagere med omgivelsene i en silisiumsovn. Det er uønsket at dette skjer for høyt oppe i ovene, da det kan føre til en mer kompakt blanding av materialer. Det kan resultere i en lavere permabilitet for gasser som strømmer oppover i ovnen. Mykning og smelting kan også påvirke reaksjonshastighetene mellom kvarts og andre materialer. En dypere forståelse av mykning og smelting av silika kan føre til en mer grunding utvelgelse av nye råstoffer, og til en mer effektiv ovnsdrift. Kostnader og energibruk kan reduseres.

Denne rapporten fokuserer på hvordan følgende parametre påvirker mykning og smelting: temperatur, oppvarmingshastighet, kvartstype, holdetid og partikkelstørrelse. Metoden som er brukt er basert på S.C.I.C.E. (stationary charge in controlled environment) teknikken. Karbondigler ble fylt med kvarts og silisiumkarbid, og så varmet i en induksjonsovn. Temperaturkontroll var viktig for forsøkene, så derfor ble det gjennomført flere eksperimenter for å fastslå usikkerhet i temperaturmålingene. Etter avkjøling ble diglene kuttet i to halvdeler, slik at hver overflate kunne skannes og områdene med myknet og smeltet silika målt.

Den nye metoden for å studere mykning og smelting av kvarts ga tilfredstillende resultater. Fra eksperimentene kan det ses at en mer uren kvartstype vil føre til mer mykning og smelting enn en renere kvartstype. Å øke holdetiden ved maksimaltemperaturen vil også føre til en økning av mykning og smelting. Effekten av partikkelstørrelse var noe inkonsistent, men ved høyere temperaturer vil mykning og smelting øke med mindre partikkelstørrelse. Ved høyere temperaturer var variasjonene i mykning og smelting mellom de to oppvarminshastighetene testet, neglisjerbar.

Nomenclature

Symbol	**Name**	**Unit**
α	Thermal diffusivity	mm^2/s
Δ	Difference	-
g	Gas phase	-
l	Liquid phase	-
s	Solid phase	-
μ	Chemical potential	J/mol
η	Viscosity	Poise
η_0	Pre-exponential factor	-
$G*$	Activation energy	J/mol
R	Gas constant	J/K·mol
T	Temperature	°C
H	Enthalpy	kJ/mol
SEM	Scanning Electron Microscope	-

Contents

Chapter 1

Introduction

The focus of this report has been the melting and softening properties of silica used in the silicon industry. Quartz is a stable phase of silica at room temperature and atmospheric pressure. When heated, the quartz can go through phase transformations before it softens or melts. The work presented in this report can be considered a continuation of earlier studies by Jusnes[1]. Different samples of quartz will be heated in a carbon crucible to varying temperatures in an induction furnace, while parameters such as heating rate, particle size and quartz type are changed. The method is based on earlier and similiar work done with manganese ores[2]. The method has already been tested for the purpose of studying quartz properties, and has showed adequate quantitative and qualitative results. The method will be further improved. One and one parameter will be altered to study the effect. After cooling, the crucibles will be filled with epoxy and cut through the middle. The inner surface can then be studied and areas of softened and melted silica measured. Then the effect of varying parameters will be observed. Experiments in a wetting furnace will be used to improve the method in the induction furnace, and to compare the two methods. SEM will be used to study the microstructure of softened, melted and unreacted silica.

1.1 Background

Quartz is the raw material for the production of silicon, a semiconducting element. It was first recognized in the early 1800s, and was from the middle of this century used as element or in alloys. Today silicon is used in a broader specter of applications such as raw material for the semiconductor industry, raw materials for the chemical industry and as silicon carbide, one of the most important abrasives[3] [4].

To produce silicon, quartz, a carbon source and energy is needed. The raw materials are added to a submerged arc furnace, where three electrodes provide the energy. The simplest equation to explain the process is given by reaction 1.1.

$$SiO_2 + 2C = Si + 2CO \tag{1.1}$$

Figure 1.1 shows a typical silicon production plant. The raw materials are added at the top of the furnace where the temperature is varying from 700 °C to 1300 °C. They descend through the furnace while they are heated. The temperature in the inner zone of the furnace can be up to 3000 °C. In this zone the silicon is produced[3]. The melting point of silica is 1713 °C[5], so silica can melt while it is descending. Before the silica is melting, it can soften. This may influence the reaction rates in the furnace. Softening and melting of silica too high in the furnace can also cause a more compact charge in the upper part of the furnace. Gas from the inner zone of the furnace is ascending. It is favourable that the gas takes longer time to leave the furnace. In that way, more SiO gas can be recovered from the process. If the silica has softened or melted it will decrease the gas permeability, which can cause less recovery. The silicon yield will then be lowered, and costs increased.

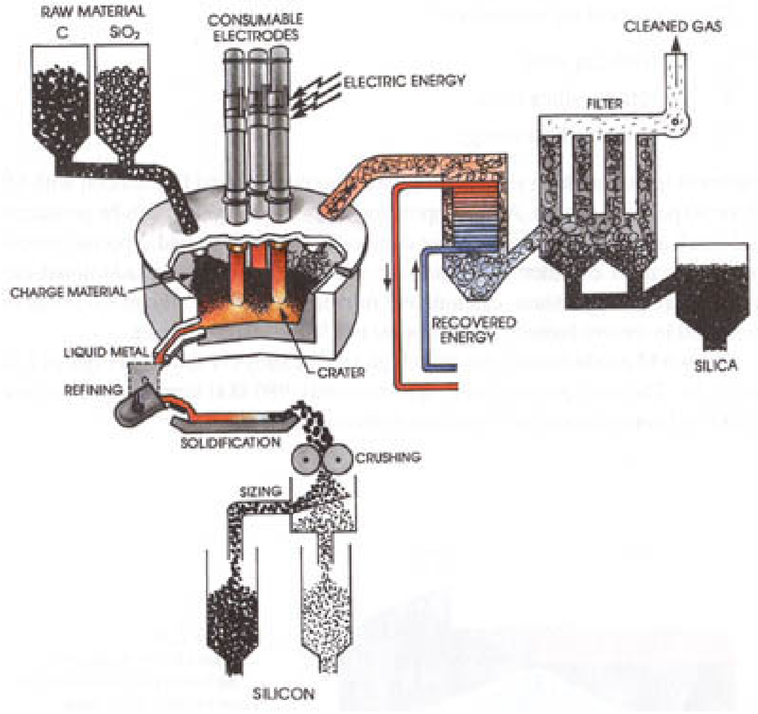


Figure 1.1: A typical silicon production plant. The illustration is reprinted from Schei et al.[3].

Energy can be recovered from the process, and the off-gas can be cleaned to filter out small pieces of silica, called microsilica. The silicon is tapped from the lower part of the furnace through a taphole. After tapping, the silicon can be refined before it solidifies.

In reality the production of silicon goes through several reaction steps, not only reaction 1.1. The quartz properties can influence the reaction rates. Compared to carbon properties, which are widely studied, the importance of quartz properties is missing[6]. A deeper knowledge on how the quartz is behaving in the furnace, can lead to a more thorough selection of new raw materials and more efficient furnace operations. More knowledge can therefore lead to decreased energy consumption, and hence a lower cost for the industry.

1.2 Objectives

The main goal for this master thesis is to describe the progress of softening and melting of selected quartz types used in the silicon industry. This should be done by further developing a new method which allows for the effect of different parameters on softening and melting to be studied. The objectives are divided into the following points:

- Further develop and improve the method tested in earlier project work. The method should give qualitative and quantitative results on softening and melting.
- Determine the effect of varying parameters on the softening and melting of silica. The parameters varied will be temperature, quartz type, particle size, holding time and heating rate.
- Study softening and melting in smaller scale in wetting furnace and use these results to optimize the method for larger scale experiments.
- Find a mathematical expression for softening as a function of the most important parameter(s).
- Study and describe progress of softening and melting in microscale using SEM.

Chapter 2

Theory

2.1 Silicon production

The theory presented here is based on the work by Schei et al.[3]. As described in the introduction, quartz and carbon are added to a submerged arc furnace to produce silicon. The overall reaction equation for the process, being reaction 1.1. The main source of SiO_2 used in silicon production comes from quartz[3].

2.1.1 Chemical reactions in the silicon furnace

Reaction 1.1 is a result of a number of reactions happening in a silicon furnace. Silicon carbide, SiC, and silicon monoxide, SiO, are also stable components in a system containing silicon, carbon and oxygen. The interaction of these three components make the process a lot more complex.

Quartz and carbon sources are added at the top of the furnace where the temperature is between 700 °C and 1300 °C. While the raw materials are descending in the furnace their temperature will increase. The upper part of the furnace is the low temperature zone, and the lower part is the high temperature zone with temperatures well above 2000 °C. The quartz can react in both solid and liquid form with silicon and silicon carbide to produce SiO gas and CO gas according to reaction 2.1 and 2.2.

$$\mathrm{SiO_2}(s,l) + \mathrm{Si}(l) = 2\mathrm{SiO}(g) \qquad \Delta H_{2000^\circ\mathrm{C}} = 599\,\mathrm{kJ/mol} \tag{2.1}$$

$$\mathrm{SiO_2}(s,l) + \mathrm{SiC}(s) = 3\mathrm{SiO}(g) + \mathrm{CO}(g) \qquad \Delta H_{2000^\circ\mathrm{C}} = 1364\,\mathrm{kJ/mol} \tag{2.2}$$

The SiO gas produced will react with carbon according to reaction 2.3.

$$\mathrm{SiO}(g) + 2\mathrm{C}(s) = \mathrm{SiC}(s) + \mathrm{CO}(g) \qquad \Delta H_{1800\,^\circ\mathrm{C}} = -78\,\mathrm{kJ/mol} \tag{2.3}$$

This reaction is a solid-gas reaction, and the SiO-reactivity to the carbon source affects the reaction rate. Silicon will be produced according to reaction 2.4.

$$\mathrm{SiC}(s) + \mathrm{SiO}(g) = 2\mathrm{Si}(l) + \mathrm{CO}(g) \qquad \Delta H_{2000\,^\circ\mathrm{C}} = 167\,\mathrm{kJ/mol} \tag{2.4}$$

It is believed to be beneficial for the silicon yield that the silica do not react too high in the furnace where the temperature is lower. The SiO gas produced in reaction 2.1 and 2.2, is participating in reaction 2.4, producing silicon. Hence, if the SiO gas is produced near the top of the charge it will easier escape the furnace since the distance out is shorter. In that case, it will not contribute to the silicon production. The behavior at high temperature of silica is therefore important for the silicon production[7]. On the other hand, it is not beneficial for the furnace operation that large pieces of solid silica reach the high temperature zone. Cold material will decrease the temperature in the lower part of the furnace, where a high temperature is needed to produce silicon[8]. Also, reactions 2.1 and 2.2 are endothermic, which will contribute to the energy consumption in the high temperature area. Since reaction 2.2 requires almost three times the energy as reaction 2.1, the energy distribution in the furnace will depend on kinetics of these reactions[9].

For reaction 2.4 to produce silicon, the partial pressure of SiO must be above 0.67 atm and the temperature above 1811 °C. This is shown in figure 2.1, which shows equlibrium SiO pressure above condensed phase combinations C-SiC, SiO_2-C, SiO_2-SiC, SiC-Si and SiO_2-Si. Gas compositions above the condensation reactions are unstable. If the temperature is too low, the SiO gas will react according to reaction 2.3 or 2.5, which will increase the temperature in the lower temperature zone of the furnace.

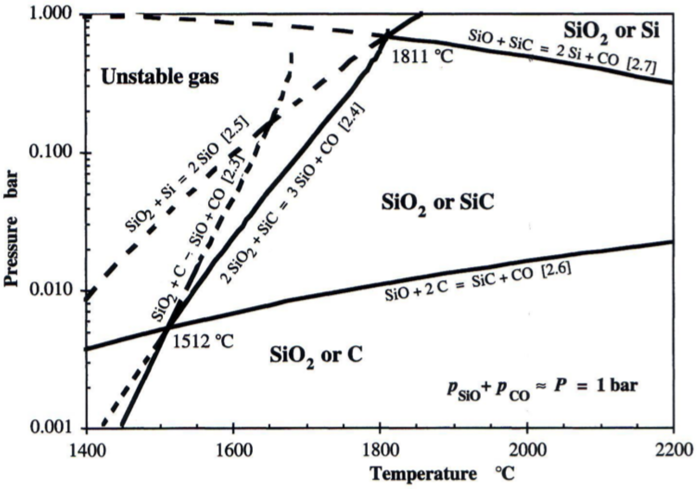


Figure 2.1: Partial pressure of SiO gas in equilibrium with SiO_2, SiC and C as a function of temperature. Total pressure of SiO and CO is 1 atm[3].

Excess SiO gas and CO gas produced will rise to cooler areas. SiO gas will dissociate according to the following reaction:

$$2\mathrm{SiO}(g) = \mathrm{Si} + \mathrm{SiO_2}(s) \qquad \Delta H_{1800^\circ\mathrm{C}} = -606\,\mathrm{kJ/mol} \tag{2.5}$$

The SiO and CO gas can also react to produce silica and silicon carbide according to reaction 2.6.

$$3\mathrm{SiO}(g) + \mathrm{CO}(g) = 2\mathrm{SiO_2}(l) + \mathrm{SiC}(s) \tag{2.6}$$

If the SiO or CO gas reaches the top of the charge without reacting, they will both oxidize according to reaction 2.7 and 2.8 respectively. The product from reaction 2.7 is microparticles of silica, which can be collected in the off-gas and sold for suitable applications.

$$2\mathrm{SiO}(g) + \mathrm{O_2}(g) = 2\mathrm{SiO_2}(s) \tag{2.7}$$

$$2\mathrm{CO}(g) + \mathrm{O_2}(g) = 2\mathrm{CO_2}(s) \tag{2.8}$$

2.1.2 Silicon furnace operations

Certain quartz properties are important for optimizing the conditions and the product in the silicon furnace. The industry has developed a list of requirements to the quartz as raw material. Some of the requirements are yet not fully understood. A better ore will give a better product, therefore the following properties are important[3]:

- Chemistry (e.g. Al, Ti, P, Fe, Ca)
- Lump size (10-150mm)
- Mechanical strength
- Thermal strength
- Softening properties

Figure 2.2[3] shows the traditional understanding of a typical silicon furnace around one of the three electrodes. The product is tapped through the tap-hole at the bottom. A cavity will form under and on the sides of the electrode. Due to a mixture of SiO_2, SiC and condensate from reaction 2.5, a bridge of material will form. This causes the cavity. Descending of raw materials will be prevented because of the bridge, and a pool of liquid silicon and SiC particles will be present underneath. Drops of SiO_2 will fall into the pool and react. The size of the cavity affects the reaction rates. If the distance between the charge top and the cavity is too short, the area for preliminary reactions is smaller, and hence reaction 2.1 and 2.2 will be limited. Also, the recovery reaction for SiO with carbon will be affected. This is because of higher temperature at the top of the charge, which will force reaction 2.3 to the left, producing less SiC and CO gas. There is also a smaller number of carbon particles to react with. Operators have to stoke the furnace regularly to break down the cavity[4].

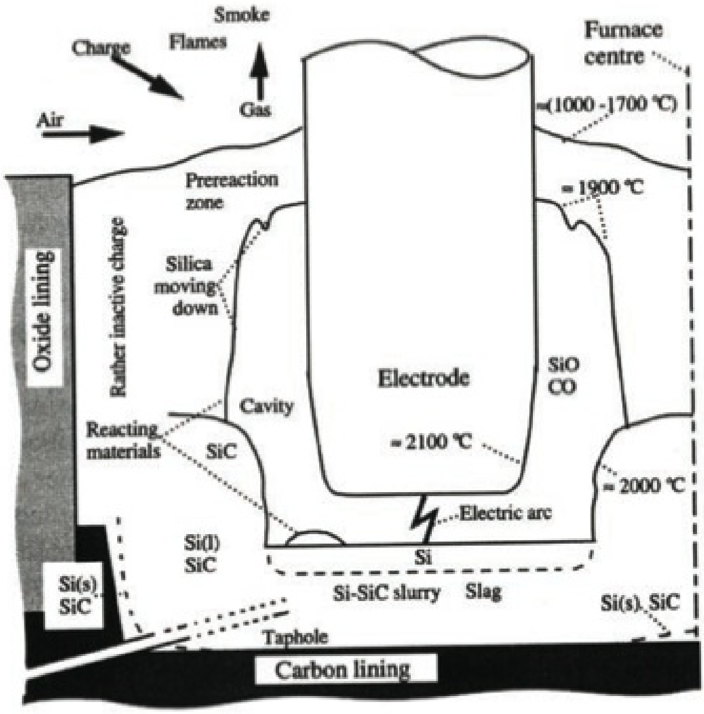


Figure 2.2: The inner structure of a silicon furnace as illustrated by Schei et al.[3].

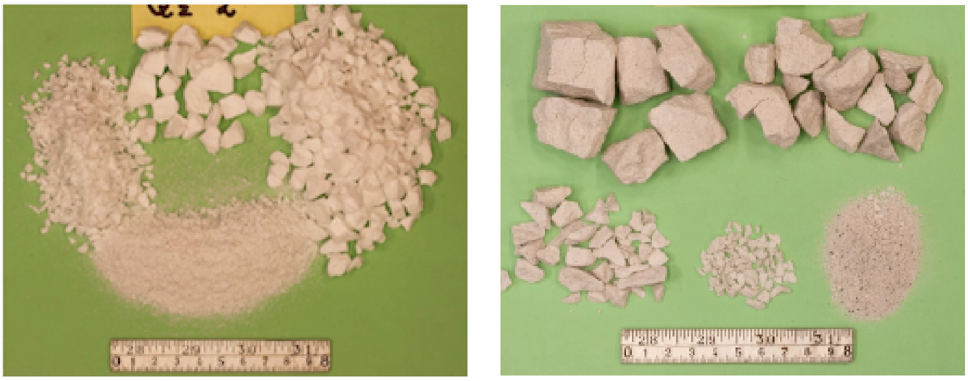
2.1.2.1 Material and gas flow

It is important for the furnace operation that there is an even flow of raw materials and ascending gas. This requires good gas permeability. Several factors are affecting the gas permeability[7] :

- Too much fine particles
- Clogging by SiO condensation
- Clogging caused by softening and melting of silica

Increased SiO condensation will contribute to the blocking. If reaction 2.1 and 2.2 were to happen outside the high temperature zone, the partial pressure of SiO would increase, favouring the condensation[9]. This zone of condensated material is experienced in furnace excavations[10] [11]. Softening and melting of silica also affects the gas permeability. Silica can react in both liquid and solid form, where the softening and melting affect the reaction rates. This could happen because the contact area towards other particles can change. The total effect of the softening and melting on the reaction rates are still being investigated[9].

When a piece of quartz is heated it may disintegrate. Too many fine particles in a silicon furnace may contribute to clogging and decreased gas permeability. Shock heating experiments have been performed by several researchers[7] [6] [12]. Paulsen and Bakken[12] and Ringdalen[7] used the same sample size, around 40 mm × 60 mm and the same maximum temperature, 1500 °C, and a holding time of 10 minutes. Aasly used samples that were only 40 mm × 40 mm and a maximum temperature of 1300 °C. The holding time at maximum temperature was 10 minutes for Aaslys experiments as well. Figure 2.3 shows one of Ringdalens experiments. It can be seen from the figure that the behaviour between quartz samples is not the same. Some samples produce more fine particles than others.



(a) Ringdalens experiments[7], with maximum temperature 1500 °C, Qz2 sample.

(b) Ringdalens experiments[7], with maximum temperature 1500 °C, Qz16 sample.

Figure 2.3: The formation of fines after shock heating quartz in preheated crucible[7].

Ringdalen's[7] and Bakken and Paulsen's[12] results for all their thermal shock heating experiments are gathered in figure 2.4, which shows the relationship between particle size and the cumulative amount of this size. Test 17a, 17b and 17c are parallels from the same sample. Variations are seen between them, but they still fall into the same group which generates around 40-75 % <10 mm. Ringdalen suggests that the amount of fines generated could not yet be correlated with other properties of the quartz samples.

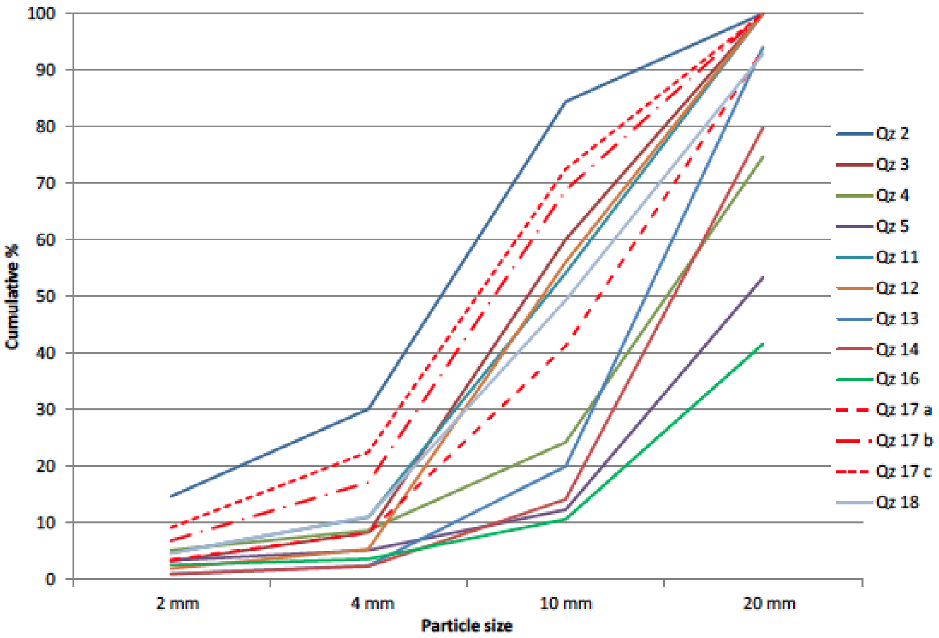


Figure 2.4: Cumulative % in different size fractions after shock heating at 1500 °C[7].

2.2 Silica

Silicon is the second most abundant element on earth, after oxygen. It is mainly bounded as silicon oxides or silicates. As raw material for the silicon production, silica rich minerals are used[6]. Pure quartz contains 100 % silicon dioxide. Quartz can also contain impurities, which are responsible for the differences between quartz types. In figure 2.5, two types with different impurity content can be seen.

Figure 2.5: Two types of quartz. The one to the left has a higher impurity content. The photo is taken by the author for use in this thesis.

2.2.1 Solid phase properties

2.2.1.1 Polymorphism

The phases discussed here are the most distinct and important phases for the silicon production.

The stable phase of silicon dioxide at room temperature and atmospheric pressure is quartz. During heating the quartz will transform into different phases. Some of these phase changes are accompanied by a change in volume as well. The phase diagram for silicon dioxide is given in figure 2.6

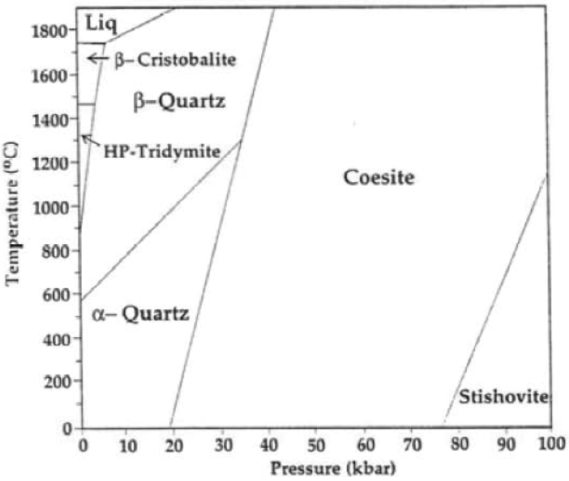


Figure 2.6: Phase diagram for silica. Reprinted from Aasly[6].

The melting point for silicon dioxide varies between different litterature. SI Chemical Data[5] reports a melting point of 1713 °C and a boiling point of 2230 °C. Before the melting point is reached, several phase transformations will occur at atmospheric pressure. From figure 2.6 it can be seen that the first transformation is from α-quartz to β-quartz. This transformation is spontaneous and reversible, and will occure at 573 °C[13]. There is no significant impact on the thermal stability of the quartz from the α to β transformation[14].

According to the phase diagram in figure 2.6, HP-tridymite is a stable phase of silicon dioxide. The existence of this phase is debated, and some suggests that certain impurities are needed for this phase transformation to happen[15]. Tridymite is not further discussed here.

The β-quartz to β-cristobalite transformation is a very slow and reconstructive reaction, and does not start before the temperature has reached 1400 °C according to Stevens et al.[15] In order to form cristobalite, chemical bonds between Si and O have to break and rebind[6]. If the heating rate is too high the β-quartz will reach the melting temperature before any β-cristobalite is formed. It is suggested by Stevens et al.[15] that the transition from β-quartz to β-cristobalite will go through an amorpheous transition phase.

The last transformation of silica is from β-quartz or β-cristobalite to liquid silica. For silicon production, this transformation should occur as low in the furnace as possible. The best position would be just above the electric arc[14].

Even more phases exist, such as several forms of tridymite at 1 atmosphere pressure, and coesite and stishovite at higher pressure[13]. Meta stable phases can also occur. One example is cristobalite at room temperature. The cristobalite formed upon heating will remain during cooling to room temperature unless the cooling rate is very slow[16].

2.2.1.2 Silicon dioxide structure

Characteristically for all the silicon dioxide polymorphs are the building blocks, $SiO_4{}^{-4}$-tetrahedrons. Four oxygen atoms are placed in the corners and a silicon atom in the middle. The tetrahedrons are bonded togehter in the corners, making the ratio two oxygen and one silicon atom. Figure 2.7 illustrates this[17].

(a) Silicon-oxygen tetrahedron, $SiO_4{}^{-4}$.

(b) The arrangement of silicon and oxygen in a unit cell of cristobalite[17].

Figure 2.7: Silicon dioxide structure.

The different polymorphs of silicon are made up of different arrangements of layers of tetrahedrons. The structures that are most stable at room temperature, are relatively open structures with low denisty. The density of quartz is 2.53 g/cm^3[17]. When quartz samples are heated, they will go through an amourphous phase before they transform into cristobalite, which is the most stable phase at temperatures above 1400 °C[15]. In the non-crystalline phase, the $SiO_4{}^{-4}$-tetrahedrons will be randomly placed[17].

2.2.1.3 Volume expansion

A volume expansion of silica during heating is observed in several investigations[6] [14]. The theoretical volume expansion from α-quartz to cristobalite is 17 %[18], but earlier experiments show that the volume expansion could vary between 10 and 110 % with different quartz types. Also between samples of the same quartz types, large differences have been observed. The volume increase is related to the amount of cristobalite formed during heating[14]. Cristobalite has the largest specific volume of the solid phases, and the transformation to this phase from quartz has the largest volume increase. The formation of cristobalite varies between quartz types. This was shown by Kjelstadli[19] during investigation of phase transformations in quartz. Figure 2.8 shows the amount of cristobalite in three different quartz types as a function of holding time at 1600 °C. The amount of cristobalite varied between 1 % and 9 %. The theoretical volume increase from quartz to liquid silica at 1713 °C is 22 %[18].

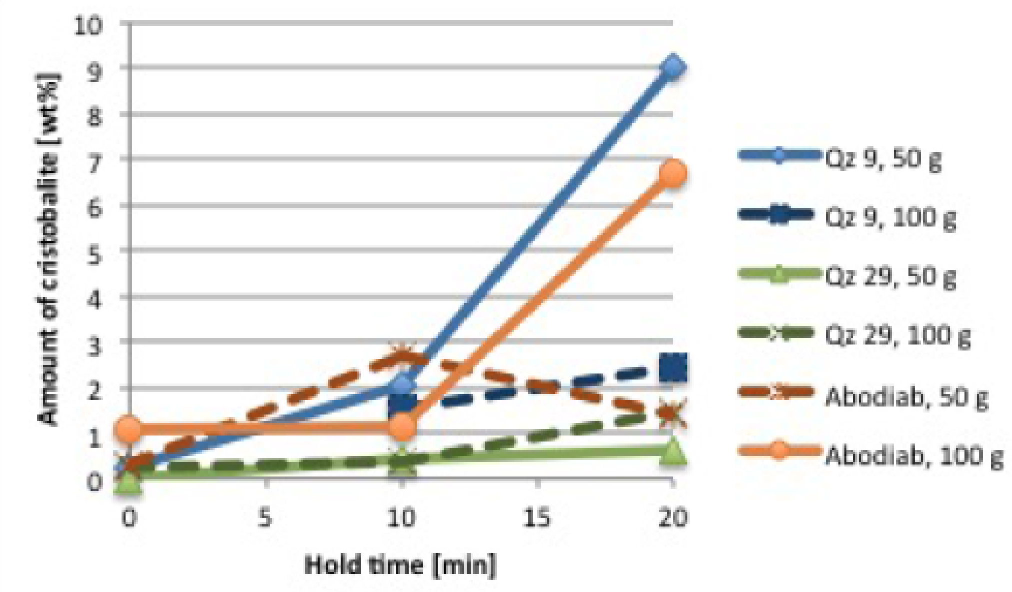


Figure 2.8: The amount of cristobalite in different quartz types as a function of holding time at maximum temperature 1600 °C[19].

Ringdalen et al.[18] and Andersen[14] measured the volume increase as a function of temperature for several different quartz types. The volume expansion in their experiments performed in sessile drop furnace had large variations. The maximum volume was observed from 1650 °C to 1800 °C. Figure 2.9 shows this.

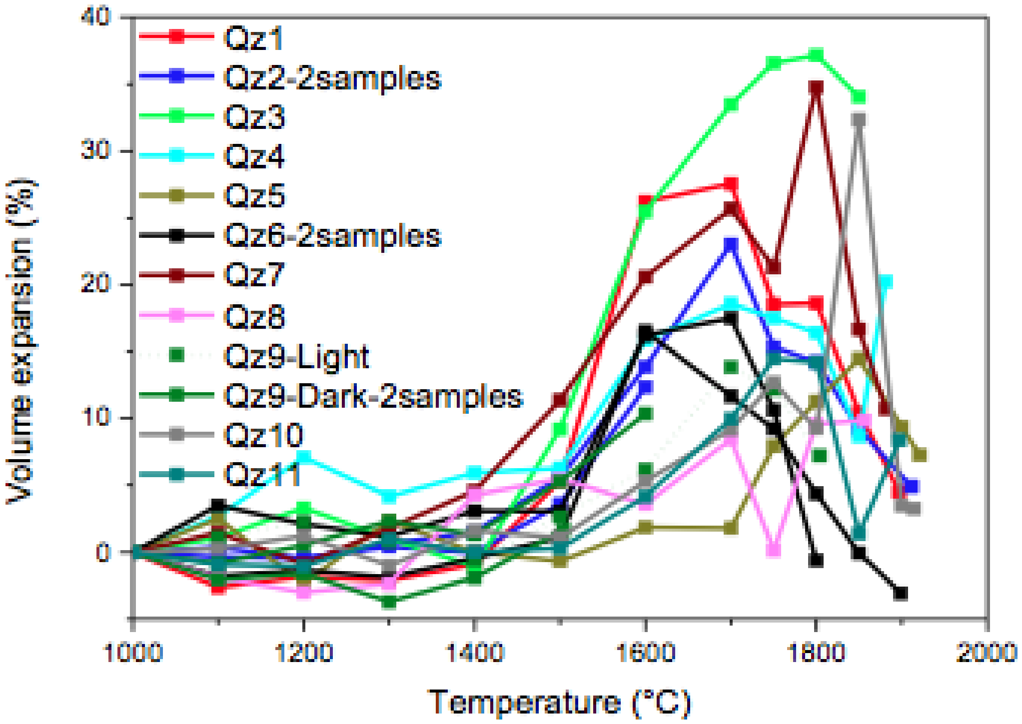


Figure 2.9: Volume expansion as a function of temperature for several quartz types. The figure is based on results from Ringdalen[20].

For some quartz samples the volume expansion has been measured with varying heating rates as well[18]. As can be seen from figure 2.10, different quartz samples show the largest difference in volume expansion. The figure also shows that for Qz27 and Qz9 decreased heating rate increases the volume expansion. Qz27 was heated twice with the same heating rate, 5.5 °C/min, and the volume expansion was close. This strengthens the reliability of the method used.

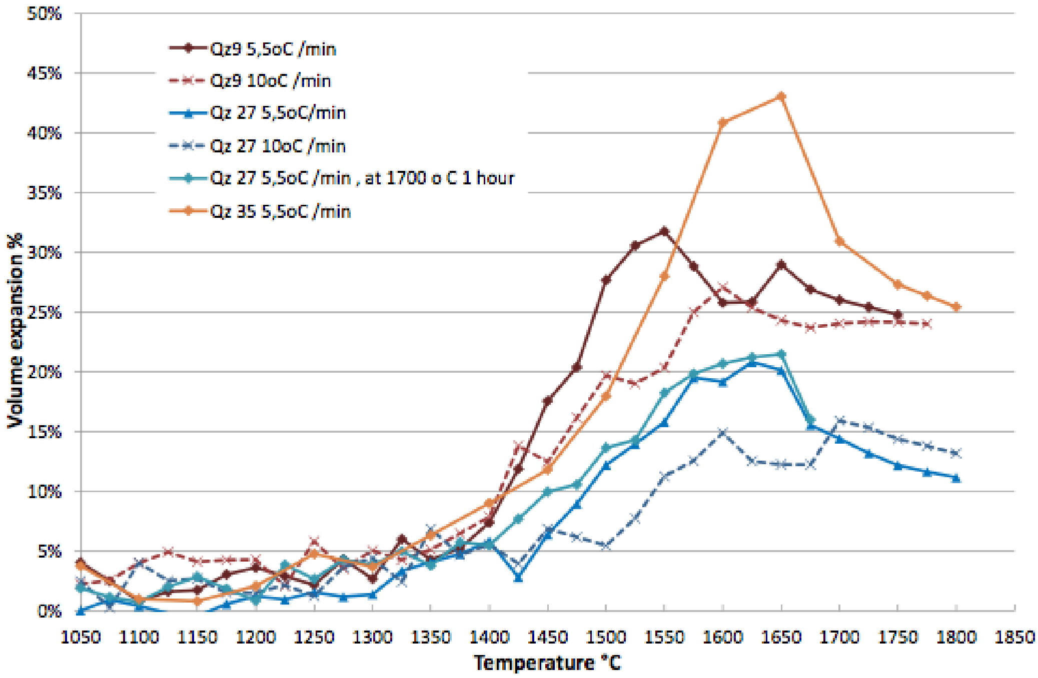


Figure 2.10: Volume expansion as a function of temperature for several quartz types and different heating rates[18].

2.2.1.4 Heating of solid silica

Thermal diffusivity

The thermal diffusivity of silica will decrease with increasing temperature up to 573 °C. This was shown by Ksiazek[21] for two quartz samples. Figure 2.11 shows this. After about 573 °C, when α-quartz has transformed to β-quartz, the thermal diffusivity tends to be constant for D quartz at a value of 0.75 mm^2/s. The other quartz type increases its diffusivity slightly after this.

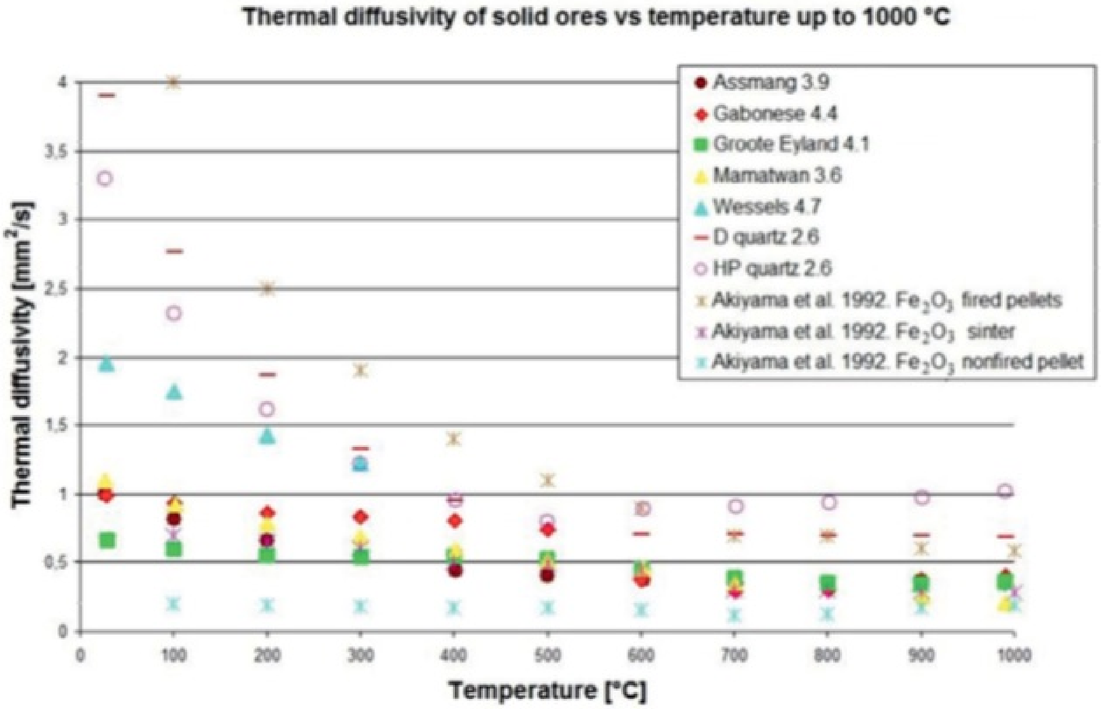


Figure 2.11: Thermal diffusivity of different manganese ores, and two quartz types, as a function of temperature. Numbers behind the legend names indicated the density of the sample in g/cm^3 [21].

Temperature distribution

Kjeldstadli[22] with assistanse from Michal Ksiazek modelled the temperature in the center of a quartz sample, as a function of time. Samples with different radii were modelled up to 1700 °C. As can be seen from figure 2.12, it takes about 30 minutes before the temperature in the middle of a sample with radius of 1 cm reaches 1700 °C. The samples were heated together with the furnace. It took 30 minutes for the furance to reach 1700 °C, which means a heating rate of 57 °C/min. The model does not take into account changes in thermal diffusivity with different silica phases. Thermal diffusivity for quartz is used for all temperatures.

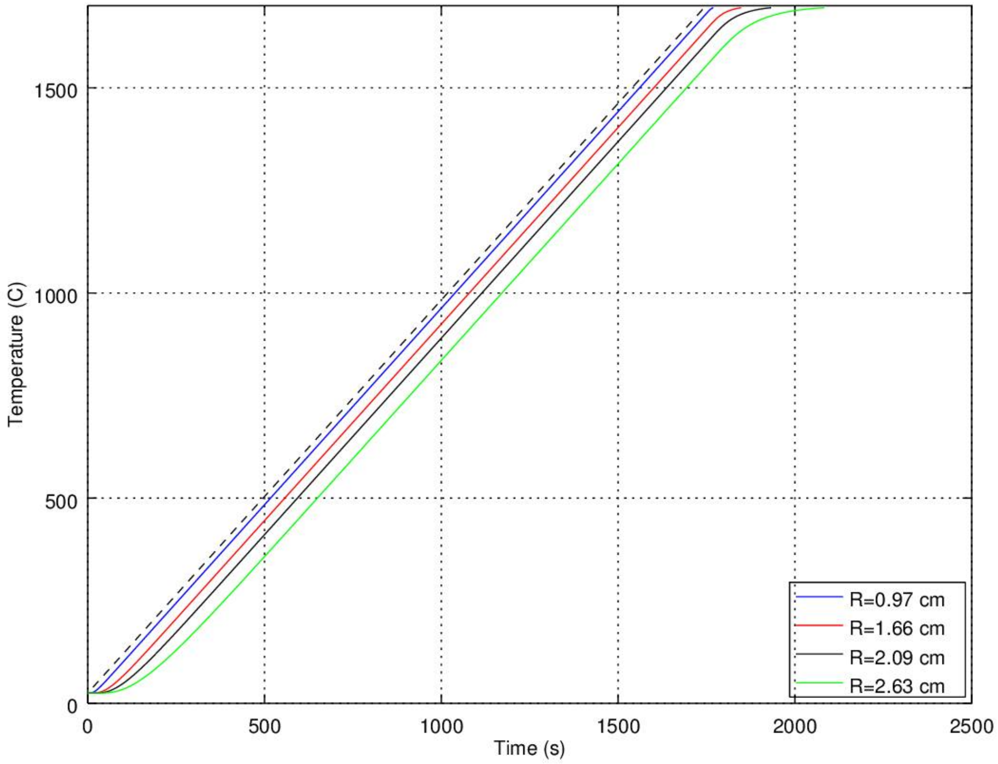


Figure 2.12: Temperature in the center of quartz samples with varying radii as a function of temperature[22].

2.2.2 Softening and melting of silica

2.2.2.1 Softening

The softening and melting properties of silica have not been widely investigated earlier, as e.g. carbon properties have[6]. In a silicon furnace, softening should ideally happen close to the melting temperature. If the quartz starts to soften too early it may cause a more compact charge in the furnace, and lower the gas permeability. Also at a lower temperature, the quartz will be located at a higher point in the furnace. Together, these factors will decrease the recovery of SiO gas in reaction 2.5 and 2.3, and lower the Si-yield for the process. A compact charge can also cause the pressure inside the furnace to increase. This could lead to a sudden blow of gas. Then the gas will force its way out of the furnace, and give little time for the SiO gas to recover[3].

When silica samples are approaching its melting point, they can start to soften[18]. Softening is defined by Ringdalen et al.[9] as when the shape of a quartz sample loses its sharp edges. According to Dash[23], a material can start to premelt before bulk melting starts. The disorder and mobility of atoms at the surface of a bulk sample will increase as the temperature approaches the melting temperature. This disordered region will initially be very thin and possess the solid bulk properties. As the region thickens, the outer surface will change its properties to liquid properties more and more. This wetting of an initially dry surface on a bulk solid below its melting temperature, could lower the systems free energy. Despite the energy cost of converting a small amount of material from solid to liquid, this is not prohibitive. The cost of this conversion also determine the theoretical thickness of the pre melted layer. For Ar and Ni the layer is approximately five to six atomic layers[23].

Doris Kuhlmann-Wilsdorf[24] suggests that amorphous substances are understood as liquids of high viscosity. This is explained by high frictional stress on the dislocation cores in the structure. When the free energy of a dislocation core becomes negative, it will enter the melted phase. Several of these dislocation cores with negative or zero free energy will build up the liquid phase of a structure. Thermal motion reduces the frictional stress on dislocation cores in a solid, and helps to overcome it. This can explain gradual softening of amorphous substances on heating. Also Presser and Nickel[25] present that silica will become increasingly fluid-like at temperature above 1677 °C.

An earlier test method for investigating softening temperatures was the Seger cone test. The material with unknown softening temperature was compared with other materials with known softening temperature. Nearly geometrical identical cones were made of all the materials, and then they were heated toghether. By comparing the bending downwards of the cones, the softening temperature could be determined[16].

2.2.2.2 Melting

In brief, cohesive forces keep the atoms close to each other in solids and liquids. In solids, the atoms have fixed positions, and are vibrating around these. When a solid melts, energy is added and makes it possible for the atoms to jump around the fixed positions in the solid. The energy needed to overcome the binding forces in a solid, is called the latent heat[26]. At the equilibrium phase transition temperature, the chemical potential, μ, of the different phases are the same[27]:

$$\mu^s = \mu^l \tag{2.9}$$

If the temperature is increased or the pressure decreased from this point, the liquid state becomes the state with lowest energy, and hence the more favourable state to be in. Figure 2.6 shows the phase diagram. The lines are illustrating the conditions where the chemical potentials for two or more phases are the same. Just above 1700 °C, a line is separating the β-cristoabalite phase and the liquid phase of the silica.

The mechanism of melting

Even if the macroscopic and thermodynamical consepts of melting are well established, the mechanism and microscopic aspects are not fully understood. Several theories have been presented since 1910 when Lindemann presented a theory based on vibrational instability[28]. Some theories are presented here.

One theory of melting is based on the claim that melting occurs when the free energy of dislocation cores becomes negative. When this happens, dislocations cores are generated, and will fill the crystal. This process requires significant amount of latent heat, and the solid will lose all its resistance against shear forces. The temperature of melting is, by definition, the point where the dislocations cores loses its free energy[24].

Another theory also based on dislocations, suggests that the transition between a solid and a liquid phase attributes to a sudden catastrophic proliferation, or spreading, of dislocations[29]. This theory implies the acceptance that a liquid is a crystal saturated with dislocation cores. On the atomic level melting could be explained by lattice instability at sufficient high temperature. Thermal vibration and thermal expansion will eventually cause a dispersion, or bifurcation, of the on-site potential energy near an atom. This suggests that melting might be a result of separation instability, and that a liquid state is the result of a series of these bifurcations of potential energy. The atoms will eventually move further apart from each other, until they reach the point where the attracting energy between them is close to zero[29]. The crystal will reach the bifurcation instability point, when the lattice no longer maintains its structural integrity and has become a liquid[30].

More recent studies[31] suggest that the earlier theories have too many simplifications, and that melting is a process that contains multiple and competing pathways involving formation and migrations of dislocations and point defects. These pathways are a result of barrier-crossing events which are arising from several metastable states of the solid material. A liquid nucleus will form, and eventually grow. Atoms at the surface of a solid, are more fluid-like and therefore it is more likely that the liquid nucleus will form and expand as the solid crystal becomes smaller and smaller.

Melting kinetics

A studies by Ainslie et al.[28] claims that all observations so far indicate that melting is a heterogeneous process. A liquid film will form on the free surfaces of a crystal, and propagate inwards. This will happen at slight superheating. Further, they also suggest that the nucleations of a liquid nucleus on a surface are an easier process than the opposite, crystallization. The viscosity of a fluid will affect its melting kinetics. If a melt has low viscosity and is quite fluid, the heat absorptions will be so fast that the interior of a crystal will not become superheated before it melts. For melts that have high viscosity, the heat absorptions will be slower, and high superheating can be obtained. It is shown by Mackenzie[32] that quartz can sustain superheating of 300 °C a considerable period of time. A result from Ainslie et al.[28] is shown in figure 2.13 which shows a section of a quartz crystal heated to 1730 °C. The formation of cristobalite was supressed in these experiments, which means that the formation of a glassy silica phase could start as low as 1400 °C. It can be seen from figure 2.13 that the glass phase has formed on the external surface of the crystal. The interior is still quartz. This was the case for all the experiments, except when cracks were present in the crystal. The viscosity of the glass phase at 1730 °C is still very high, so that the shape is not considerably altered during heating. The thickness of the glass layer could therefore be measured quite accurately, and a relationship between the thickness of the melted layer and time could be constructed. This heating rate can be seen in figure 2.14. Within reasonable uncertainty limits, the fusion-time relationship is linear.

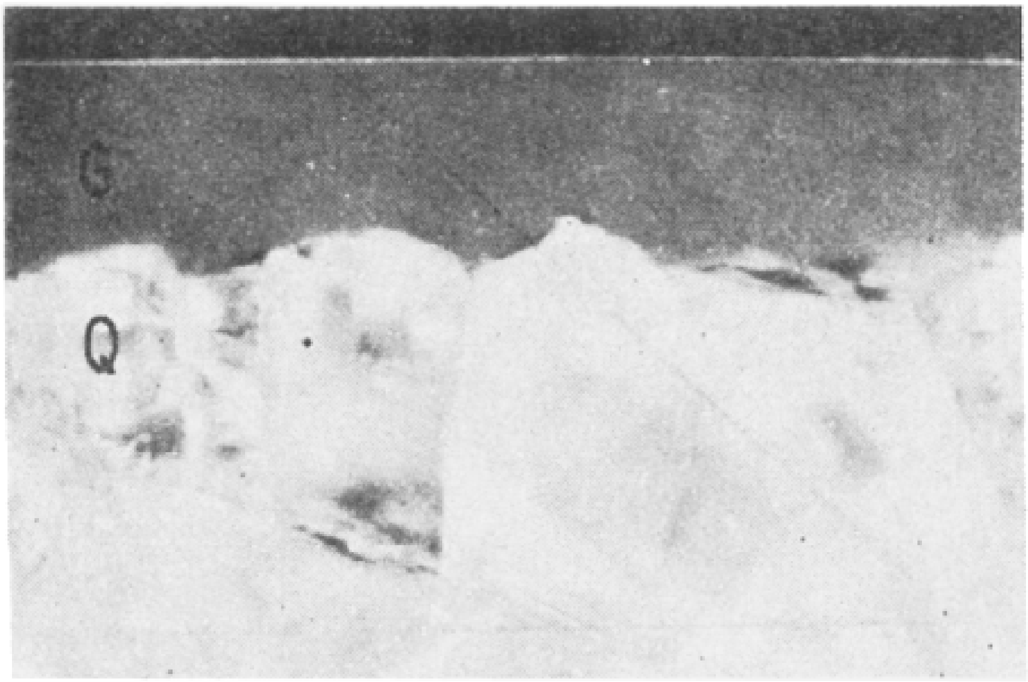


Figure 2.13: Section of quartz crystal heated to 1730 °C for 15 minutes in air. The formation of glass phase, G, is over the quartz substrate, Q. The image is enlarged 200 times[28].

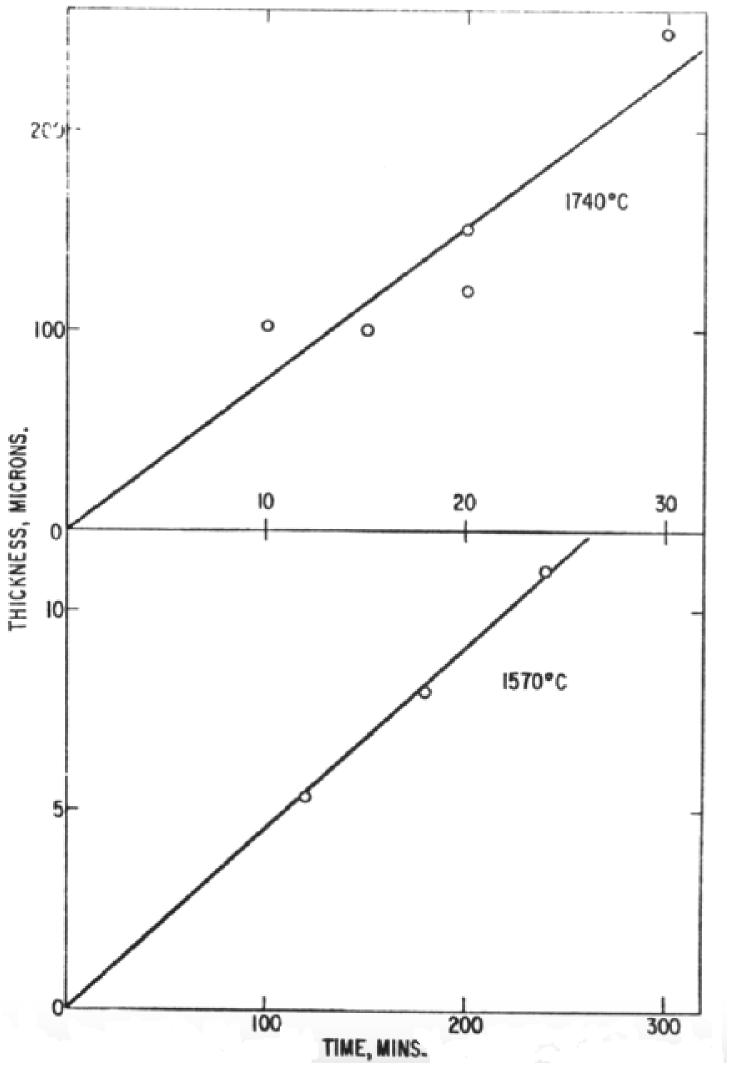


Figure 2.14: The melting rates of quartz at 1740 °C and 1570 °C, respectively[28].

Wiik[33] suggests that the phase transformation from quartz to cristobalite is homogeneous, and do not start at the surface of a sample like Ainslie et al.[28] argues. The phase transformation to cristobalite origins from nucleation sites evenly spread throughout the sample. Because quartz is of higher density than the transition phase between quartz and cristobalite, the transition phase will occupy a larger volume. This causes tension in the sample, that will cause cracks in the parts still being quartz. The reconstructive transformation involving the breaking of Si-O bonds will result in an extensive fragmentation of the transition phase. Some studies have found that partiailly converted quartz samples, containing large portions of transition phase but no cristobalite, were easily crumbled under pressure from the fingers. This supports the theory that the transition phase is fragmentated, and therefore a large number of homogeneously distributed internal nucleation points for nucleation and growth of cristobalite would be available[33]. The formation to cristobalite would then occur througout the whole volume of the transition phase, not only on the outer surfaces as suggested by Ainslie[28].

The effect of impurities
Impurities in the quartz can alter the melting temperature. The effect depends on the nature of the impurity. A mix of several impurities can have a complex impact. If a binary system is considered, the impurity can either lower or raise the melting point depending on what composition range the two components are in. The effect can either be eutectic-like or peritectic-like[27].

Doris Kuhlmann-Wilsdorf[24] claims that in a dilute mixed crystal of an alloy, the energy will be less than in a pure crystal. This is because every binding between dislocation cores and substitutional and interstitial atoms decreases the core energy. Hence, the energy is closer to the point where the free energy of dislocation cores vanishes, and the melting point will be decreased. Also Turnbull and Cohen[34] found that in crystals which are covalently bound, impurities will catalyze the movement of the interface between crystal and liquid.

2.2.2.3 Viscosity

At its melting temperature, silica is highly viscous, around $2 \cdot 10^7$ Poise[35]. Compared to liquid water, which has a viscosity of 0.01 Poise, silica at 1713 °C behaves nearly as a solid. The viscosity of quartz determines the melting conditions, temperature of working and annealing, rate of removal of bubbles, maximum temperature of use and crystallization rate[36]. Several experimental evidence has shown that the temperature affects the viscosity, and that it is usually represented by an Arrhenius-type relationship given in equation 2.10.

$$\eta = \eta_0 \cdot exp\frac{G*}{RT} \tag{2.10}$$

η_0 is the pre-exponential factor, G* is the activation energy, R is the gas constant and T is the temperature. Depending on the form of equation 2.10, the pre-exponential fractor η_0 may vary[37].

Figure 2.15[37] shows the viscosity for pure silica in addition to other silica melts. From the figure it can be seen that the viscosity is highly dependent on temperature. As the temperature increase the viscosity decreases. The same trend is seen for all the different silica melts, containing other components often found in slag from silicon production. All the silica melts with impurities have a lower viscosity than pure silica.

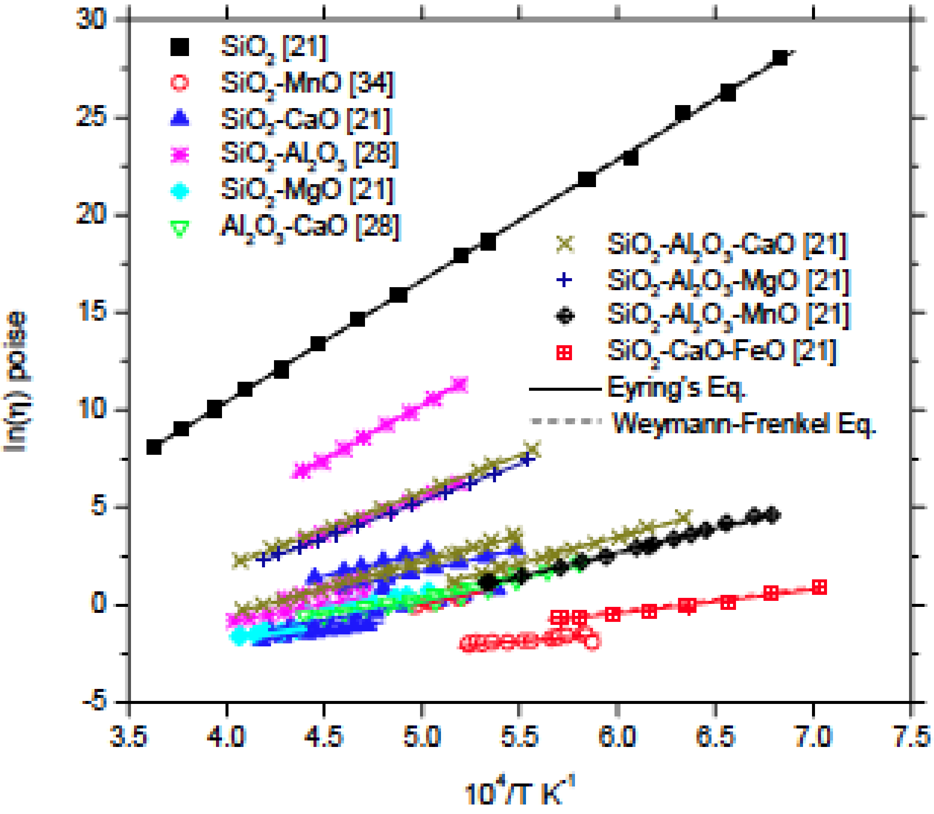


Figure 2.15: Viscosity for different silica melts[37].

2.2.2.4 Superheating of a crystalline solid

A crystalline solid can be superheated above the melting point. This is possible when melting at the surface is suppressed. The most important and early explanation of this phenomenon was proposed by Lindemann and Born. They suggested that bulk melting is caused by instability due to vibrations in the crystal lattice. The instability arises when the average displacement between atoms has reached a critical fraction of the total distance between two neighbouring atoms. Later Born also proposed that the vanishing of elastic modulus during heating caused the stiffness of a material to disappear, which could determine the melting point of bulk material when surfaces were limited[27].

Recent explanations for the upper limit of superheating are based on the heat capacity. When a substance is heated, the heat capacity increases rapidly because of vacancy formation. Also, Fecht and Johnson argued that the limit for superheating was a result of the isoentropic temperautre, where the entropies for the superheated crystal and the liquid become equal[27].

2.2.2.5 Softening and melting temperature - earlier experiments

Experiments in the mg-scale

The melting point of silica will vary between different quartz types, due to impurities. Experiments to determine the softening temperature in wetting furnace have been performed by Ringdalen[18] and Andersen[14]. Most of the experiments were perfomred under CO-atmosphere, and a few under Ar-atmosphere.

From figure 2.16 it can be seen that the softening and melting temperatures vary between quartz samples and heating rate. According to Ringdalen et al.[18] it was first believed that a higher heating rate might cause a higher melting and softening temperature. There is some overlap, but the indicative trend is that the softening and melting point do increase with increasing heating rate.

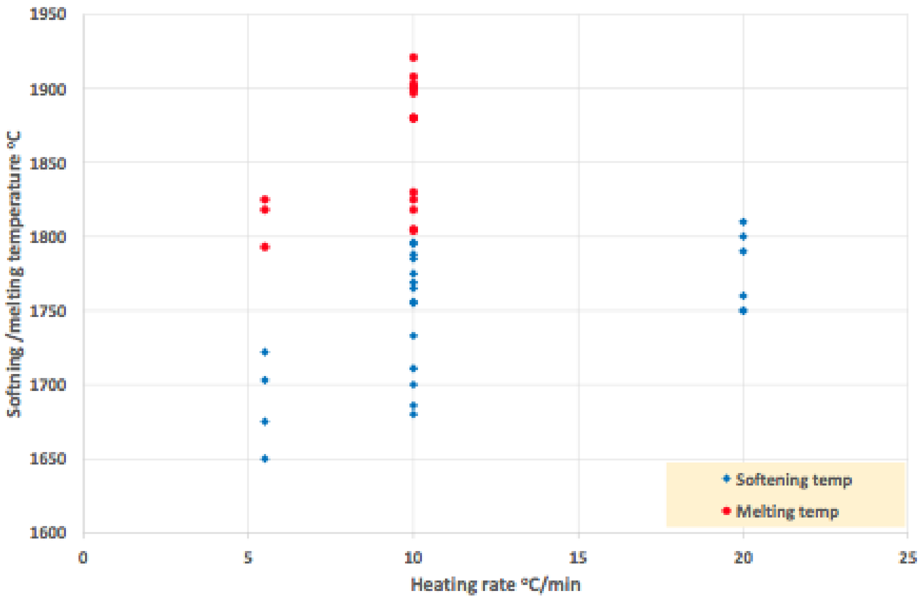


Figure 2.16: Softening and melting temperatures for different quartz samples as a function of heating rate. The figure is reprinted from Ringdalen et al.[18].

Effects of impurties

According to experiments by Ringdalen et al.[18], the content of FeO in quartz will affect the softening temperature. Figure 2.17 shows that the softening temperature mostly decreases with increasing FeO content.

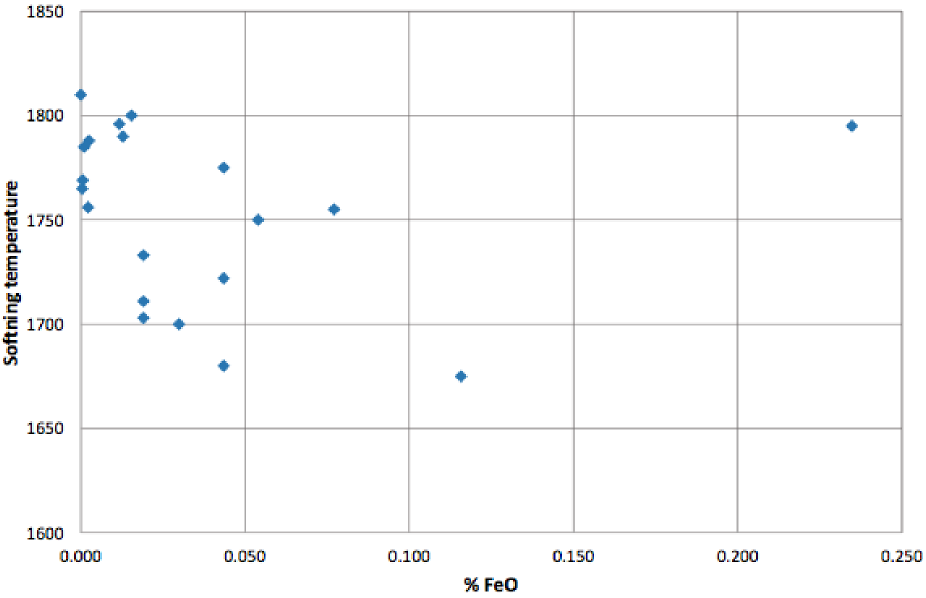


Figure 2.17: Variations in softening temperature as a function of FeO content in different quartz samples[18].

Experiments in the kg-scale

In Jusnes'[1] study quartz was heated to different temperatures, and the amount of softened, melted and unreacted silica measured. Figure 2.18 shows crucibles with quartz heated to a maximum of 1500 °C to 1850 °C. The amount of softened and melted quartz was visually inspected on the surfaces.

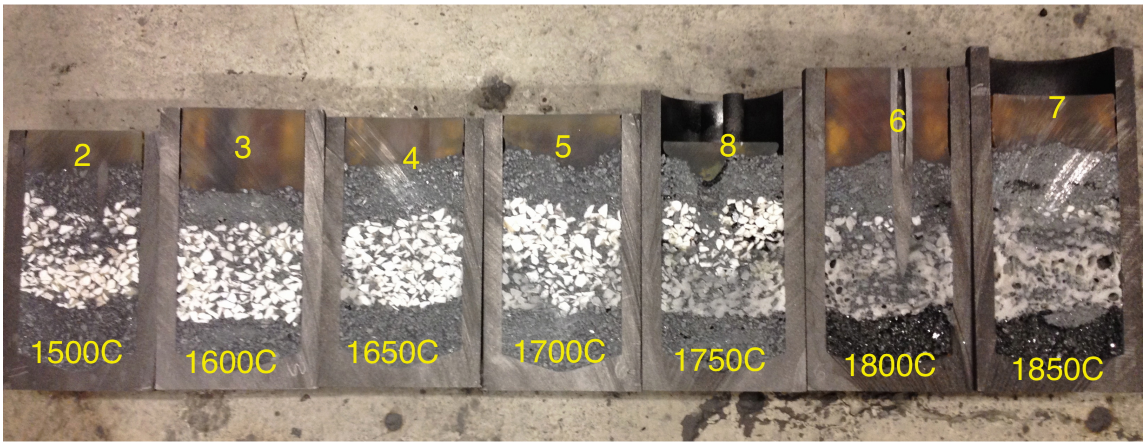


Figure 2.18: Quartz of the type Qz27 heated to different maximum temperatures. The amount of softened silica will increase and then decrease as the silica is melting[1].

Figure 2.19 shows the percentage of surface area that was softened, melted or unreacted as a function of temperature in the experiments performed by Jusnes[1]. From the figure it can be seen that the amount of unreacted silica is steadily decreasing, and the amount of melted silica is increasing, as expected. The softening of silica is first increasing and then decreasing as it is melting instead.

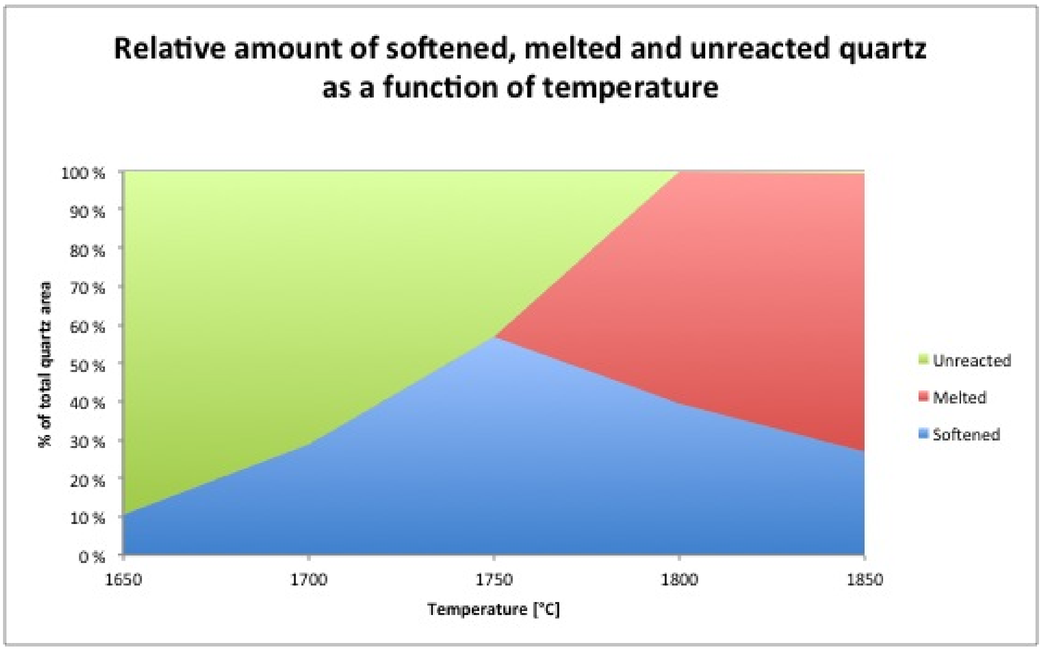


Figure 2.19: The relative amount of softened, melted and unreacted silica as a function of temperature[1].

Chapter 3

Experimental

In total 13 experiments in the induction furnace and 4 experiments in the wetting furnace have been executed in this study. The details for each experiment are given in table 3.2 and 3.4 respectively.

In Jusnes'[1] earlier work with the development of a method for measuring softening and melting of silica, some improvements were suggested. These were as follows:

- **Equipment:** Check thermocouple consistensy for thermocouples used in the experiments, and manually control the induction furnace in an attempt to minimize the variations in heating rate.
- **Set up:** SiC particles should have the same size as the quartz particles. Also the SiC:quartz ratio should be adjusted.
- **Conditions:** There should be a holding time at maximum temperature.

All these suggestions for improvements have been executed.

3.1 Materials

Quartz
Two different types of quartz have been used to further develop and optimize a method for investigating softening and melting of silica. The two samples, Qz27 and Qz35, were provided by the industry. Qz27, also used in earlier similiar experiments, was purer than Qz35 which contained a considerable amount of impurities. The composition of Qz 35 is given in table 3.1. Before the experiments started, lumps of quartz were crushed and sieved to obtain

the desired particle size. Most of the samples were sieved between 4.76 and 9.52 mm. This sample size was chosen to minimize any effect the carbon crucible might have on the contents. The sample size should be under 10 % of the diameter of the crucible to minimize any effect from the crucible.

Content Qz35	
Element	**Amount %**
SiO_2	93.85
MnO	0.14
Mn	0.1
Fe	0.09
FeMET	0.09
P	0.013
Cr	0.0339
Ti	0.0235
Al_2O_3	1.19
MgO	0.05
CaO	0.09
BaO	0.0017
K_2O	0.18
S	0.007

Table 3.1: The composition of Qz35 quartz. Only the impurities with a content above 0.001% are included here.

Silicon carbide

Silicon carbide, SiC, was also used in the experiments. The size of the silicon carbide pieces were in the same range as the quartz samples, 5-10 mm. Washington Mills was the provider of the SiC. It has a density of 3.21 g/cm^3 [38].

CO gas

CO gas was used in the wetting furnace experiments to obtain a CO atmosphere inside the heating chamber. The gas was provided by AGA, and was of the type instrument carbon monoxide 3.7.

3.2 Experiments in induction furnace

3.2.1 Equipment

Carbon crucible

Carbon crucibles with an inner diameter of 11 cm and a height of 38 cm were used in the experiments. A new crucible was used each time. The thickness of the crucible wall was 2.3 cm.

Thermocouples

Thermocouples of type C were used. The principle of operation is based on the thermoelectric effect. A voltage is generated in a conductor exposed to a temperature gradient. Two wires of different conductivity are connected by soldering in a hot junction and to a voltmeter in the other end. A small difference in voltage is created and recorded by the voltmeter. This voltage difference is converted to a temperature. The wires are protected by alumina protective sheet and alumina protective tube[39]. A carbon tube is also used as protection outside the alumina tube. For type C thermocouples the wires are made of tungsten, 74 wt% and rhenium, 26 wt%. This type can withstand temperatures well above 2000 °C[40].

A type S thermocouple which was secondary calibrated was also used. The type S thermocouple can withstand temperatures up to 1500 °C, and the wires are made of platinum-10%rhodium and platinum[40].

Induction furnace

An induction furnace is based on the principle that an alternating current will create a varying magnetic field, which again will create a current in conducting material. Due to resistance in the material, the current will cause an increase in temperature. For the induction furnace used in these experiments, a copper coil is winded around a carbon crucible. A power supply generates the current through the coil, which induces a magnetic field which is directed through the crucible. A carbon crucible can be placed inside the furnace from the top. The furnace used in these experiments can be seen in figure 3.1. The crucible is placed in the circular opening in the middle of the furnace. The opening has a diameter of 18 cm. Water cooling is essential for the equipment. Also, the inside of the furnace needs a protective layer of graphite wool if the temperature is exceeding 1600 °C.

Figure 3.1: The induction furnace used for the experiments. A carbon crucible fits in the furnace opening, which is 18 cm.

The power input to the furnace can be adjusted, but there will always be a delay before the recorded temperature responds to the power adjustment. This means that in most cases, the heating rate will not be constant, but have small local variations in time. The power input was manually controlled in all the experiments.

3.2.2 Method

Heating

The experimetnal setup was based on similiar experiments performed by Slizovskiy et al.[2]. They used the setup to investigate melting temperatures for manganese ores under different conditions. Jusnes[1] adjusted the method for investigation of quartz. It was important to use a method that reproduced the operating conditions inside an industrial furnace, and to develop a method that could be used for later comparising of quartz types. The method is based on the S.C.I.C.E. (stationary charge in controlled environment) technique, since this method allows for repetative experiments and controllable heating conditions. For the experiments done in this study, the initial method was further developed.

Several experiments with different varying parameters were done. The details for each experiments are seen in table 3.2. Heating rate, particle size, type of quartz and temperature were varied one at the time, to see the effect of each parameter. Table 3.3 shows the parameters that were kept constant during all the experiments.

Carbon crucibles of 11 cm diameter and 38 cm height were used. They were filled with 5 cm layer of SiC in the bottom, then a 10 cm layer of SiO_2 and SiC, and a 5 cm layer of SiC at the top. The ratio of the middle layer was 1:2 moles of quartz compared to SiC. This ratio was based on the overall reaction equation, reaction 1.1, where 2 moles of carbon react with 1 mole of SiO_2. The carbon will react by reaction 2.3 to produce SiC. This reaction will happen at a lower temperature than the temperature at which the quartz reacts. This means that at the time when the quartz starts to react, all the carbon have reacted to SiC. Figure 3.2 shows an illustration of the carbon crucible and its content. A Kalwool layer was placed on top of the crucibles as an attempt to decrease heat loss.

No.	**Quartz type**	**Max. temp. [°C]**	**Heating rate [°C/min]** **(after1000°C)**	**Particle size [mm]**
9	Qz27	1650	5.5	4.76-9.52
10	Qz27	1800	5.5	4.76-9.52
11	Qz27	1750	5.5	4.76-9.52
12	Qz27	1700	5.5	4.76-9.52
13	Qz35	1650	5.5	4.76-9.52
14	Qz35	1750	5.5	4.76-9.52
15	Qz35	1700	5.5	4.76-9.52
16	Qz27	1650	11	4.76-9.52
17	Qz27	1750	11	4.76-9.52
18	Qz27	1700	11	4.76-9.52
19	Qz27	1750	5.5	15-20
20	Qz27	1700	5.5	15-20
21	Qz27	1650	5.5	15-20

Table 3.2: The variable parameters used in this experiment.

Constant	**Value**
Heating rate up to 1000 °C	40 °C/min
Holding time at max. temp.	30 min

Table 3.3: The constant variables used for all the experiments.

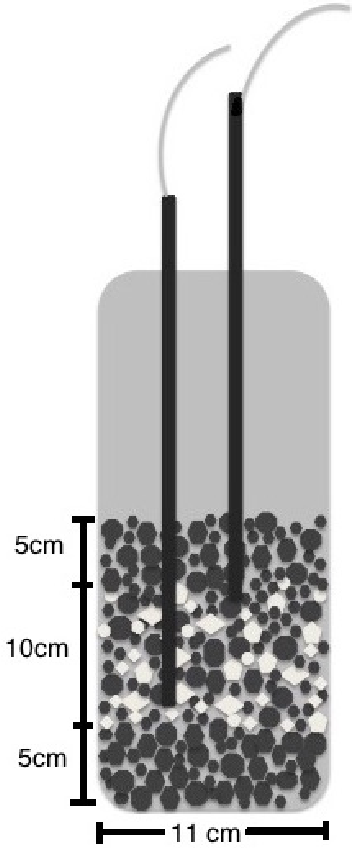


Figure 3.2: An illustration of the carbon crucibles filled with SiC, black particles, and quartz, white particles. The wires at the top are connected to a temperature recorder. The inner diameter of the crucible is 11 cm, and the height 38 cm.

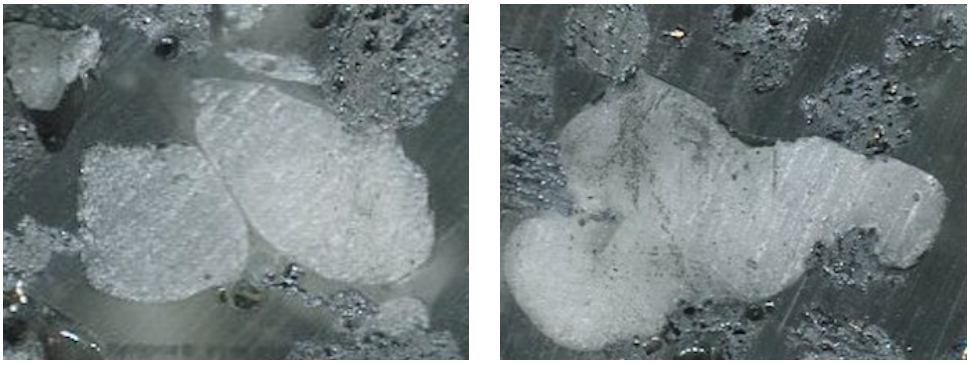
Post heating treatment

After cooling, the crucibles were filled with epoxy of the type Weber floor 4710N base and hardener, and left over night to harden. The crucibles were then cut vertically through the middle using a diamond saw.

The inside surfaces of each crucible were scanned using an Epson Perfection V30 scanner and the belonging software. To measure the area of softened, melted and unreacted quartz Adobe Acrobat was used. Each area was marked using the measuring tool in the software, and divided into the three groups softened, melted and unreacted. In this context, unreacted means neither softened or melted. The criterias for determining between softened and melted phase were based on the following:

- Melted particles have more round shape than softened.
- Melted particles have adjusted themselves to the surroundingd, softened has not.
- Melted particles may have melted togheter, forming one larger particle. If there still exists a boundary bewteen the particles, they are softened.

Figure 3.3 tries to illustrate a case on the very limit between melting and softening.



(a) Softened particles.

(b) Melted particles.

Figure 3.3: Examples clarifying the limit between softened and melted silica.

Temperature control

To check the consistency between the C-thermocouples used in the experiments, they were compared with a secondary calibrated S-thermocouple at 1500 °C. The three thermocouples were mounted in a crucible filled with SiC. They were positioned with the same distance to the crucible wall and to each other to equalize any possible impact this might have on the temperature. In figure 3.4 the set up can be seen. The heating rate was set to 40 °C/min up to required temperature, and then a held for 20 minutes.

Figure 3.4: Set up for comparison of C-thermocouples and S-thermocouple at 1500 °C. The opening in the furnace has a diameter of 18 cm, and the crucible has an inner diameter of 11 cm.

The temperature in the induction furnace varies with position. In Jusnes'[1] earlier experiments it was shown that the vertical temperature gradient in the crucible was around 200 °C across the quartz layer. Figure 3.5 shows the relationship between the temperature and the vertical position in the crucible.

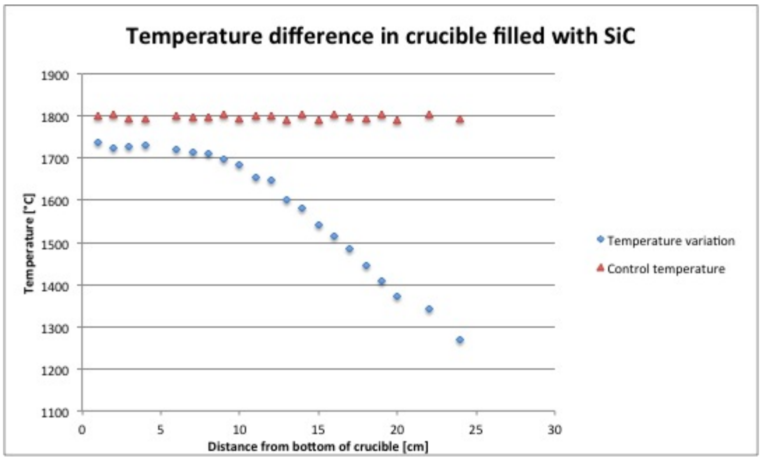


Figure 3.5: Temperature in a crucible filled with SiC held at 1800 °C as a function of distance from the bottom of the crucible[1].

Tangstad et al.[41] also measured a temperature gradient in crucibles containing SiC, silica and Si heated in the induction furnace. Their temperature gradient shows similiar results as Jusnes'[1]. In figure 3.6, a crucible with the decreasing temperature marked is seen. This crucible was heated to 1710 °C, and had a temperature gradient of 260 °C during 30 minutes holding time at maximum temperature. The uncertainy of the method developed is large, but since it is known, the softening and melting can still be measrued within reasonable limits, and compared with each other.

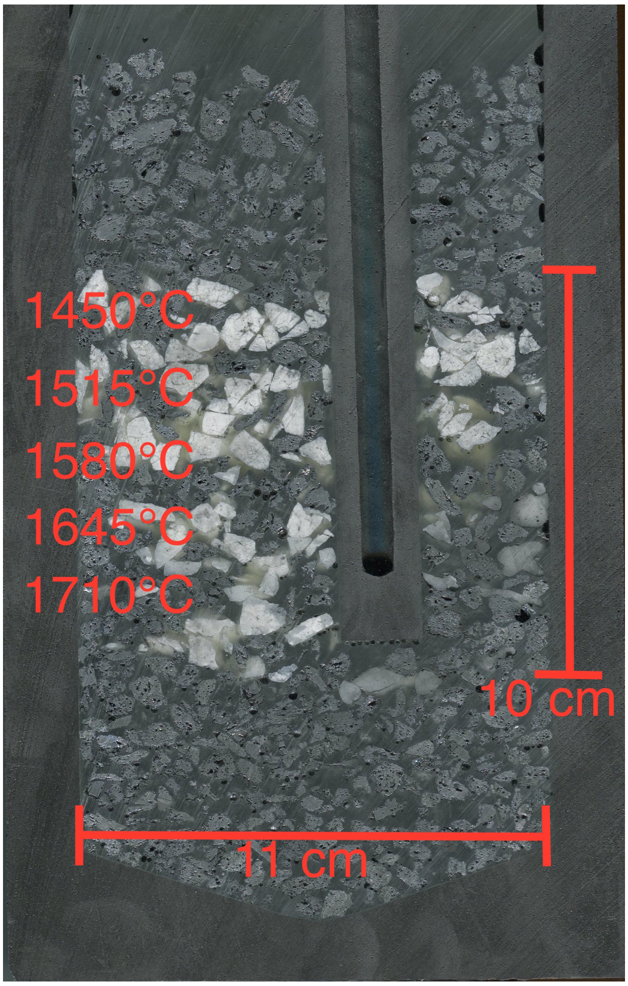


Figure 3.6: Crucbile heated to 1710 °C. The temperature is decreasing upwards in the crucible as marked on the left hand side. The quartz area in the crucible is 10 × 11 cm.

For the experiments performed for this project the radial temperature gradient was also measured. The crucible was filled with the same material and amounts, as all the other experiments, seen in figure 3.2. Kalwool was also used on the top of the crucible. Three thermocouples were mounted in the bottom of the quartz layer, at the same vertical position but with different horizontal position from the crucible wall. In total three measuring points were possible to fit in the crucible. The setup can be seen in figure 3.7. Maximum temperature for this experiment was set to 1700 °C. The heating rate was 40°C/min, and a holding time for 30 minutes at maximum temperature.

Figure 3.7: The crucible placed in the furnace to measure the radial temperature gradient. There were three measuring points from the crucible wall to the center of the crucible. The opening in the furnace where the crucible is placed is 18 cm in diameter.

3.3 Experiments in wetting furnace

Equipment

The wetting furnace was used to investigate the softening and melting temperatures and the volume change during heating for different quartz samples. A wetting furnace consists of a closed chamber, horizontally directed and with graphite heat elements. The heater is surrounded by graphite radiation shields, and is water cooled. The quartz sample was placed on a carbon substrate with a molybdenum shield to protect it from the heat. Figure 3.8 gives a schematic overview of the furnace. A video camera is mouted in front of a window in the heater, and allows digital recordings of the melting process. These pictures are later used to determine the softening and melting temperature and calculate the volume change. Also in this furnace a type C thermocouple was controlling the temperature. A pyrometer was used as an extra temperature control. During the experiments, the temperature difference in the thermocouple and the pyrometer was recorded. Over time, the thermocpuple will degrade, causing a deviation in the temperature. The reason is that the thermocouple can not withstand high temperatures in CO atmosphere[14].

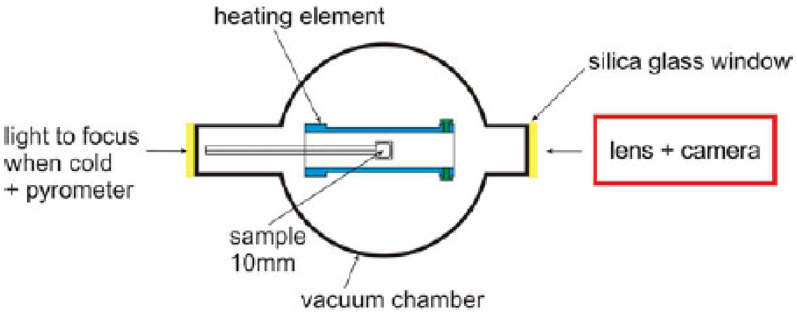


Figure 3.8: Schematic overview of the wetting furnace. Reprinted from Andersen[14].

Method

Four experiments were done in the wetting furnace to check the softening and melting temperature, and to calculate any volume variations during heating. Specifics for each experiments are given in table 3.4. The results from these experiments were used to obtain a deeper understanding of the behavior of the quartz types used, and furthermore to compare results with the experiments done in the induction furnace.

The samples for these experiments were drilled out from larger lumps of quartz. Sylinders of 4 mm were then cut with a height of 4mm, making the sample a sylinder with the same diameter and height. The initial volume was calculated based on this geometrical form. For each experiments, pictures were taken each second and the temperature at this instant recorded.

Quartz type	**Heating rate up to 900 °C**	**Heating rate 900-1200 °C**	**Heating rate from 1200 °C**
Qz27	300	50	5.5
Qz27	300	50	11
Qz35	300	50	5.5
Qz35	300	50	11

Table 3.4: Details for each experiment in the wetting furnace. All heating rates are in °C/min.

The softening temperature was determined based on when the sharp edges of the samples started to loose its sharpness, and become more round. Melting was determined to be when the sample had become close to a sphere, or when the sample showed a clear glassy structure throughout larger parts of the sample.

3.4 Microscale investigations

To investigate the difference in softened, melted and unreacted quartz on microscale, three samples were prepared for investigation in scanning electron microscope, SEM. The samples were taken from crucibles heated in earlier experiments by Jusnes[1]. These experiments were done in collaboration with Siri Marie Bø, who also used the results in her master's thesis.

The three samples were taken from an unreacted, softened and melted zone, heated to respectively 1500 °C, 1750 °C and 1850 °C maximum. All the samples were Qz27. The samples were drilled out of the crucible halves, molted in epoxy and polished before a conducting carbon layer was put upon them.

Scanning Electron Microscope

SEM of the type Zeiss Supra V was used. The sample is placed in a low vacuum chamber, and a thin electron beam swipes the surface. It is possible to obtain several different signals when the electron beam hits the sample. The signals can give valuable information about chemical composition, topography, crystallography etc.[42]. In these experiments the backscattered electrons were detected, and a chemical analysis of the surface was done. Images of the surfaces at different magnifications were also taken.

Chapter 4

Results

4.1 Development of method

The results for the method developed for studying softening and melting of quartz are first presented.

4.1.1 Thermocouple consistency

To check the reliability of the two C-thermocouples used in the experiments, they were compared to a secondary calibrated S-thermocouple. Figure 4.1 shows the temperature of the three thermocouples as a function of time, when they were mounted in the bottom of a crucible filled with SiC. All three thermocouples show good consistency both during heating and when held at approximately 1500 °C. The average difference between the two C-thermocouples from 36 minutes and onwards was 3 °C. If the heating from room temperature is included, the average difference is 14 °C. For the controlling C-thermocouple and the S-thermocouple, the average difference was 14 °C from 35 minutes and onwards, and 42 °C if the heating from room temperature is included.

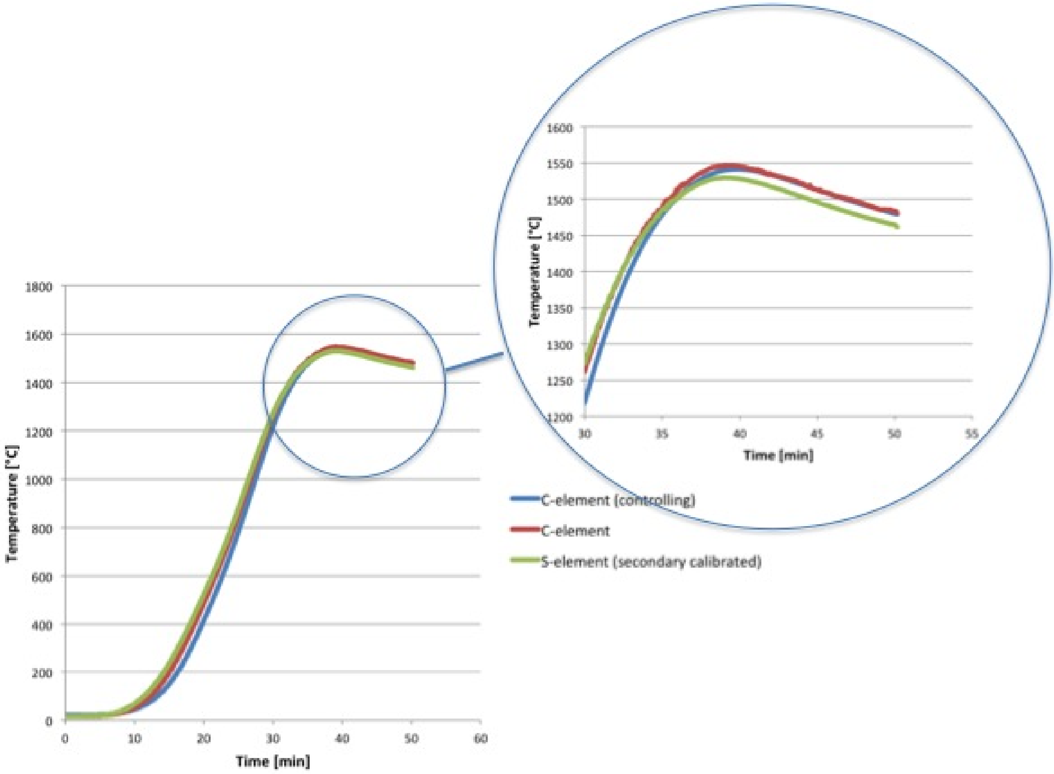


Figure 4.1: Consistency check of C-elements against a S-element, which was secondary calibrated. The crucible was heated to 1500 °C, and held for 20 minutes.

4.1.2 Vertical temperature gradient in crucible

The temperature in the crucibles heated in the induction furnace was measured at two points, one in the bottom of the quartz layer and one at the top. Table 4.1 shows the average temperature difference for the last 30 minutes for each experiment. In this time interval the temperature was set to be constant. The table also contains the average temperature during holding time, compared to the planned temperature.

Table 4.1: Average temperature during holding time, and average vertical temperatur difference from each experiment.

No	**Set temperature [°C]**	**Average temperature [°C]** (during holding time)	**Average ΔT [°C]**
9	1650	1652	233
10	1800	1802	244
11	1750	1750	205
12	1700	1706	205
13	1650	1650	199
14	1750	1755	189
15	1700	1707	211
16	1650	1650	191
17	1750	1752	143
18	1700	1715	230
19	1750	1749	246
20	1700	1703	227
21	1650	1655	182
Average:			208

Figure 4.2 shows the crucible surface for experiment 9. The maximum temperature in the bottom of the silica layer, and the the temperature at the top of the silica layer is marked on the figure. A similiar temperature gradient across the silica layer exists for all experiments in the induction furnace.

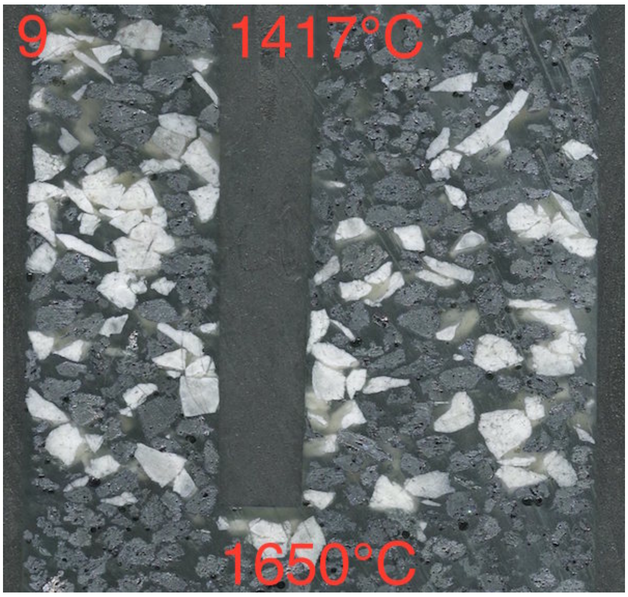


Figure 4.2: Quartz area from crucible 9, where the average maximum temperature was 1650 °C, and the average temperature gradient was 233 °C. This would cause the top of the quartz layer to experience an average temperature of 1417 °C during holding time.

4.1.3 Radial temperature gradient in crucible

The radial temperature gradient was also investigated. The result can be seen in figure 4.3. In the graph running from 0 °C, it can be seen that the outermost thermocouple is experiencing the highest temperature during heating. The inner thermocouple shows a lower temperature than the other two. At the holding temperature at 1700 °C, the enlarged section of the graph reveals that the peaks are slightly delayed compared to each other. First, the outermost thermocouple has a peak in temperature. Then the middle thermocouple has a peak, before the peak is seen in the inner thermocouple. The highest temperature seems to be in the middle of the crucible, and the lowest temperature outermost. From 52 min and onward the average temperature difference between the outer and innermost thermocouple in the crucible was calculated to 14 °C.

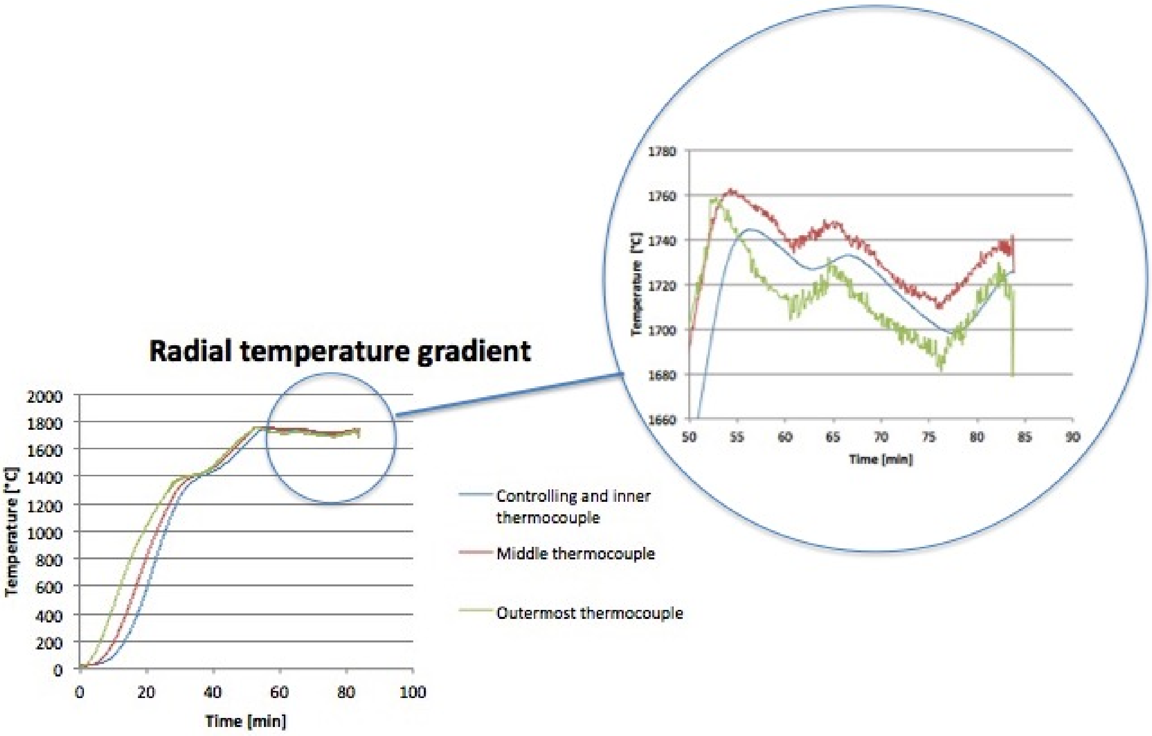
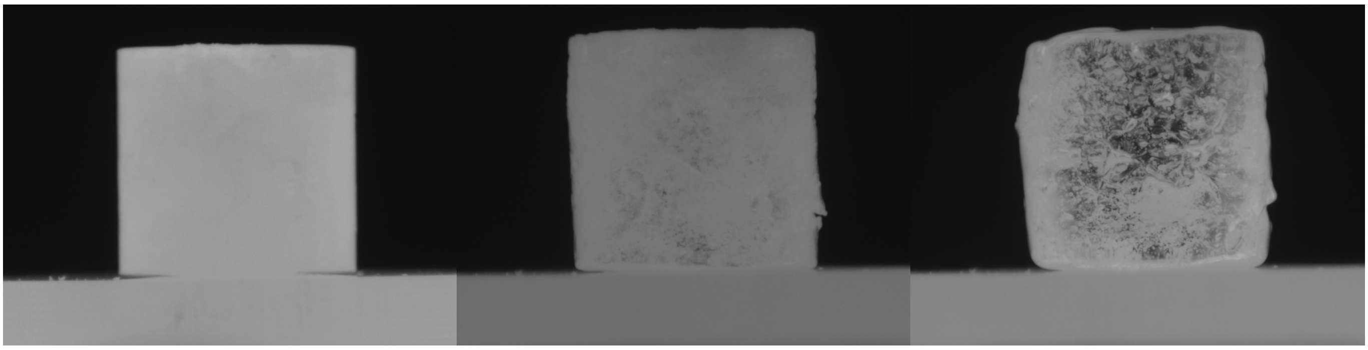


Figure 4.3: The radial temperature gradient in the crucible with inner diameter 11 cm. The section of the graph where the temperature is held at 1700 °C is enlarged.

4.1.4 Wetting furnace experiments

The following figures show the images taken during heating in the wetting furnace. Two samples were investigated, each at two different heating rates. Figure 4.4 and figure 4.5 show the results for the Qz27 sample, which have less contaminants than the Qz35 sample whose results can be seen in figure 4.6 and 4.7. The softening and melting temperature of the samples are determined to the nearest 10 °C. For Qz27 the softening and melting temperatures for the sample heated with 5.5 °C/min was 1750 °C and 1780 °C respectively. The Qz27 sample heated with 11 °C/min had softening temperature of 1770 °C and melting temperature of 1810 °C. For this sample, increased heating rate caused a higer softening and melting temperature. For Qz35 the softening temperature at both heating rates was determined to be 1740 °C. The melting temperature was 1780 °C for the sample heated with 5.5 °C/min and 1770 °C for the sample heated with 11 °C/min. These results are summarised in table 4.2.

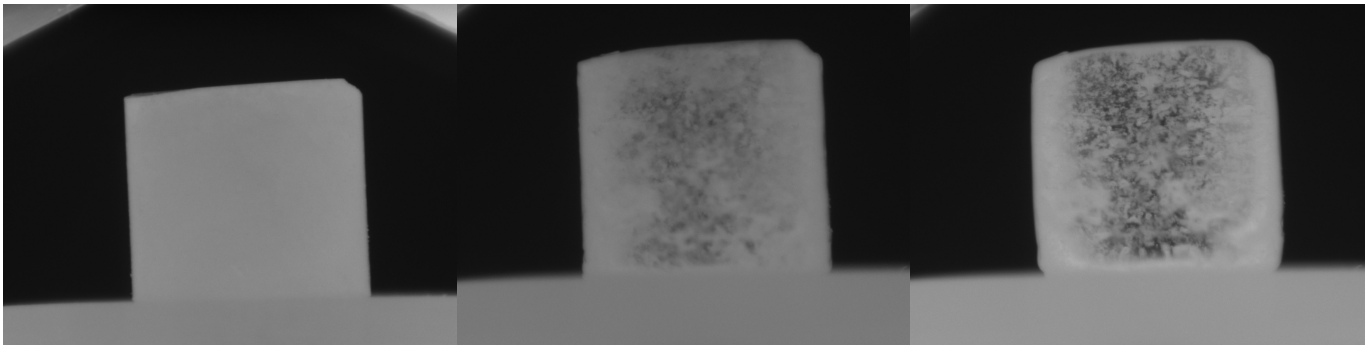


(a) Qz27 sample at 1149 °C, before any shape changes have been observed.

(b) Softened sample at 1750 °C.

(c) Melted sample at 1780 °C.

Figure 4.4: Quartz sample Qz 27, heated in wetting furnace with a heating rate of 5.5 °C/min from 1200 °C.

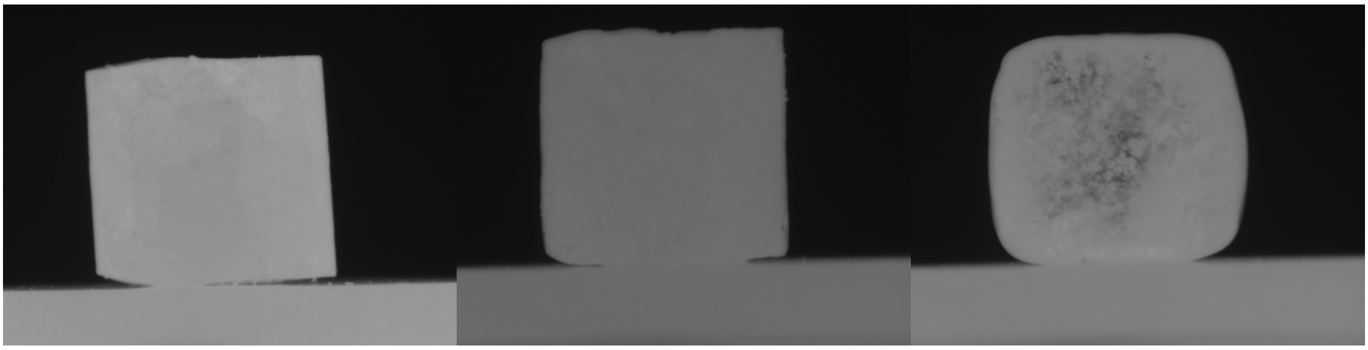


(a) Qz27 sample at 1128 °C, before any shape changes have been observed.

(b) Softened sample at 1770 °C.

(c) Melted sample at 1810 °C.

Figure 4.5: Quartz sample Qz 27, heated in wetting furnace with a heating rate of 11 °C/min from 1200 °C.

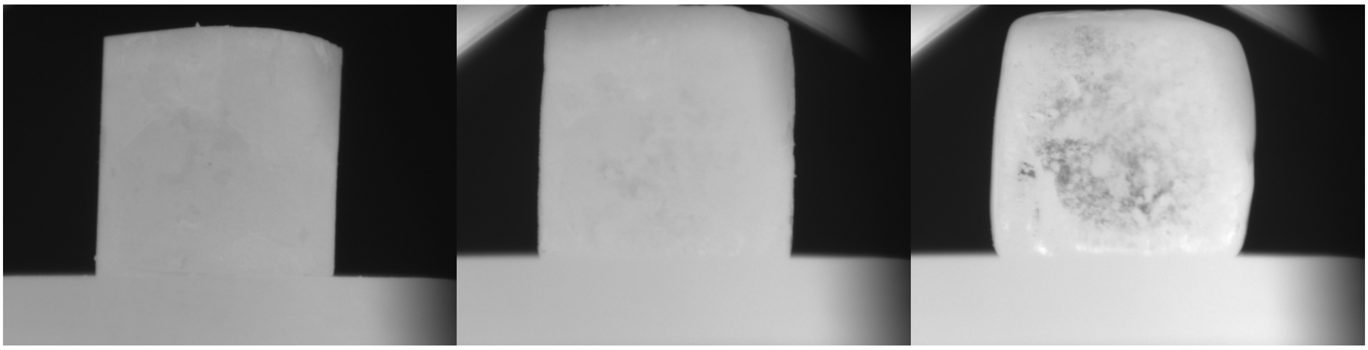


(a) Qz35 sample at 1145 °C, before any shape changes have been observed.

(b) Softened sample at 1740 °C.

(c) Melted sample at 1780 °C.

Figure 4.6: Qz 35 sample, heated in wetting furnace with a heating rate of 5.5 °C/min from 1200 °C.



(a) Qz35 sample at 1150 °C, before any shape changes have been observed.

(b) Softened sample at 1740 °C.

(c) Melted sample at 1770 °C.

Figure 4.7: Quartz sample Qz 27, heated in wetting furnace with a heating rate of 5.5 °C/min from 1200 °C.

Table 4.2: Softening and melting temperature of quartz samples. The temperature is rounded to the nearest 10 °C.

Quartz type	**Heating rate [°C/min]**	**Softening temperature [°C]**	**Melting temperature [°C]**
Qz27	5.5	1750	1780
Qz27	11	1770	1810
Qz35	5.5	1740	1780
Qz35	11	1740	1770

4.1.5 Volume change

Height difference in quartz layer

The height difference measured in the crucibles are presented in tabel 4.3. A measuring tape was used to measure the height from the charge top to the crucible top before and after heating. The difference and % change in volume was then calculated. All the experiments show that the quartz layer expanded during heating. Figure 4.8 shows the different volume changes as a function of temperature. It is not observed any clear correlation between the data points.

Table 4.3: Height difference of quartz layer in crucibles before and after heating.

No.	**Temp. [°C]**	**Qz type**	**ΔHeight [cm]**	**% change of initial volume**
9	1650	Qz27	+0.2	1.9
10	1800	Qz27	+0.7	7.3
11	1750	Qz27	+0.2	2.0
12	1700	Qz27	+0.7	7.2
13	1650	Qz35	+0.9	8.4
14	1750	Qz35	+0.7	7.6
15	1700	Qz35	+0.5	5.1
16	1650	Qz27	+0.5	5.1
17	1750	Qz27	+0.8	8.9
18	1700	Qz27	+0.6	6.1
19	1750	Qz27	+0.9	9.4
20	1700	Qz27	+0.6	5.7
21	1650	Qz27	+0.8	8.3

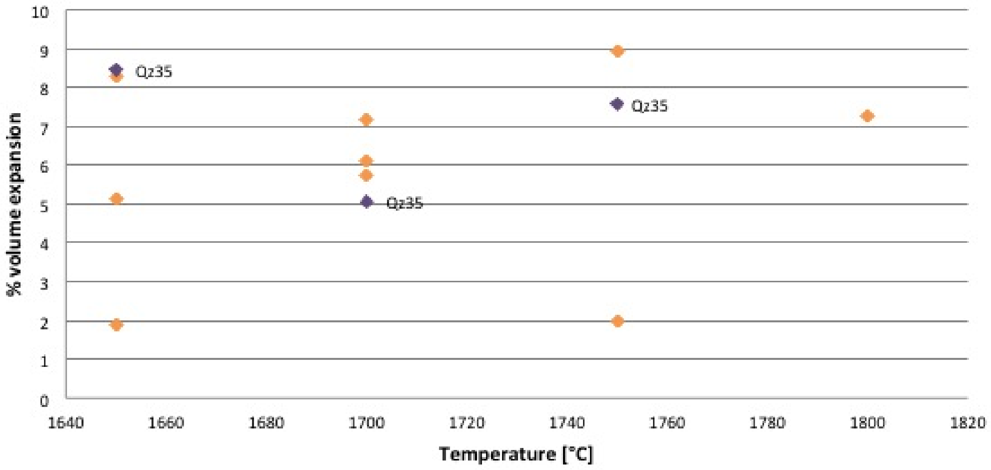


Figure 4.8: Volume expansion of quartz layer in crucibles as a function of temperature. The purple data points are Qz35, with a higher amount of impurities than the orange data points, which are Qz27.

Volume expansion in wetting furnace

The volume increase was also measured in the wetting furnace, and the results can be seen in figure 4.9. Volume calculations for Qz35, 11 °C/min are underestimated because of movement of the sample during heating. This caused the sample to expand out of the image frames. All the samples experienced volume increase during heating. The maximum volume expansion is seen between 1600 °C and 1700 °C. After 1750 °C the volume seems to decrease again.

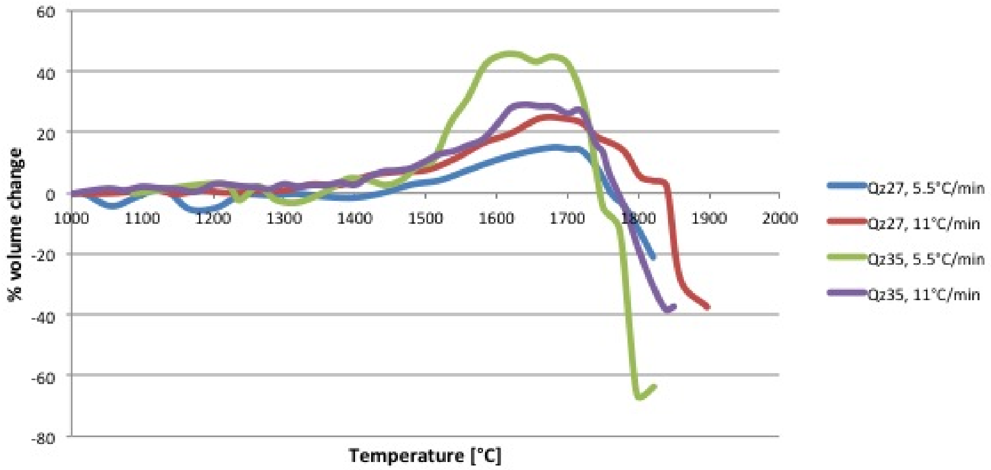


Figure 4.9: Volume expansion as a function of temperature of silica samples heated in a wetting furnace with different heating rates.

4.1.6 Visual inspection of heated quartz samples

One of the crucibles used to measure the radial temperature gradient contained quartz pieces of the type Qz27. These were heated to 1720 °C and held there for 30 minutes. After the experiment they were poured out and visually inspected. On the following figures, some interesting observations can be made. Since the samples were poured and partly knocked out of the crucible, their position in the crucible is not known. Based on the average temperature gradient in the other crucibles heated to similiar temperatures, it is reasonable to say that the silica samples on the picture have experienced a temperature approximately between 1520 °C and 1720 °C.

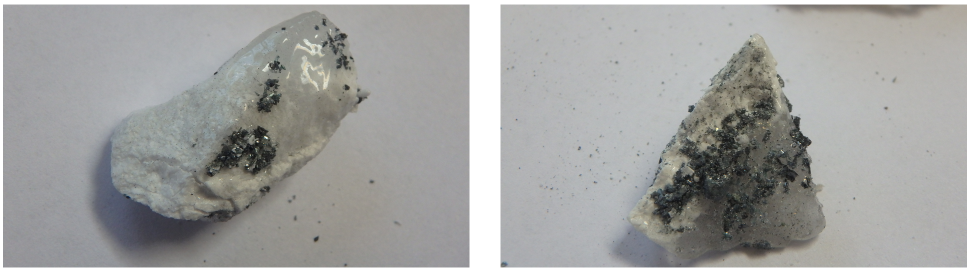
Figure 4.10 shows parts of the content. The silica pieces are smaller than 2 cm. Both melted, softened and unreacted silica can be seen. The unreacted silica was highly porous, and could easily be crushed into smaller pieces.

(a) Crucible content after heating to 1720 °C. Some samples are still solid silica, while some are softened and melted.

(b) A silica sample that has neither softened or melted. The sample is very porous.

Figure 4.10: Crucible content after heating to maximum 1720 °C.

Some of the silica pieces seem to have a more glassy apperance on the surface, like the sample in figure 4.11a. For the sample in 4.11b, one side of the sample is glassy while the other side seems to neither be softened nor melted. Also, smaller SiC-particles are glued to the surface to both samples in figure 4.11.

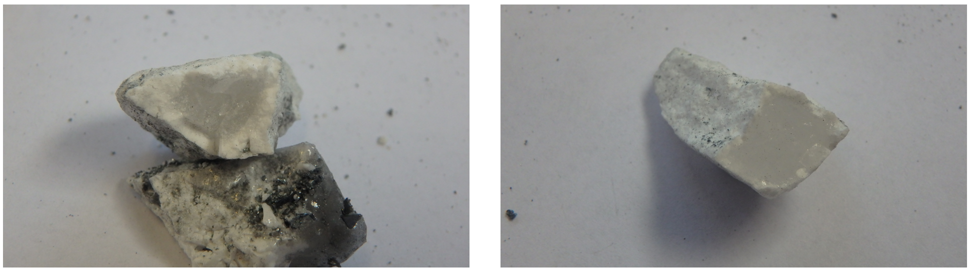


(a) Heated silica with SiC particles glued to the surface.

(b) Heated silica with one side partly glassy. Also with SiC particles glued to the surface.

Figure 4.11: Silica pieces with a partly glassy surface. Other particles are glued to the surface. The samples are heated to maximum 1720 °C.

In figure 4.12, the interior of the particles have a glassy apperance, while the surface still looks unreacted. The particles in figure 4.12a also have SiC-particles glued to the surface, and the particles are glued to each other.

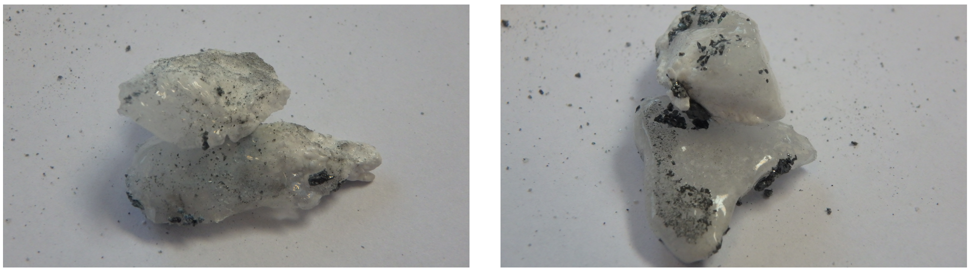


(a) Heated silica, with a glassy interior and SiC particles glued to the surface.

(b) Heated silica with a glassy interior, but a compact white surface.

Figure 4.12: Silica pieces heated to maximum 1720 °C.

The particles in figure 4.13 have a more or less glassy surface, and are glued to each other. In addition their shape has a more rounded form.



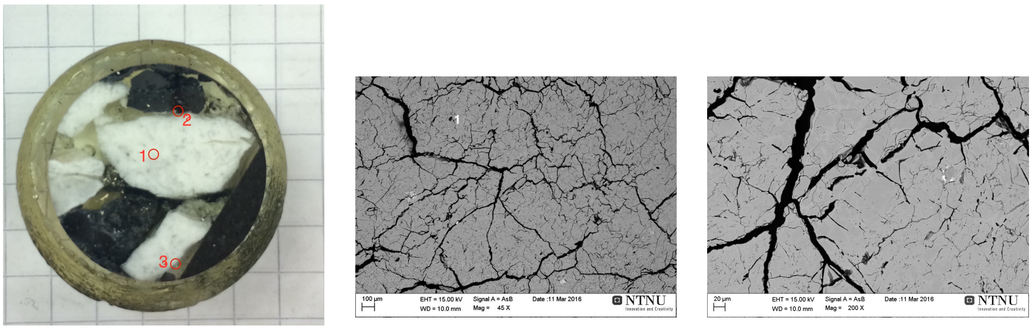
(a) Silica pieces with a melted surface, causing the pieces to be glued together.

(b) Silica pieces with a melted and rounded surface.

Figure 4.13: Melted particles that are glued to each other. Also, smaller SiC-particles are glued to the surface. The samples are heated to maximum 1720 °C.

4.1.7 Apperance of silica on microscale

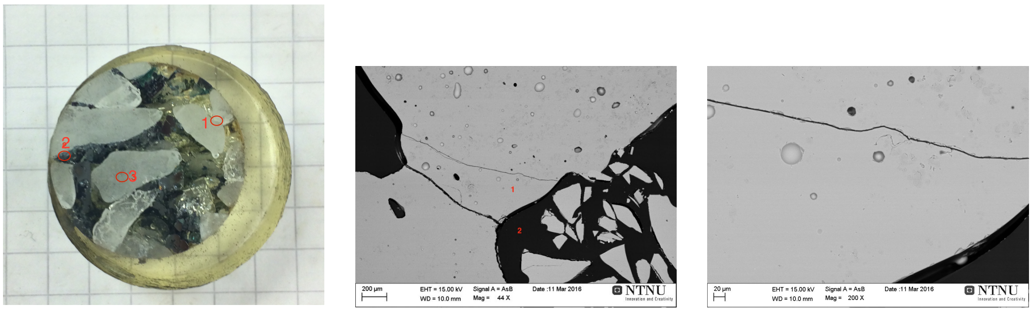
Unreacted, softened and melted silica were investigated using Scanning Electron Microscope. Figure 4.14 shows the results, and also the macroscopic position of the area that was enlarged to 45X and 200X magnification. The surface of the unreacted silica has severe cracks, which can be seen at both magnifications. For the softened silica, the sample is much more compact, and no cracks can be observed. Some bubbles have started to form, and some darker particles are visible. On the melted sample the amount of bubbles have increased, and they have grown. The darker particles are still present, but nothing certain can be said about the amount or the size of them.



(a) Macroscopic view of silica samples heated to 1500 °C. Position 1 is from an unreacted silica particle.

(b) 45X magnification of position 1 on figure 4.14a.

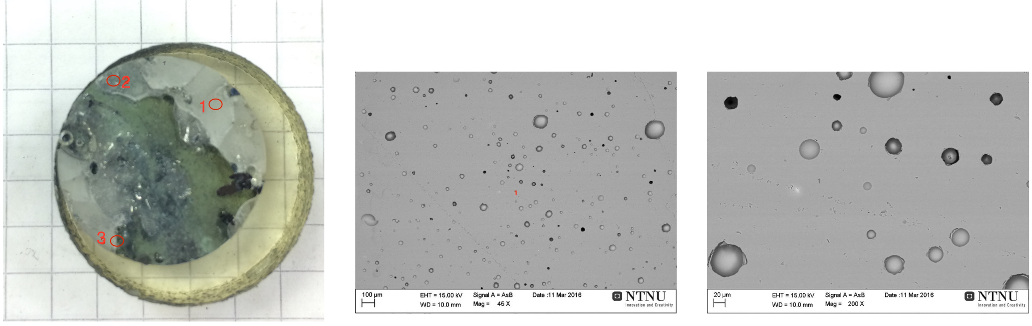
(c) 200X magnification of position 1 on figure 4.14a.



(d) Macroscopic view of silica samples heated to 1750 °C. Position 1 is from a softened silica particle.

(e) 45X magnification of position 1 on figure 4.14d.

(f) 200X magnification of position 1 on figure 4.14d.



(g) Macroscopic view of silica samples heated to 1850 °C. Position 1 is from a melted silica particle.

(h) 45X magnification of position 1 on figure 4.14g.

(i) 200X magnification of position 1 on figure 4.14g.

Figure 4.14: Investigations of softened, melted and unreacted silica in SEM.

4.1.8 Heating rates

Figure 4.15 shows the heating rates for all experiments in the induction furnace. As can be seen from the figure, the heating rates are showing some variations, but the overall trend is the same.

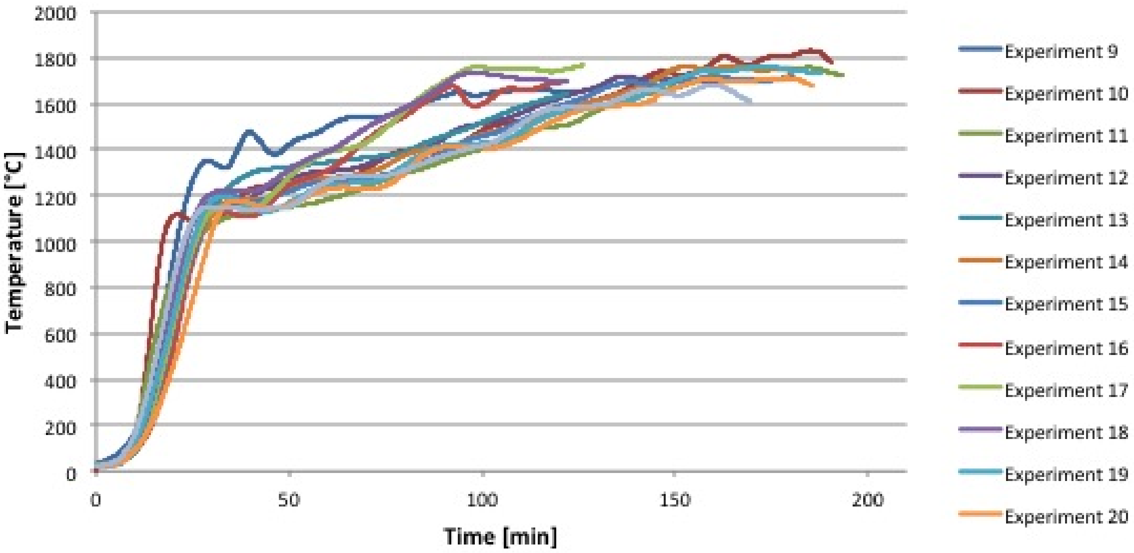


Figure 4.15: Heating rates for all experiments in the induction furnace.

4.1.9 Summary of development of method

- Vertical temperature gradient in crucible, in avergage 208 °C.
- Radial temperature gradient in crucible, aroximately 14 °C.
- Softening and melting point determined in wetting furnace for two diferetn quartz types at two different heating rates. These can be seen in figure 4.2. These results are used for comparison with the results from the induction furnace.
- Heating rates have the same trend for all experiments, but show some local variations.

4.2 Parameters affecting softening and melting

Table 4.4 shows the areas measured from the heated crucibles. From these numbers the fractions of softened, melted and unreacted silica are calculated. These results are given in table 4.5. For clarification, in this case unreacted means not softened nor melted. The sample might still have altered some of its other properties. These are not investigated here.

Table 4.4: Areas of softened and melted silica on the crucible surface. All areas are measured in mm^2.

No.	Temp. [°C]	Total area	Softened area	Melted area	Unreacted
9a	1650	2381	13	-	2368
9b	1650	2920	242	-	2678
10a	1800	2472	239	2125	108
10b	1800	2423	364	1951	109
11a	1750	2460	616	1301	544
11b	1750	2191	624	909	658
12a	1700	2667	928	293	1446
12b	1700	2448	842	146	1460
13a	1650	2774	1038	-	1737
13b	1650	2468	840	-	1628
14a	1750	2406	394	1507	505
14b	1750	2728	414	1736	577
15a	1700	2789	1286	731	772
15b	1700	2786	1471	542	774
16a	1650	2530	715	-	1815
16b	1650	2673	608	-	2066
17a	1750	2311	713	955	643
17b	1750	1922	536	859	529
18a	1700	2000	673	431	896
18b	1700	1393	434	417	542
19a	1750	2399	632	876	891
19b	1750	2292	401	824	1067
20a	1700	2234	33	-	2201
20b	1700	2134	126	-	2008
21a	1650	2885	430	-	2455
21b	1650	2007	369	-	1638

Table 4.5: Fraction of softened and melted area of each crucible.

No.	**Qz type**	**Temp. [°C]**	**% Softened**	**% Melted**	**% Unreacted**
9	Qz27	1650	4.4	-	95.6
10	Qz27	1800	12.4	83.2	4.4
11	Qz27	1750	26.8	47.2	26.1
12	Qz27	1700	34.6	8.5	56.9
13	Qz35	1650	35.7	-	64.3
14	Qz35	1750	15.8	61.4	21.1
15	Qz35	1700	49.5	22.8	27.7
16	Qz27	1650	25.5	-	74.5
17	Qz27	1750	29.4	43	27.6
18	Qz27	1700	32.4	25.7	40.0
19	Qz27	1750	21.9	36.2	41.8
20	Qz27	1700	3.7	-	96.3
21	Qz27	1650	16.7	-	83.4

The softened and melted areas was also measured for the bottom 5 cm and bottom 1 cm for some of the crucibles. These results are seen in table 4.6 and 4.7 respectively.

Table 4.6: Fraction of softened and melted area the bottom 5 cm of the crucibles.

No.	**Qz type**	**Temp. [°C]**	**% Softened**	**% Melted**	**% Unreacted**
9	Qz27	1650	5.8	-	94.2
10	Qz27	1800	-	100	-
11	Qz27	1750	21.3	78.7	-
12	Qz27	1700	70.3	22	7.7
13	Qz35	1650	61.5	-	38.5
14	Qz35	1750	-	100	-
15	Qz35	1700	49.9	44.9	5.2
16	Qz27	1650	61.5	-	38.5
17	Qz27	1750	17.7	82.2	0.1
18	Qz27	1700	34.3	60.7	5.0
19	Qz27	1750	26.6	73.4	-
20	Qz27	1700	5.8	-	94.2
21	Qz27	1650	43.2	-	56.8

Table 4.7: Fraction of softened and melted area for the bottom cm of the crucibles.

No.	Qz type	Temp. [°C]	% Softened	% Melted	% Unreacted
9	Qz27	1650	16.2	-	83.8
10	Qz27	1800	-	100	-
11	Qz27	1750	19.1	80.9	-
12	Qz27	1700	9.1	90.9	6.8
13	Qz35	1650	93.2	-	6.8
14	Qz35	1750	-	100	-
15	Qz35	1700	27.5	72.5	-
16	Qz27	1650	62.1	-	37.9
17	Qz27	1750	-	100	-
18	Qz27	1700	8.1	91.9	0

All the crucibles surfaces for each quartz type are shown in figure 4.16 for Qz27, and in figure 4.17 for Qz35. These figures show the overview of all the experiments done. Details for each parameter studied is presented later in this section.

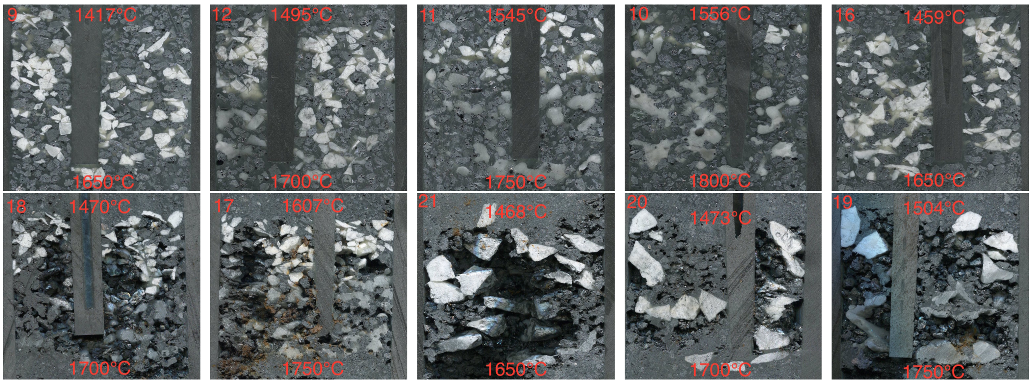


Figure 4.16: All crucibles with Qz27. The temperature at the bottom and top of the quartz layer are indicated on each crucible. All the quartz areas are 11cm × 10 cm.

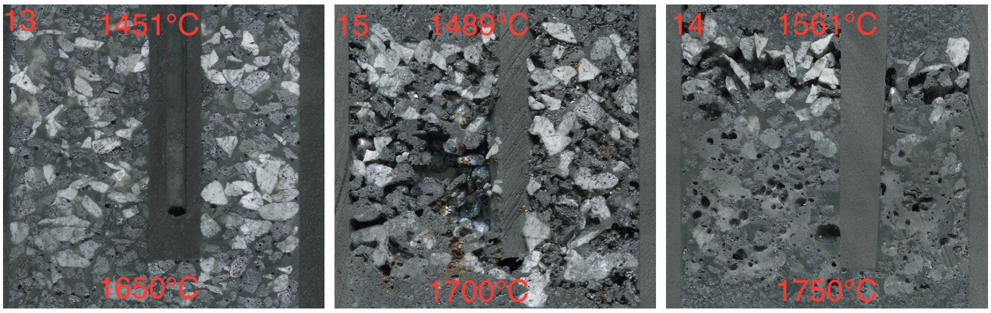


Figure 4.17: All crucibles with Qz35. The temperature at the bottom and top of the quartz layer are indicated on each crucible. All the quartz areas are 11cm × 10 cm.

4.2.1 Quartz type

Figure 4.18 is showing the differences in amount softened, melted and unreacted quartz in Qz27 and Qz35. The holding time, heating rate and particle size were kept constant for these experiments. The details for each experiment are given in table 3.2. Experiment number 9, 11 and 12 are compared to 13, 14, 15 respectively. It can be seen from the figure that softening and melting is more extensive for Qz35 than Qz27.

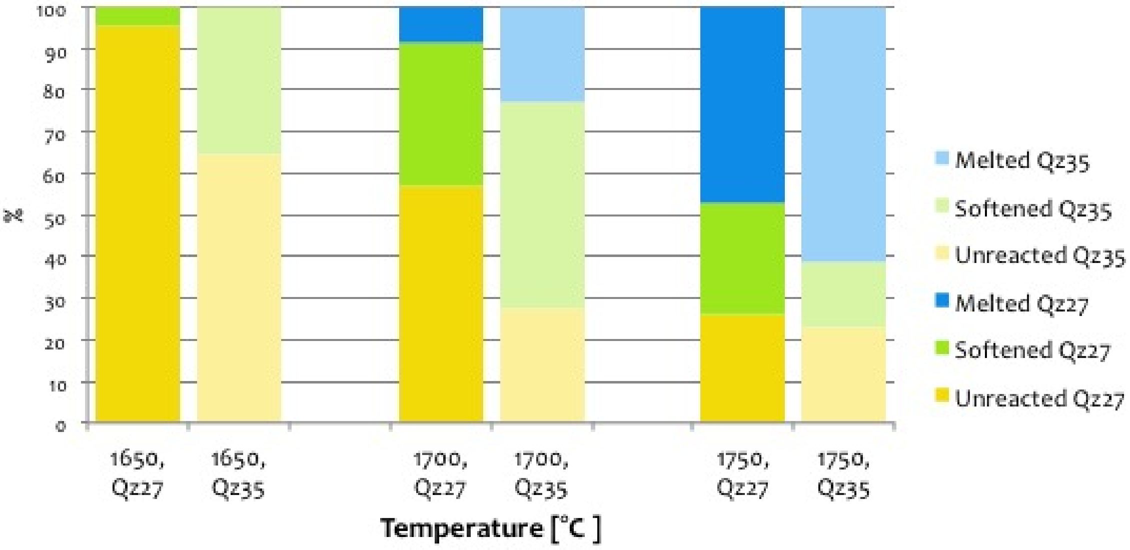


Figure 4.18: Amount of softened, heated and unreacted silica with varying quartz type.

For the lower half of the areas, the amount of softened, melted and unreacted silica can be seen in figure 4.19.

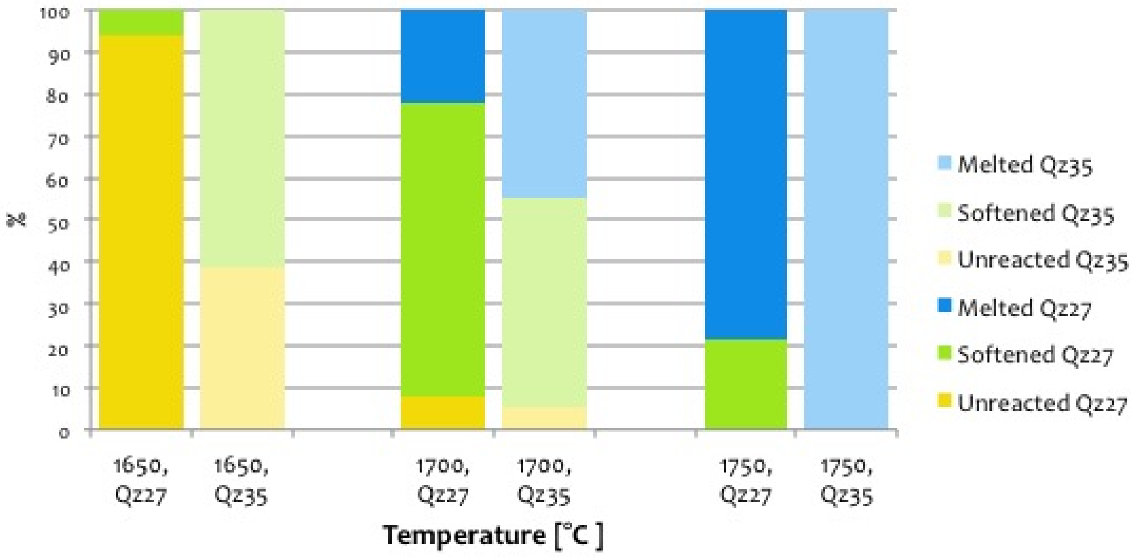
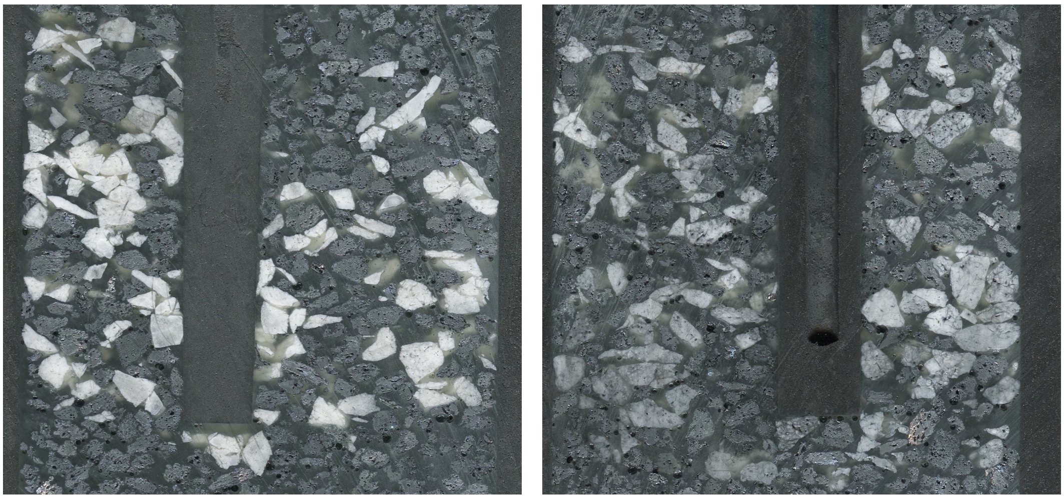


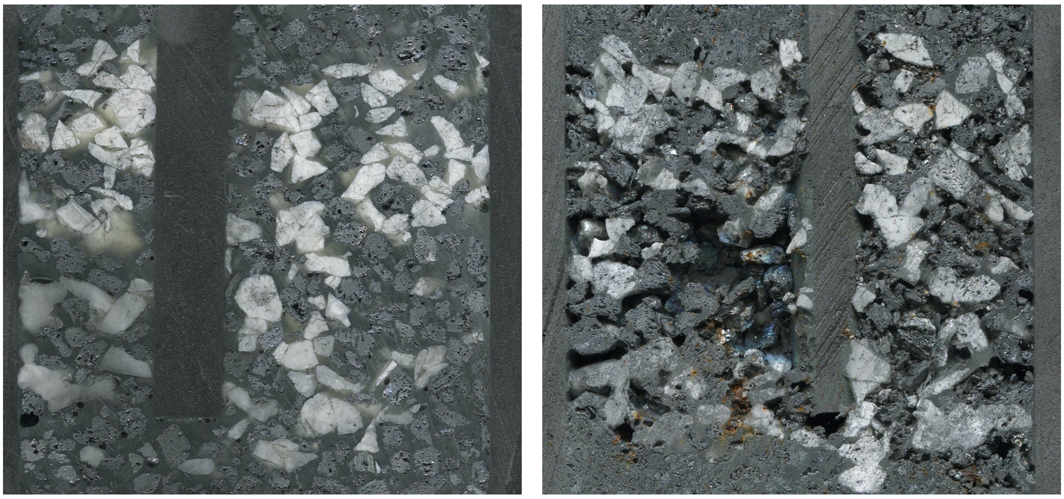
Figure 4.19: Amount of softened, heated and unreacted silica for two different quartz types. The results are for the bottom 5 cm of the quartz area in the crucibles.

The scanned crucibles can be seen in figure 4.20-4.22. In the crucibles for Qz35 the epoxy has not completely filled the cavities. Also, the Qz35 samples have a more greyish colour than Qz27 samples.



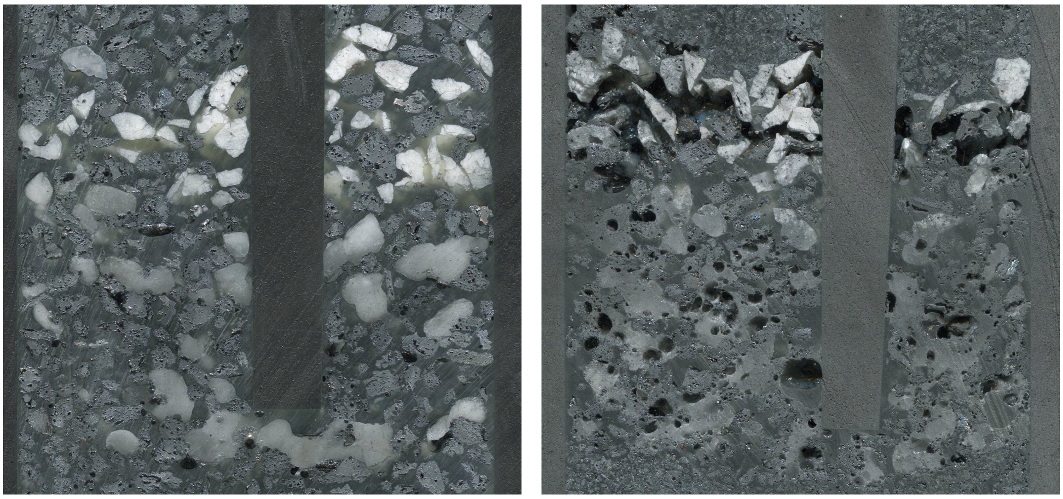
(a) Experiment 9: Qz27 (b) Experiment 13: Qz35

Figure 4.20: Crucibles heated to 1650 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 12: Qz27. (b) Experiment 15: Qz35.

Figure 4.21: Crucibles heated to 1700 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 11: Qz27 (b) Experiment 14: Qz35.

Figure 4.22: Crucibles heated to 1750 °C. All quartz areas are 10 cm high and 11 cm wide.

4.2.2 Holding time

Earlier experiments performed by Jusnes[1], where the crucibles had no holding time at maximum temperature, were compared with results from recent experiments which had 30 min holding time at maximum temperature. Number 9, 10, 11 and 12 from table 3.2 were used for comparison with 4, 5, 8 and 6 from earlier experiments, respectively. Also here, other parameters such as maximum temperature, heating rate and particle size were the same, but there were some differences in the crucible content. In the earlier experiments, the crucibles contained more quartz and less SiC. Increased holding time will cause more softened and melted silica from 1700 °C up to 1800 °C. This can be seen in figure 4.23.

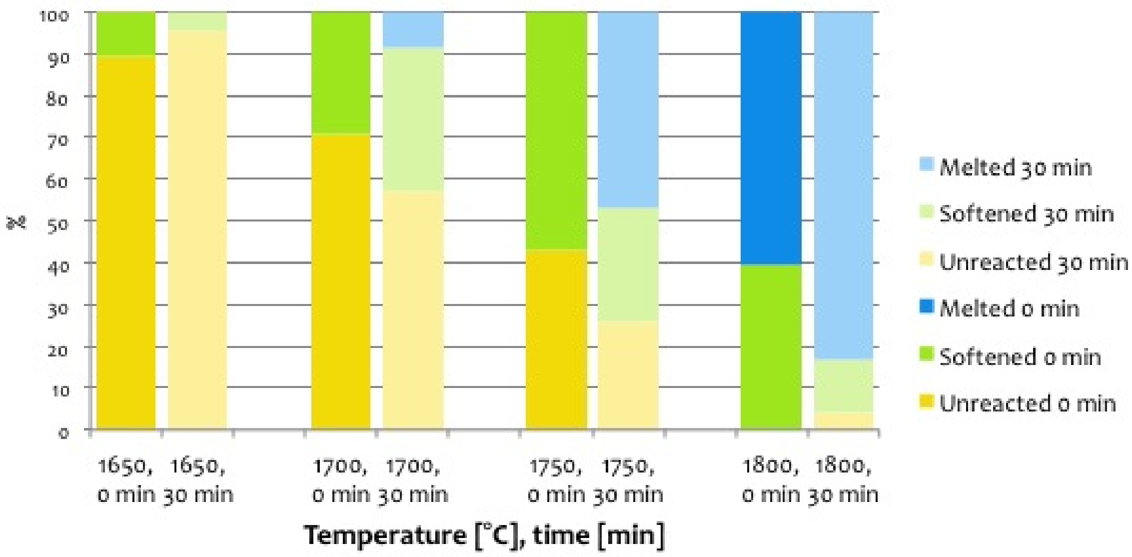


Figure 4.23: Amount of softened, heated and unreacted silica with varying holdingtime. Some of the results are from earlier work by Jusnes[1].

For the lower half of the areas, the amount of softened, melted and unreacted silica can be seen in figure 4.24.

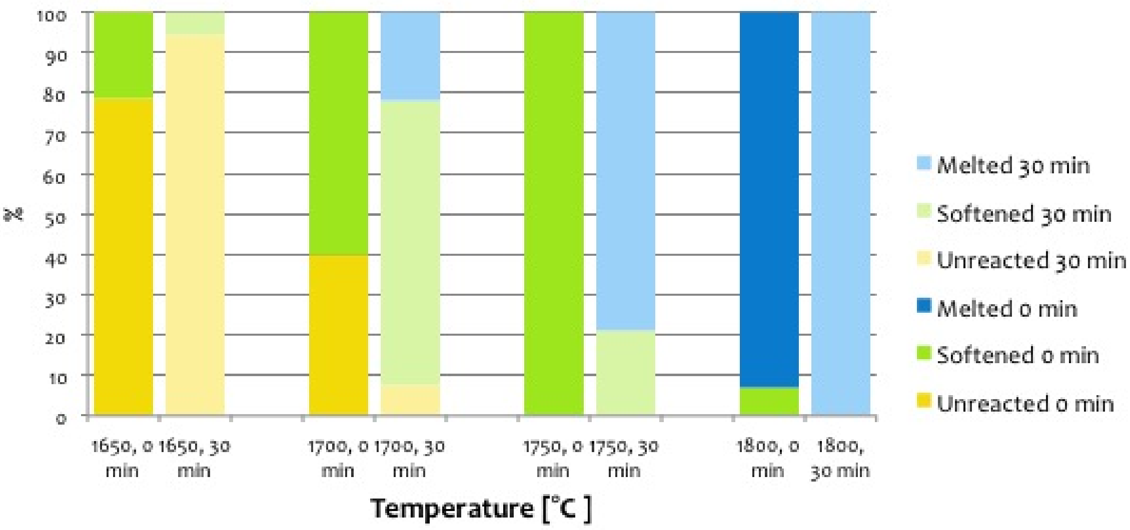


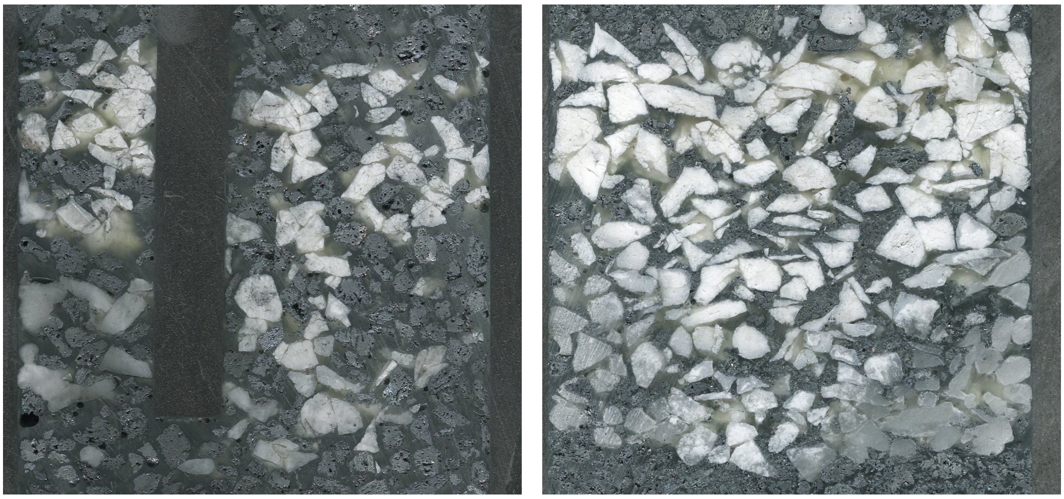
Figure 4.24: Amount of softened, heated and unreacted silica with different holding times. The results are for the bottom 5 cm of the quartz area in the crucibles.

Figure 4.25-4.28 show the crucible surfaces with varying holding time at maximum temperature. Results from recent experiments are seen in figure 4.25a-4.28a, and from earlier experiment in figure 4.25b-4.28b.

(a) Experiment 9: 30 minutes holding time.

(b) Experiment 4: 0 minutes holding time

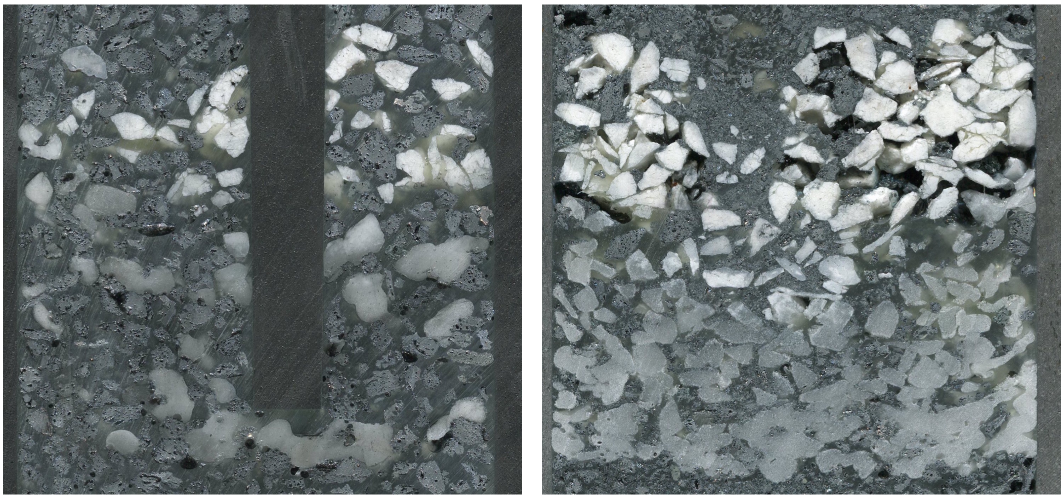
Figure 4.25: Crucibles heated to 1650 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 12: 30 minutes holding time.

(b) Experiment 5: 0 minutes holding time.

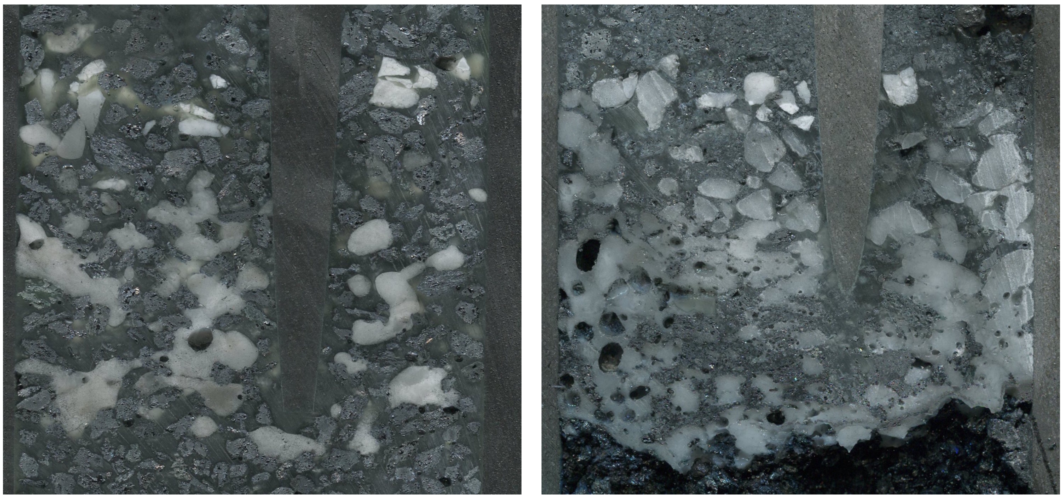
Figure 4.26: Crucibles heated to 1700 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 11: 30 minutes holding time.

(b) Experiment 8: 0 minutes holding time.

Figure 4.27: Crucibles heated to 1750 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 10: 30 minutes holding time. (b) Experiment 6: 0 minutes holding time.

Figure 4.28: Crucibles heated to 1800 °C. All quartz areas are 10 cm high and 11 cm wide.

4.2.3 Particle size

The effect of particle size was also studied. Smaller particles, 4.76-9.52 mm, and larger particles, 15-20 mm were used. Figure 4.29 shows the results from the experiments. The trend for the smaller particles are consistent. Increasing temperature gives more softened and melted silica. For the larger particles, the trend is not consistent, since the amount of softened silica decreases at 1700 °C and then increases up to 1750 °C. The overall trend seems to be that larger particles will give a smaller amount of softened and melted silica during heating. Experiment 9, 12 and 11 are compared with 21, 20 and 19 respectively.

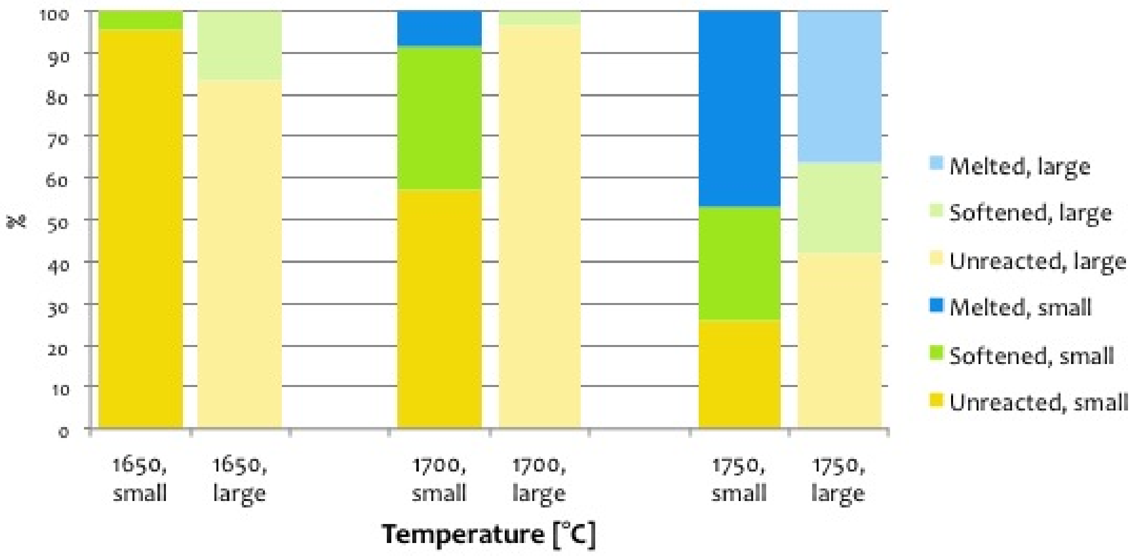


Figure 4.29: Amount of softened, heated and unreacted silica with varying particle size.

For the lower half of the areas seen in figure 4.31-4.33, the amount of softened, melted and unreacted silica can be seen in figure 4.30.

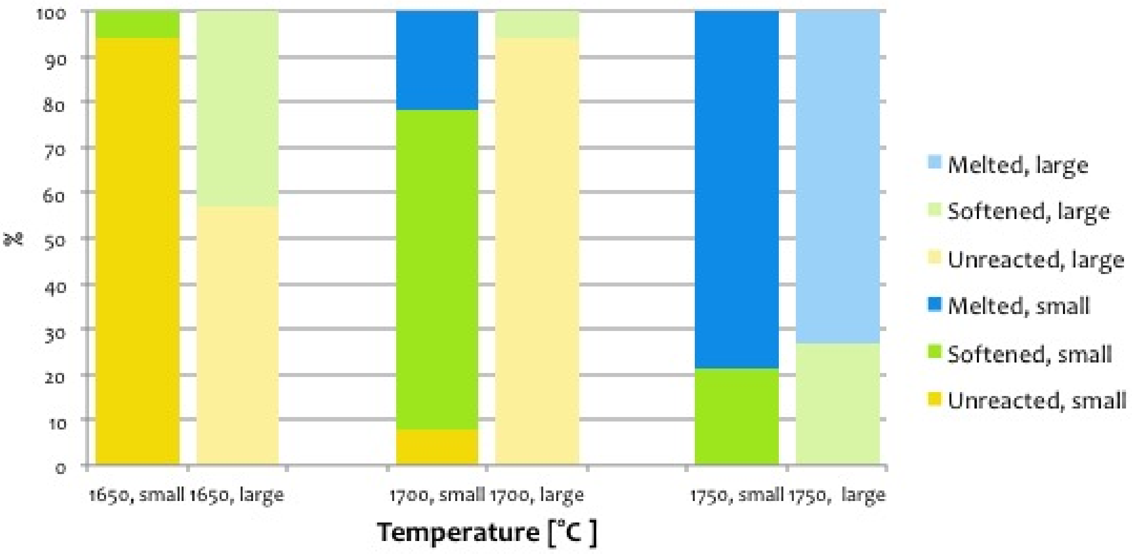


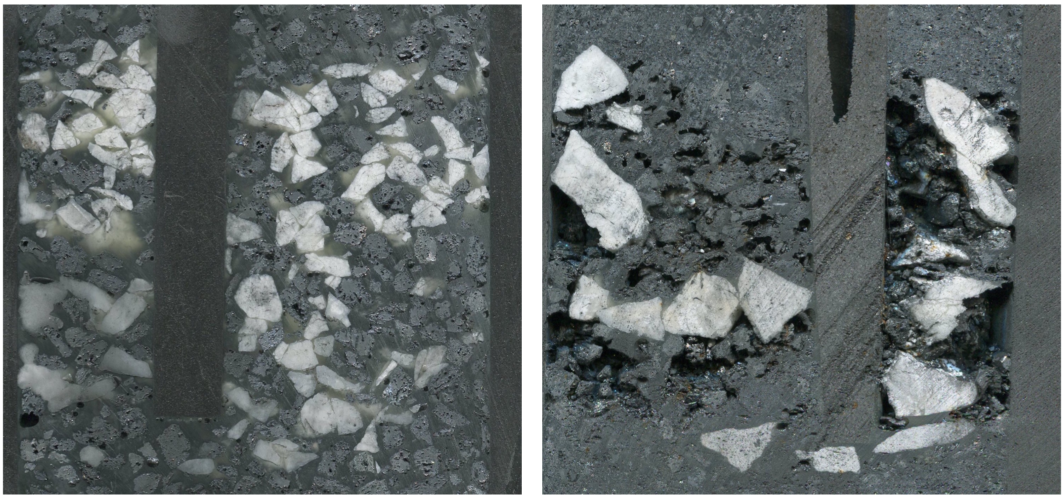
Figure 4.30: Amount of softened, melted and unreacted silica with different particle size. The results are for the lower part of the quartz area in the crucibles. All samples are Qz27. The small particles are 4.76-9.52 mm, and the large ones are 15-20 mm.

Figure 4.31-4.33 show the crucibles surfaces used to study the effect of particle size.

(a) Experiment 9: 4.76-9.52 mm particles.

(b) Experiment 21: 15-20 mm particles.

Figure 4.31: Crucibles heated to 1650 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 12: 4.76-9.52 mm particles. (b) Experiment 20: 15-20 mm particles.

Figure 4.32: Crucibles heated to 1700 °C. All quartz areas are 10 cm high and 11 cm wide.

(a) Experiment 11: 4.76-9.52 mm particles. (b) Experiment 19: 15-20 mm particles.

Figure 4.33: Crucibles heated to 1750 °C. All quartz areas are 10 cm high and 11 cm wide.

4.2.4 Heating rate

Some experiments were conducted with a faster heating rate. Figure 4.34 shows the results from the comparison with a slower heating rate. Experiment 9, 12 and 11 are compared with experiment 16, 18 and 17 respectively.

The difference is significant at lower temperatures where the fastest heated silica has softened and melted more than the silica with slower heating rate. At 1750 °C the difference is smaller.

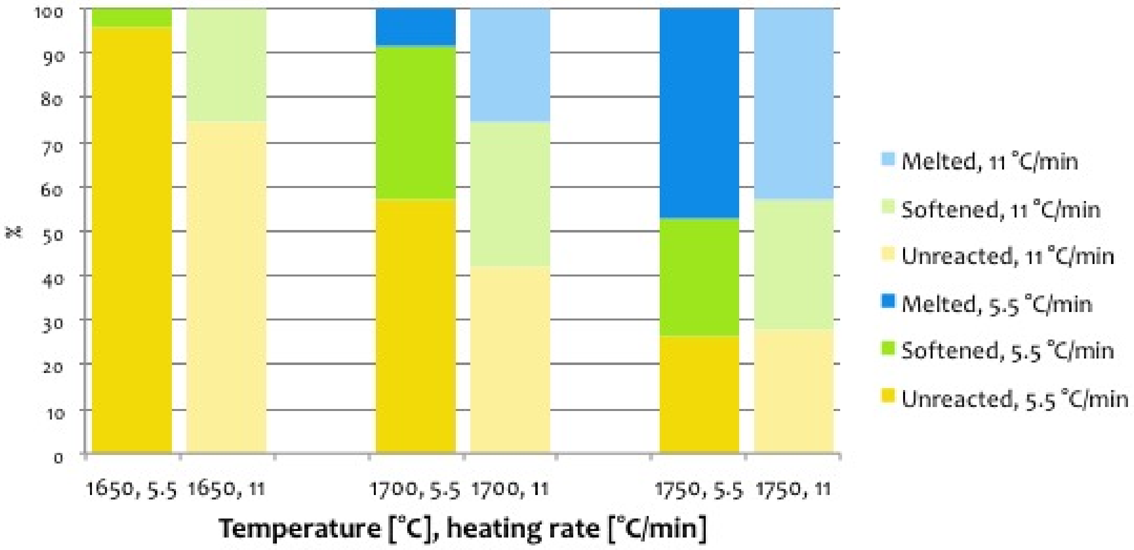


Figure 4.34: Amount of softened, heated and unreacted silica with varying heating rate.

For the lower half of the areas the amount of softened, melted and unreacted silica can be seen in figure 4.35.

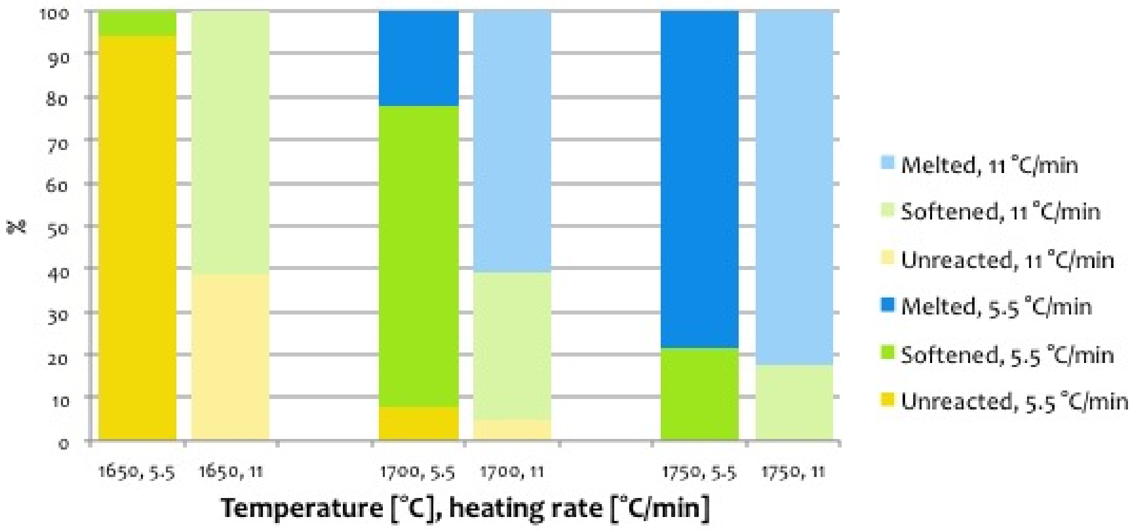
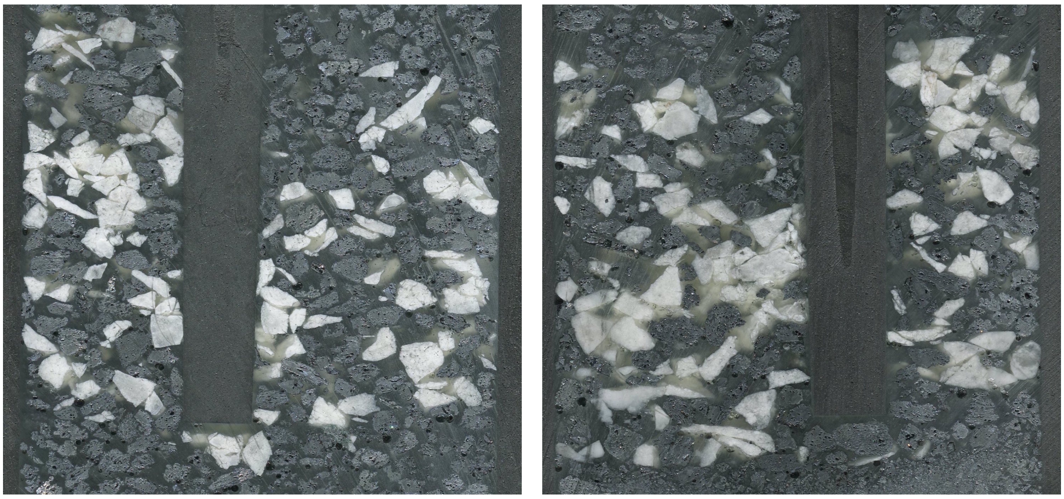


Figure 4.35: Amount of softened, heated and unreacted silica with different heating rates. The results are for the bottom 5 cm of the quartz area in the crucibles. All samples are Qz27.

Figure 4.36-4.38 show the crucible surfaces from the experiments with varying heating rate.



(a) Experiment 9: 5.5 °C/min.

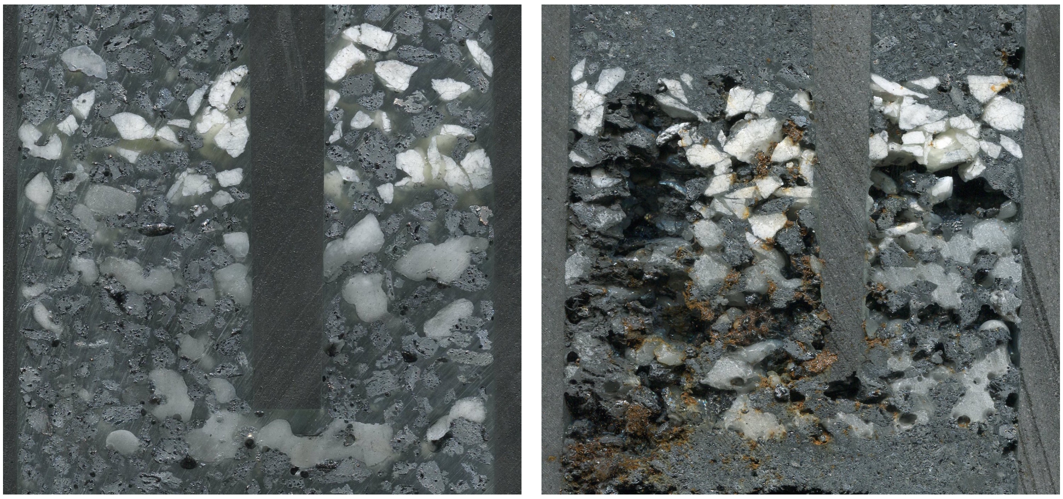
(b) Experiment 16: 11 °C/min.

Figure 4.36: Crucibles heated to 1650 °C. All quartz areas are 10 cm high and 11 cm wide.

(a) Experiment 12: 5.5 °C/min.

(b) Experiment 18: 11 °C/min.

Figure 4.37: Crucibles heated to 1700 °C. All quartz areas are 10 cm high and 11 cm wide.



(a) Experiment 11: 5.5 °C/min.

(b) Experiment 17: 11 °C/min.

Figure 4.38: Crucibles heated to 1750 °C. All quartz areas are 10 cm high and 10 cm wide.

4.2.5 The effect of different parameters

Based on the softened areas in each crucible, figure 4.39 was developed. The yellow line represents the standard measurement: Qz27, 5.5 °C/min, 4.76-9.52 mm particle size, experiment 9, 11 and 12. The effect of varying one parameter can be seen. Changing the quartz type has the largest impact on softening and melting. By the use of regression tool in excel the expression for amount of softening was determined. It can be seen in equation 4.1. The expression is valid for the standard parameters mentioned above, and in the temperature interval 1650 - 1750 °C. S is softening and T is temperature.

$$S(T) = -0.0076T^2 + 26,064T - 22310 \tag{4.1}$$

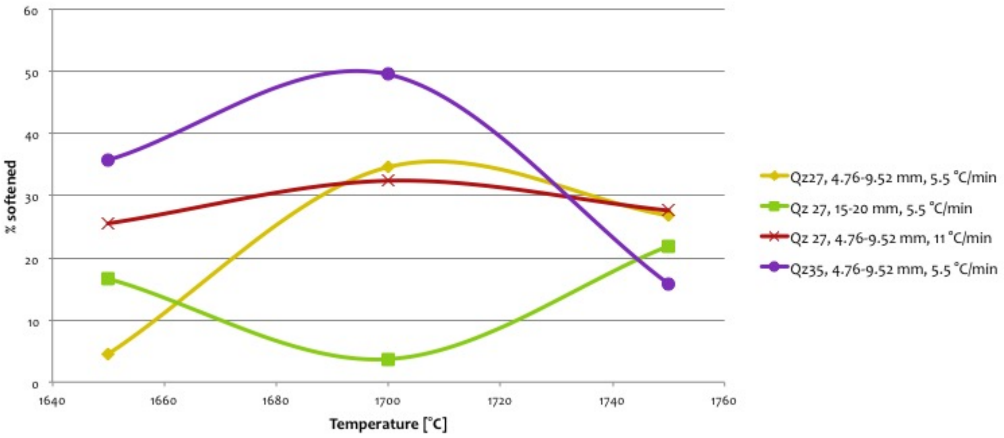


Figure 4.39: The effect of different parameters on amount of softened silica at temperatures from 1650 °C to 1750 °C. The yellow line represents the standard measurement, from where the other parameters are varied.

Chapter 5

Discussion

5.1 Development of method

5.1.1 Temperature control and accurancy of experiments

To be able to evaluate the accurancy of the results, the thermocouples used in the experiments in the induction furnace was checked at 1500 °C with a secondary calibrated S-thermocouple. The consistency was good, showing an average temperature difference of 3 °C for the two C-thermocouples when held at constant temperature. Compared with the secondary calibrated S-thermocouple, the average temperature difference was 14 °C. This indicates that the results obtained can be valid within a temperature range of approximately ±20 °C, rounded upwards to account for any larger thermocouple differences at higher temperatures. The uncertainty in the thermocouples is the most crucial source of error in these experiments.

The temperature gradient that exists through the crucibles are also important to consider when studying softening and melting of silica. Based on the average vertical and radial temperature gradient, a crucible map showing the change in temperatures with position was developed. It can be seen in figure 5.1. The highest temperature is in the middle and at the bottom of the quartz layer. The temperature was measured close to this position, to minimize the difference in the recorded maximum temperature and the actual maximum temperature. The radial temperature gradient, 14 °C, is small compared to the vertical gradient, 200 °C.

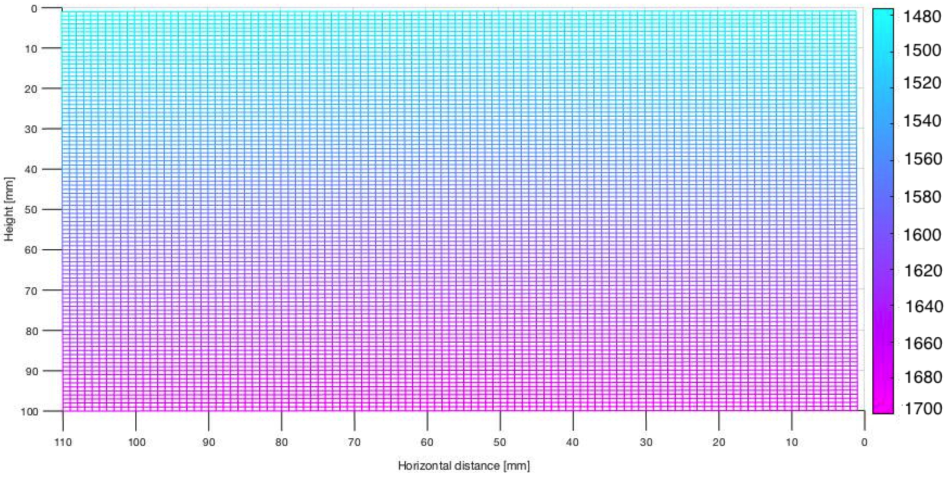
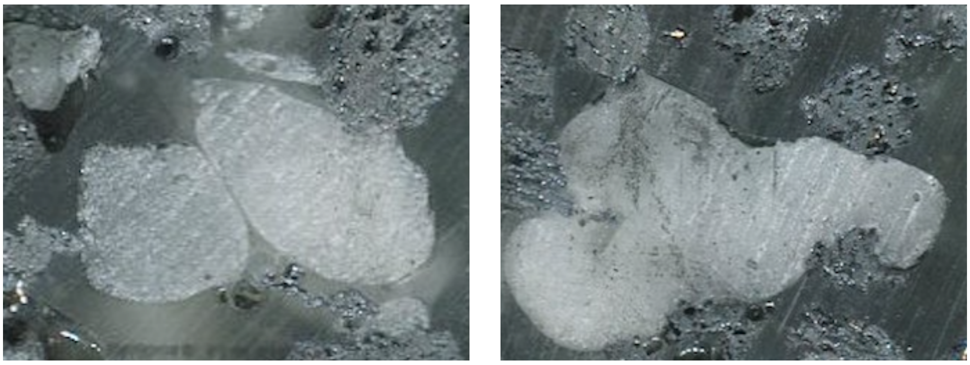


Figure 5.1: Temperature gradient in a crucible with maximum temperature 1710 °C. The area is 11 cm wide and 10 cm high.

The temperature gradient will have an impact on the uncertainty in measured softened, melted and unreacted silica areas in the crucibles. Since the temperature is not consistent, it is difficult to determine the amount of softening and melting at an exact temperature. It will be more correct to report the softened and melted silica at an average maximum temperature.

5.1.2 Determination of softening and melting

Based on the experiments in the wetting furnace, the melted phase of silica was observed to be very viscous, and maintained its shape, even when the temperature was well above the melting point. This was also observed by Ainslie et al.[28] in their investigation of melting kinetics of quartz and cristobalite. This influenced the determination criterias for melted and softened particles on the crucible surfaces. The limit is subjective, but the criterias were as follow: melted particles have a more round shape than softened, and melted particels have adjusted themselves to the surroundings, while softened particles have not. Also, melted particles can have melted together, forming one larger particle. Where the boundary between two particles no longer can be seen, they are counted as melted. Figure 5.2 illustrates two examples on the borderline between softening and melting. The figure is the same as presented in figure 3.3.



(a) Softened particles.

(b) Melted particles.

Figure 5.2: Examples clarifying the limit between softened and melted silica.

5.1.3 Wetting furnace experiments

The experiments performed in the wetting furnace was used to determine the softening and melting temperature of two different quartz types. In this furnace, the sample is only 4 mm in height and diameter, and the thermocouple is mounted just above the sample. As for the induction furnace experiments, an uncertainty in the thermocouple exists. A pyrometer was used to check the temperature. At 1500 °C the pyrometer showed about 15 °C less than the thermocouple. This difference increased as the furnace heated. At 1800 °C the difference was about 45 °C. This shows that the softening and melting temperatures has a higher uncertainty than the induction furnace experiments. The softening temperatures were determined for Qz35 and Qz27 for two different heating rates. All softening and melting temperatures were above the melting point of silica at 1713 °C from SI Chemical Data[5] . More impurities seem to lower the softening point. Ringdalen et al.[18] found the same trend in their studies. Both Kuhlmann-Wilsdorf[24] and Turnbull et al.[34] suggested that a higher impurity level would lower the energy needed for a material to melt. The effect of the two different heating rates does not seem to have a great effect on the softneing point, taken the uncertainty into account. Andersen[14] also determined the softening point based on wetting furnace experiments. His results are also showing softening temperatures above the melting point.

5.1.4 Volume increase

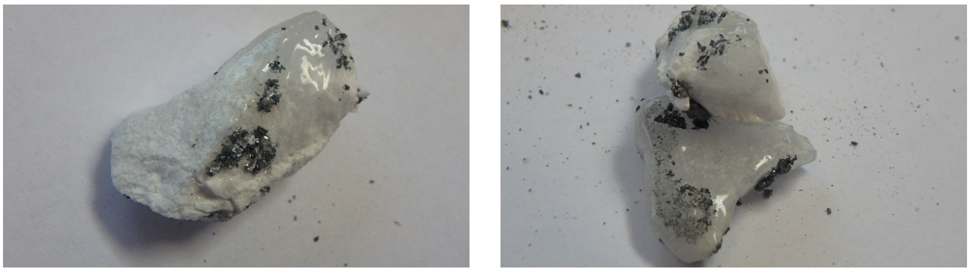
The volume increase was measured both in the induction furnace and the wetting furnace. For both methods, the same trend was seen. The silica samples will expand during heating. This is in agreement with earlier experments by Ringdalen[20], Aasly[6] and Andersen[14], who all reported a volume increase. The theoretical volume increase from quartz to melted face is 22 %[18].

5.1.5 Microscopic investigation

Softened, melted and unreacted silica was investigated using SEM. From the results in figure 4.14 it can be seen that the unreacted silica has a very cracked surface, while the softened and melted phase has a more compact apperance. There is a clear difference in the microscopic apperance of unreacted and melted silica. Softened silica looks more like melted silica. It is observed in earlier litterature by Wiik[33] that heated quartz could have cracks due to tension arising from phase transformations and differences in density.

5.1.6 Visual inspection

The silica pieces taken from a crucible heated to maximum 1700 °C, confirmed some expected results. As suggested by Schei et al.[3] and Ringdalen[7], clogging can be a problem for the gas permeability. Figure 5.3 shows a good example of this. To the left smaller SiC particles are glued to the softened and partly melted silica surface. On the picture to the right, two silica pieces are glued together. On a larger scale, this will contribute to a clogged furnace and limited gas permeability. From the visual inspection of some silica particles it can also be seen that softening occurs on the surface of particles. It is suggested by Kuhlmann-Wilsdorf[24], that amorphous substances might soften before they melt. If silica goes through an amorphous phase, like suggested by stevens et al.[15],this could explain why softening is observed.



(a) SiC particles are glued to the surface. (b) Two silica pieces are glued together.

Figure 5.3: Silica pieces heated to maximum 1720 °C.

The kinetics of melting is not determined, and both heterogeneous[28] [32] and homogeneous[33] explanations exists. From the visual inspection of heated silica, both cases can be observed. Wiik[33] reported that transition phase silica crumbled under pressure from the fingers. That was observed for the silica piece seen in figure 4.10b. Ainslie et al.[28] found that the melting of silica was a heterogeneous process starting at a free surface. From figure 4.11 this can be observed. Figure 4.12, on the other side, show glassy interior of a particles, and a neither softened nor melted surface. Based on these results, nothing certain can be said about the melting kinetics of silica.

5.1.7 Evaluation of method developed

The same setup was used for all the experiments in the induction furnace. This setup had some improvements compared to the initial setup developed by Jusnes[1]. Increased SiC content and size helped on determining the softening and melting limits, because it was easier to observe how the melted silica could partly wrap around the SiC particles. The temperature consistency check before the experiments started, improved the estimation of the temperature in the crucibles. An uncertainty excists, and one could only estimate the temperatures within a 20 °C interval.

According to Kjelstadli[22], the temperature in the center of a 2 cm sample will use about 30 minutes to reach 1700°C, when the heating rate is 57°C/min. The heating rates used for all experiments in this study is lower than 57°C/min. Based on this information it is acceptable to say that the heating rate has not been a limiting factor, when crucibles were allowed to be held at maximum temperature for 30 minutes. Also for the particles with radius 1 cm, the heat will have had opportunity to reach the center of the sample after 30 minutes.

Softening is observed as low as 1650 °C, and at 1700 °C there excists indications of melting for some experiments. For all crucibles, the average maximum temperature the last 30 minutes of each experiment was close to the set maximum temperature. This means that the temperture could have been higher for a shorter period of time in some areas of the crucible, which could explain why melting is observed below the reported melting temperature of 1713 °C[5]. Also, considering the ±20 °C, a recorded temperature of 1700 °C, could be closer to 1713 °C in reality. Since a temperature gradient exsists through the crucbile, the maximum temperature has just been reached at the bottom of the quartz layer. Compared to the wetting furnace, the softening and melting temperature estiamted are more accurate in the induction furnace. This is due to higher uncertainty in the C-thermocouple used in the wetting furnace.

Earlier test methods for softening of silica have mainly been done in a wetting furnace by Ringdalen et al.[18], Andersen[14] and Aasly[6]. The results obtained from their studies show varying softening temperature between quartz types, different heating rates and different atmospheres. In the study presented here, larger volumes of quartz have been used for each experiments, and larger sample sizes have been used. This study also includes experiments from the wetting furnace. The trend seen, is that the experiments in the wetting furnace show a higher softening and melting temperature than observed in the induction furnace experiments. This is the case for both Qz27 and Qz35. Since larger volumes are used in the induction furnace, and an average is calculated, it is acceptable to say that the induction furnace experiments have a higher reliability.

The reason for the higher softening and melting temperatures in the wetting furnace could have several explanations. One reason is that silica at its melting point is reported to behave nearly as a solid[28]. Since the softening and melting temperatures are based on visual inspection of the surface of the sample, it could be difficult to detect. Another explanation could be superheating of the sample. When surface melting is limited, quartz can sustain temperatures up to 300 °C above its melting point for a considerable amount of time according to studies by Mackenzie[32]. Also, if melting is a homogeneous process like Wiik suggests[33], melting and softening might not be detectable at the surface. The surrounding material of the quartz samples is also different in the two methods. While the sample in the wetting furnace is placed on a carbon substrate in a CO atmosphere, the sample in the induction furnace is surrounded by SiC particles and other quartz samples in all directions. The surroundings in the induction furnace is closer to the actual surroundings in a silicon furnace.

For the experiments studying the effect of different quartz types, the amount of softened, melted and unreacted silica was also meaured for the bottom centimeter of the quartz layer. Figure 5.4 shows this. Across this centimeter the temperature gradient should not be more than approximately 20 °C, and therefore the figure could show a more accurate picture of the behaviour at the maximum temperature of the crucibles. Despite this, the measurements of the bottom centimeter were uneven, and therefore the uncertainty of the results are higher than for the whole area. The trend for the different quartz types are as expected. The closer to the higher temperature areas, the more softening and melting will occure. Compared to the measurements for the whole quartz area, the trend is also the same. More impurities will decrease the softening and melting temperature, and hence more softened and melted silica at lower temperatures than for a purer quartz sample.

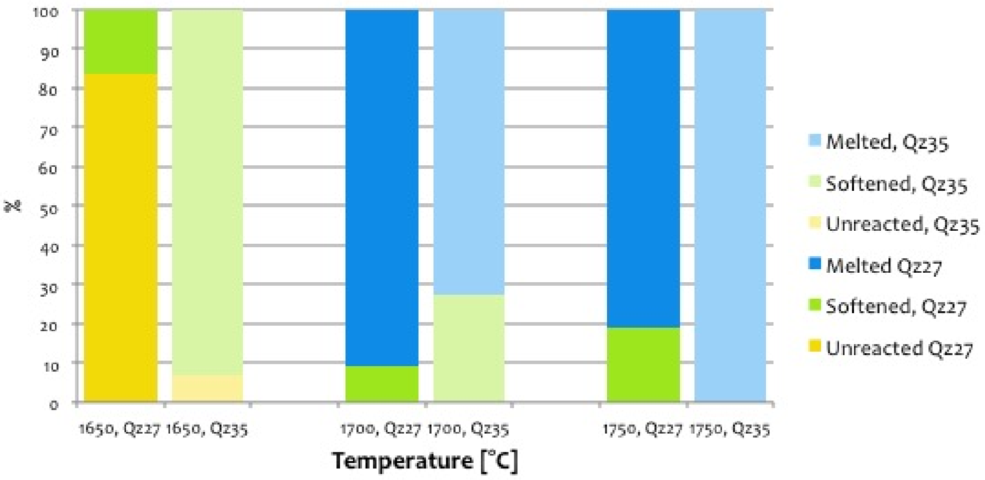


Figure 5.4: Amount of softened, melted and unreacted silica with different quartz type. The results are for the bottom centimeter of the quartz area in the crucibles.

Also for the experiments with varying heating rate, the amount of softened, melted and unreacted silica was measured for the bottom cm. The results can be seen in figure 5.5. These mesurements are also uneven, as for the bottom centimeter measurements for the different quartz types. The same trend is seen as for the whole area. Increasing heating rate will give more softening and melting.

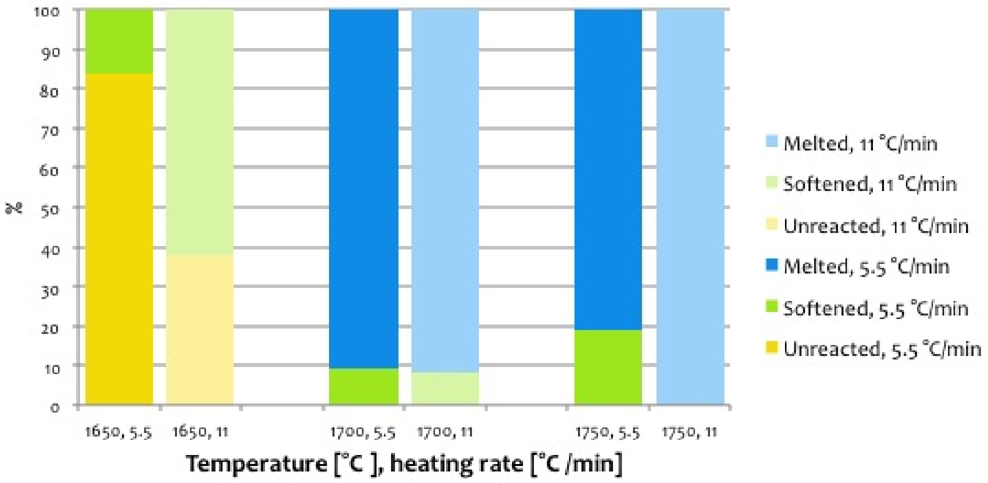


Figure 5.5: Amount of softened, melted and unreacted silica with different heating rates. The results are for the bottom centimeter of the quartz area in the crucibles.

Based on the results obtained in this study, using the method in the induction furnace to determine softening and melting of silica, is a more reliable method. The induction furnace allows for larger volumes to be heated in the same experiment, allowing for a more representative result for the quartz type. Experiments in the wetting furnace only allow for a small sample to be heated, and internal variation in this sample compared to the rest of the bulk can alter the results. Also, for the experiments in the induction furnace, the conditions are more similiar to conditions in a industrial silicon furnace. Different parameters such as particle size can be varied in an induction furnace to study any size effect. The particle size used in the induction furnace is closer to the particle size used in the industry, which is 10-150 mm[6]. The method in the induction furnace can also give a quantitatively result of the amount softening and melting, in addition to softening and melting temperature. In the wetting furnace, only the softneing and melting temperature can be determined

5.2 The effect of different parameters on softening and melting

As seen from figure 5.6, the quartz type will have the greatest impact on the softening of silica. The heating rate will have less impact. The holding time is not considered in this figure, since the experiment with no holding time also had other changing parameters. All parameters except the particle size follow the same trend for softening. The measurement at 1700 °C for the larger particles are believed to be an outlier.

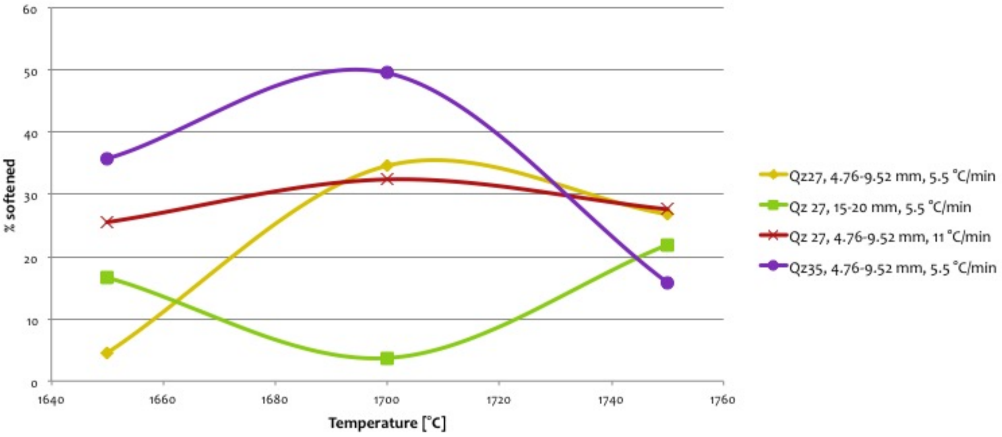


Figure 5.6: The effect of different parameters on amount of softened silica at temperatures from 1650 °C to 1750 °C. The yellow line represents the standard measurement, from where the other parameter are compared. Qz35 contains more impurities. The figure is the same as presented in the chapter for results.

Equation 4.1 could be used to estimate the amount of softening for Qz27 between 1650 °C and 1750 °C. The quation has limitations. Heating rate have to be 5.5 °C/min, particle size of average 7.5 mm and a holding time at maximum temperature for 30 min for most accurate result.

Quartz type

The softening temperature varies with type of quartz. Qz35 has a higher impurity level and lower softening and melting temperature than Qz27. Ringdalen et al.[18] studied how the FeO content in quartz affected the softening and melting temperature. The trend for their results was that the softening temperature of silica decreased as the FeO content increased. Since Qz35 contained 0.09 % Fe, it strenghtens the theory that Fe-containing impurities decrease the softening point. On a more general plane, Kuhlmann-Wilsdorf[24] and Turnbull and Cohen[34] also found that impurities will decrease the melting point of a crystal.

Holding time

For the graph showing variation in holding time, figure 4.23, it can be seen that the amount of softened silica will be higher with 0 minutes holding time at 1650 °C. From 1700 °C up to 1800 °C the 30 minutes holding time will lead to an increased amount of softening and melting. For the experiments with no holding time, the crucibles had a different content ratio, than in the experiments with 30 minutes holding time. More quartz was added to the crucibles with no holding time. This might have affected the results more than the actual holding time. Also, the criterias for determining softened and melted areas might have been more accurate for the recent experiments. This is due to the wetting furnace experiments, which showed little deformation of the silica samples at the melting temperature.

Based on results by Kjelstadli[22], increased holding time should allow for the maximum temperature to be reached throughout the silica particle, and hence for more softening and melting to develop. Therefore it is reasonable to suggest that the deviation at 1650 °C and 1800 °C are due to the crucible content or differences in the criterias for softening and melting, rather than the holding time.

Particle size

The effect of increased particle size is inconsistent. This is seen in figure 4.29. For 1650 °C, the amount of softened silica is higher for the larger particles, than for the smaller. The opposite is the case for the temperatures above 1650 °C. Also, the experiments suggest that the amount of softening will decrease from 1650 °C to 1700 °C. This is unlikely to happen, since the overall trend shows that increased temperature will cause more softening, before some of the softened silica starts to melt. This is not seen in the larger particles at 1700 °C. A reason for the deviation could be that some material has fallen out of the crucible in experiment 22. This could have caused a smaller percentage of softened quartz. Since the particles are larger, it would have taken longer time for the center of the particles to obtain the same temperature as the surface. According to the modelling of the center temperature of a quartz particle of various radii[22], it will take about 30 minutes before the center is heated. The larger radi could have prevented the center of the particle to have experienced the maximum temperature for the same amount of time as the smaller particles. This could explain the lower amount of softening and melting for the larger particles. The difference in the amount of softening at 1750 °Cis 5%, which is not a cinsiderably large difference.

Heating rate

Different heating rates were tested both in wetting furnace and induction furnace. The result from the wetting furnace showed that for Qz35, the heating rate had little influence on the softening temperature. For Qz27 the softening temperature increased with 20 °C, when the heating rate was doubled. The experiments done in the induction furnace for Qz27 show that the overall amount of softening increased with increasing heating rate. Based on the higher softening temperature, the opposite would be expected. At 1750°C, the total amount of softened and melted silica was about the same for both heating rates. Again, the modelling of temperature in the center by Kjelstadli[22] of a particle suggests that the two heating rates tested should have a negliable effect on the amount of softening and melting, since the center of the particle will be able to heat faster than the heating rates used.

Chapter 6

Conclusion

6.1 Development of method

To study the softening and melting of silica, a method developed in earlier project work has been further improved and used to investigate the effect of different parameters affecting softening and melting. The method was based on the S.C.I.C.E. (stationary charge in controlled environment) technique, and were performed in an induction furnace. The method gave adequate quantitative and qualitative results. For further experiments some minor adjustments to improve the permeabiltity of epoxy in the crucibles are suggested.

Earlier test method of softening and melting temperature of silica have been performed in a wetting furnace. Four experiments were also done in the wetting furnace for this study, to improve the new method developed. Two different quartz samples were heated with two different heating rates. The results were used to compare the softening and melting temperatures obtained, and to visually inspect the softening process.

The new method developed should be used for future measurements of softening and melting of quartz used in industrial Si production. The reasons for that are:

- An uncertainty excists in both methods, but for the new method the uncertainty is identified. The uncertainty in the thermocouples is also smaller for the thermocouples in the new method.
- The conditions are similiar to the conditions in an industrial furnace producing silicon.

- Larger quartz samples and volumes can be used in the induction furnace with the new method. This allows for a average to be calculated, decreasing statistical uncertainty.
- The new method can measure quantitatively the amount of softening as a function of temperature.

6.2 Effect of parameters on softening and melting

In total 13 crucibles were heated in an induction furnace to a maximum temperature, and with variations in one parameter at the time. Heating rate, particle size, holding time and quartz type were the parameters investigated. The silica was considered softened when the corners had a slightly rounded exterior. When the silica particles had a more rounded form, had adapted themselves to the surrounding SiC particles, or melted togheter with other silica pieces, they were considered melted. The effect of the parameters are summarised below:

- Increasing impurity content showed more softening and melting at all temperautres from 1650 °C to 1750 °C.
- Increased holding time caused an increase in amount of softened and melted silica at temperatures from 1700 °Cto 1800 °C.
- Increasing the heating rate had inconsistent results. At higher temperature the difference in amount softened and melted silica was neglible.
- Larger particles gave less softening and melting from 1700 °C to 1750 °C.

An first approximation to mathematically estimate the amount of softening as a function of temperature, is given by equation 6.1. S is softening and T is temperature. The equation is limited to the use for Qz27, 5.5 °C/min heating rate and 30 minutes holding time at maximum temperature.

$$S(T) = -0.0076T^2 + 26,064T - 22310 \tag{6.1}$$

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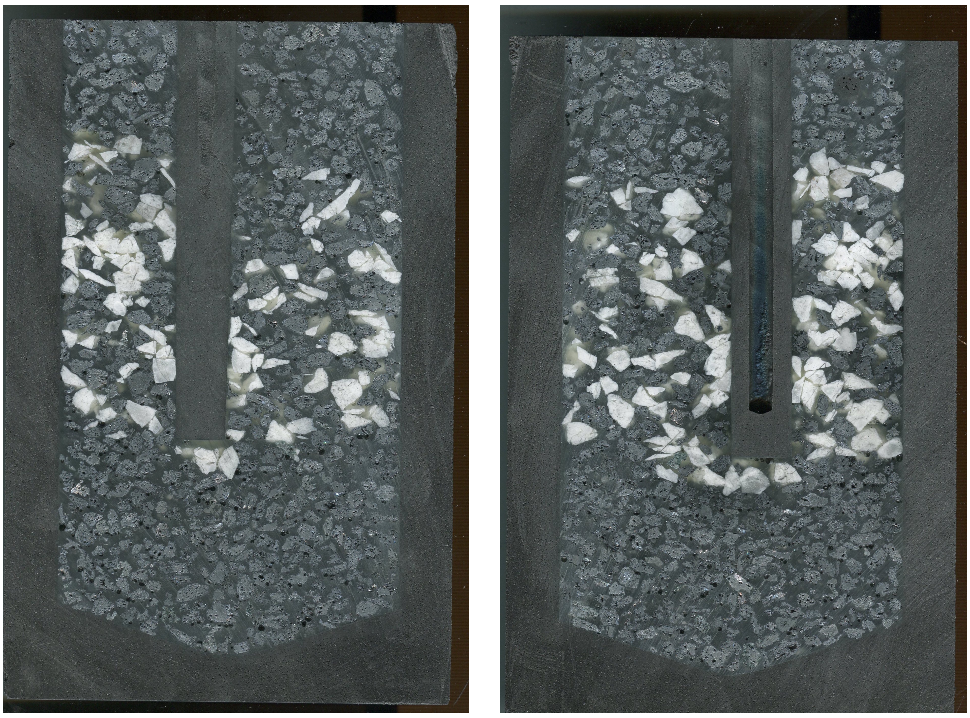
Appendix

A Scanning results and heating rates from induction furnace experiments

In the following figures, all the scanned crucible surfaces and the heating rates for all the experiments are shown.

In figure 1 the surfaces of experiment 9 are shown. Maximum temperature was 1650 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 2 shows the heating rate for crucible 9.



(a) 9a (b) 9b

Figure 1: Scanned surfaces from crucible 9.

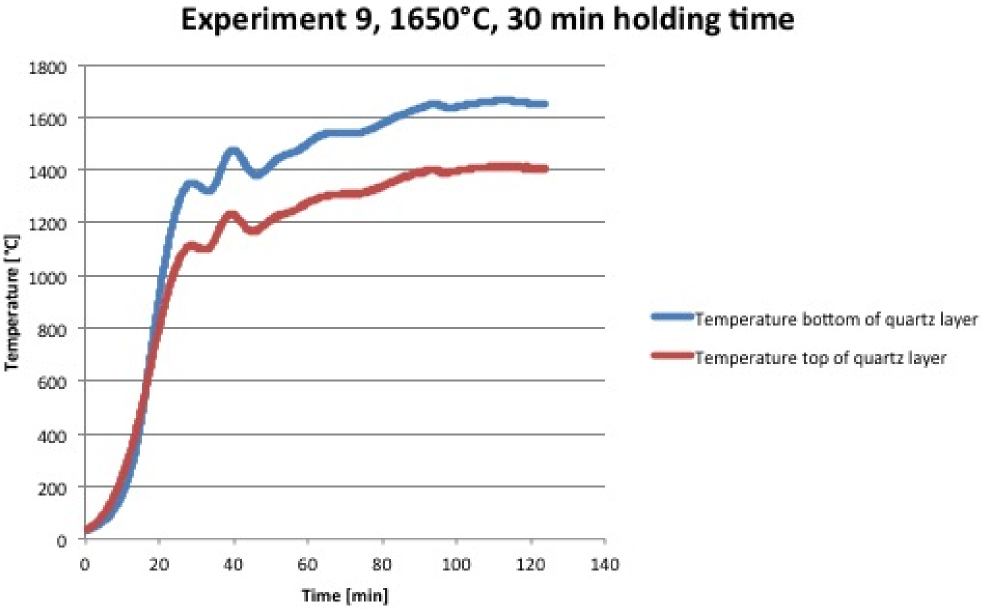
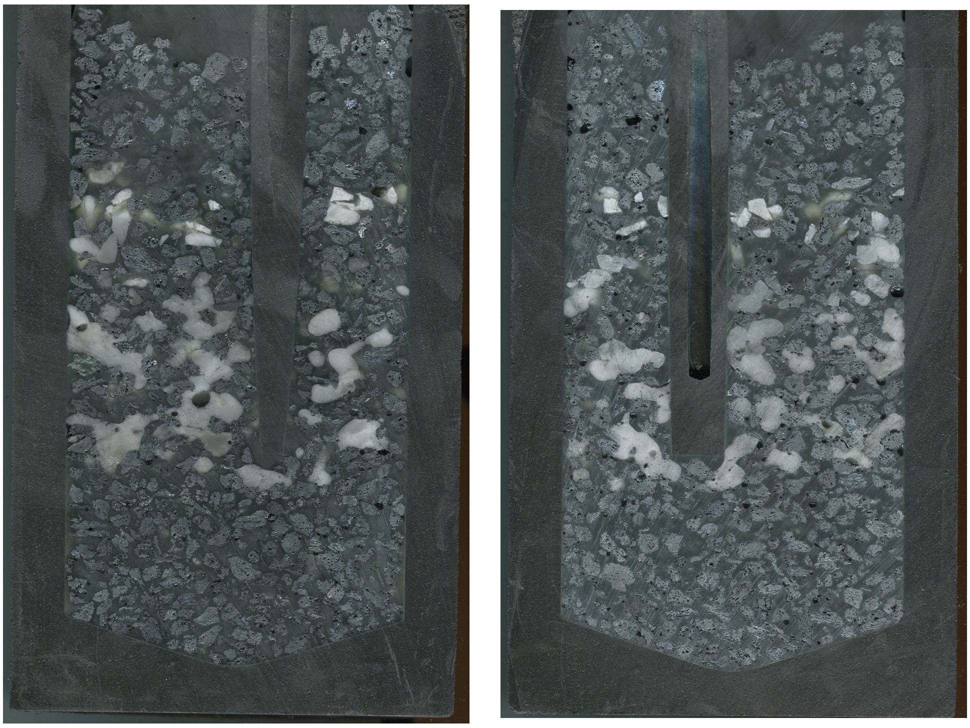


Figure 2: Heating rate for crucible 9, heated to maximum 1650 °C.

In figure 3 the surfaces of experiment 10 are shown. Maximum temperature was 1800 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 4 shows the heating rate for crucible 9.



(a) 10a (b) 10b

Figure 3: Scanned surfaces from crucible 10.

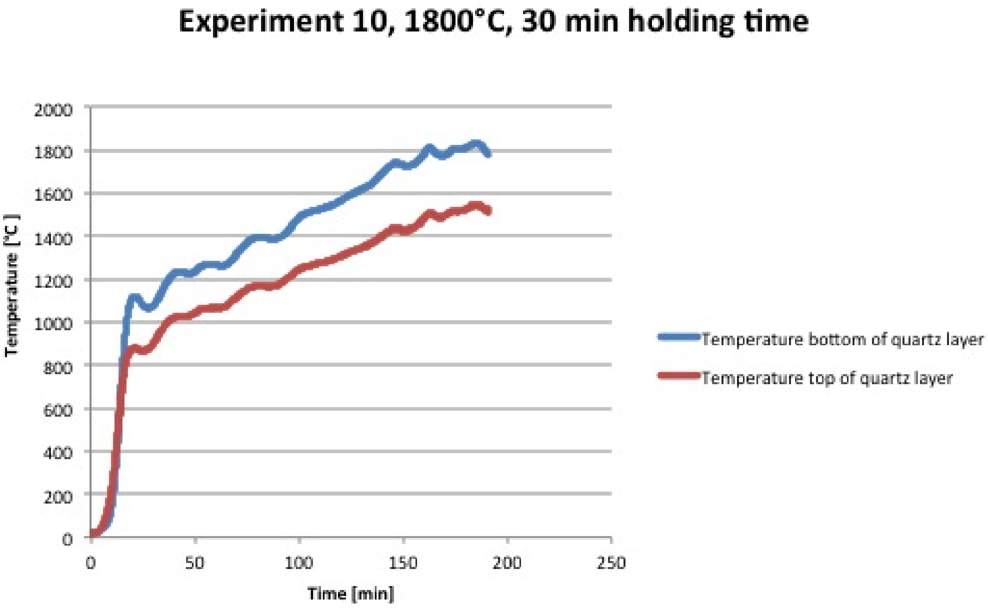
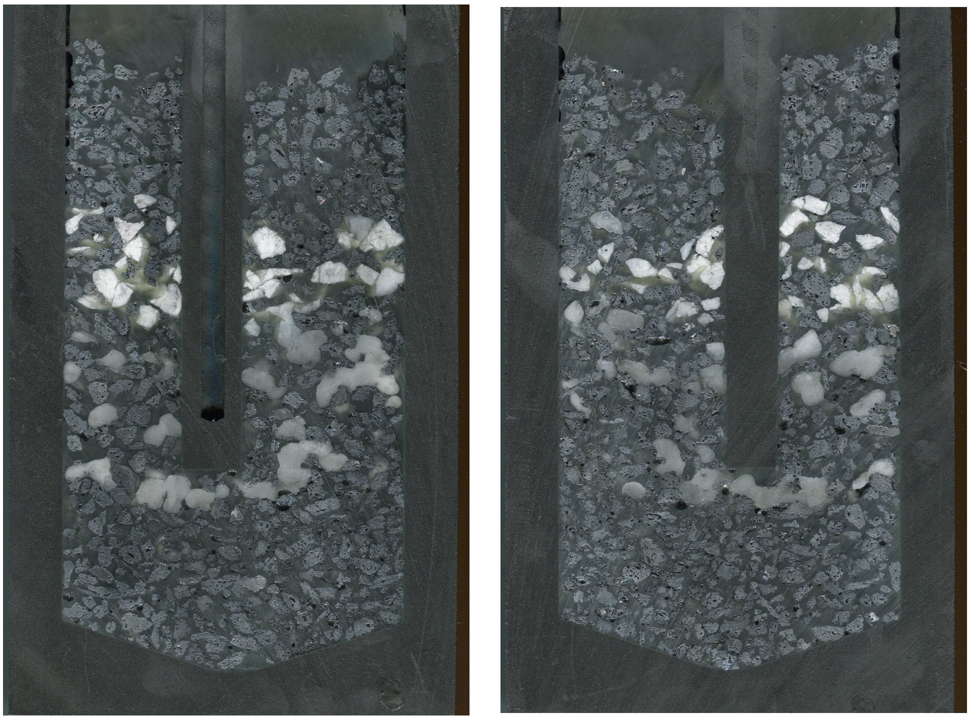


Figure 4: Heating rate for crucible 10, heated to maximum 1800 °C.

In figure 5 the surfaces of experiment 11 are shown. Maximum temperature was 1750 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 6 shows the heating rate for crucible 11.



(a) 11a (b) 11b

Figure 5: Scanned surfaces from crucible 11.

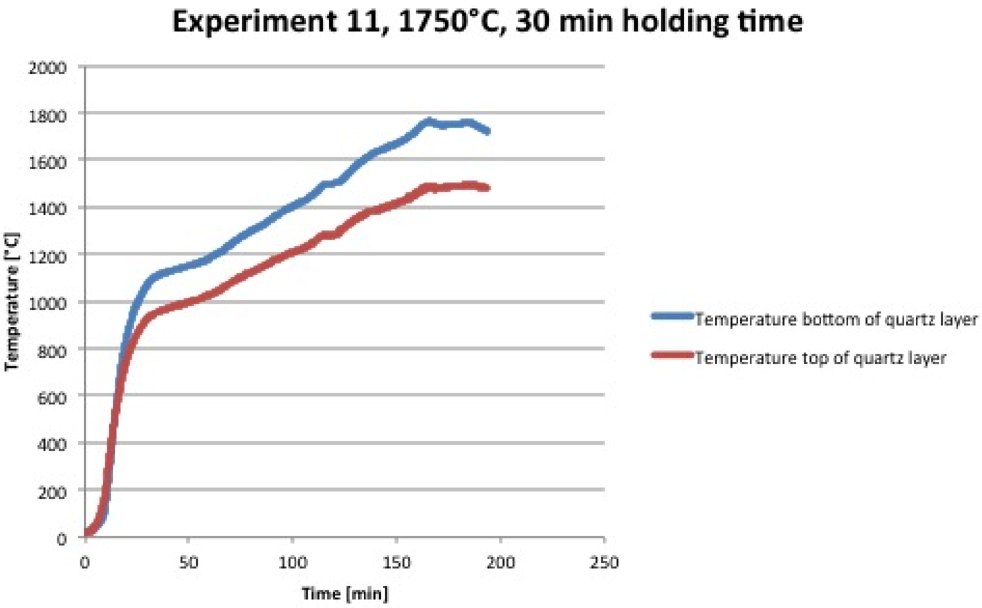
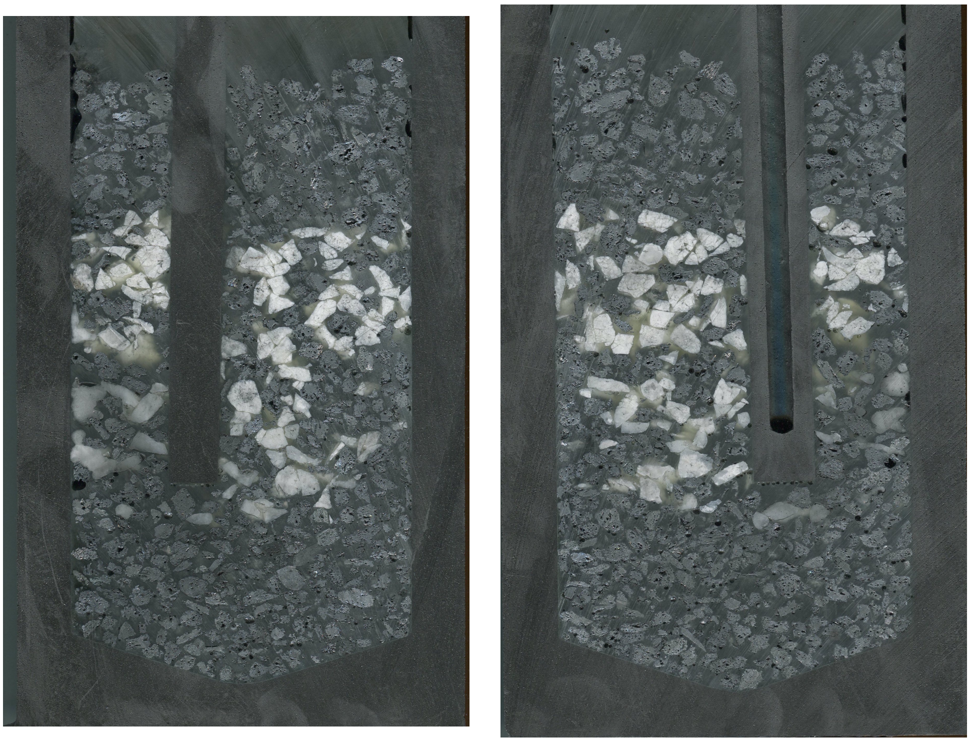


Figure 6: Heating rate for crucible 11, heated to maximum 1750 °C.

In figure 7 the surfaces of experiment 12 are shown. Maximum temperature was 1700 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 8 shows the heating rate for crucible 12.



(a) 12a

(b) 12b

Figure 7: Scanned surfaces from crucible 12.

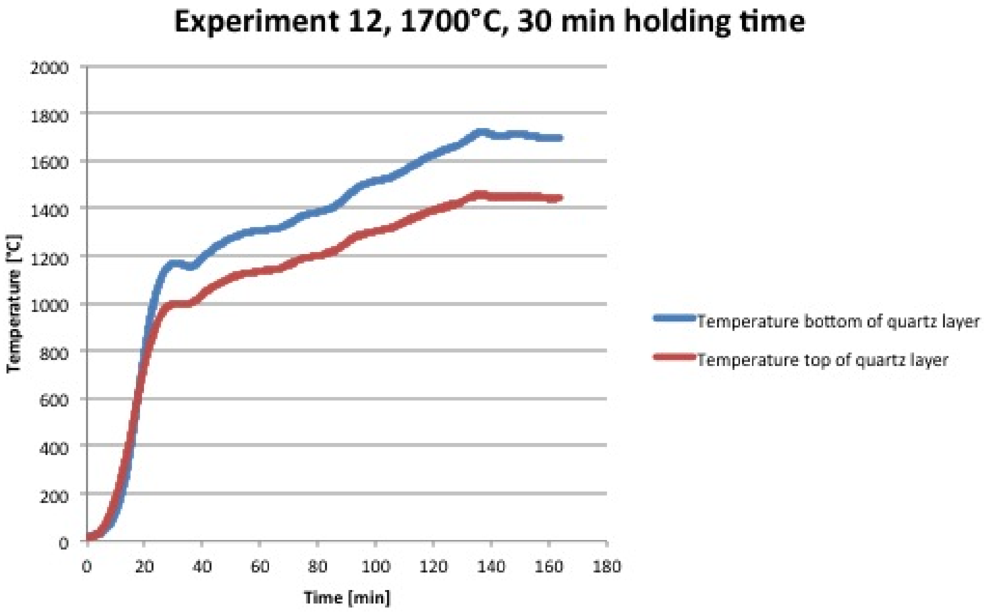
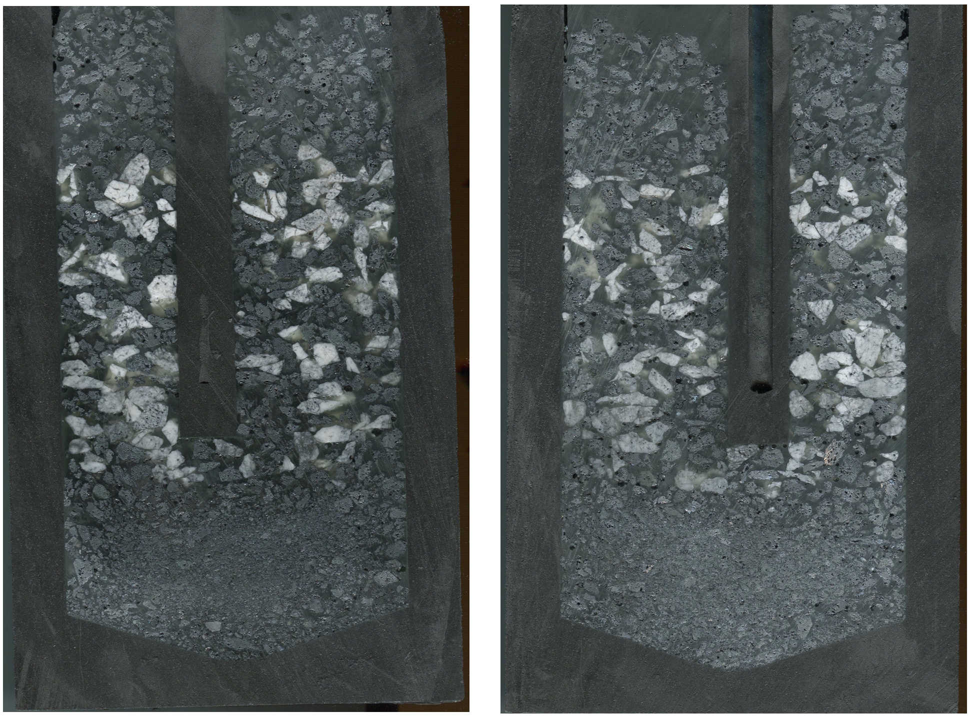


Figure 8: Heating rate for crucible 12, heated to maximum 1700 °C.

In figure 9 the surfaces of experiment 13 are shown. Maximum temperature was 1650 °C, quartz type was Qz35, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 10 shows the heating rate for crucible 13.



(a) 13a (b) 13b

Figure 9: Scanned surfaces from crucible 13.

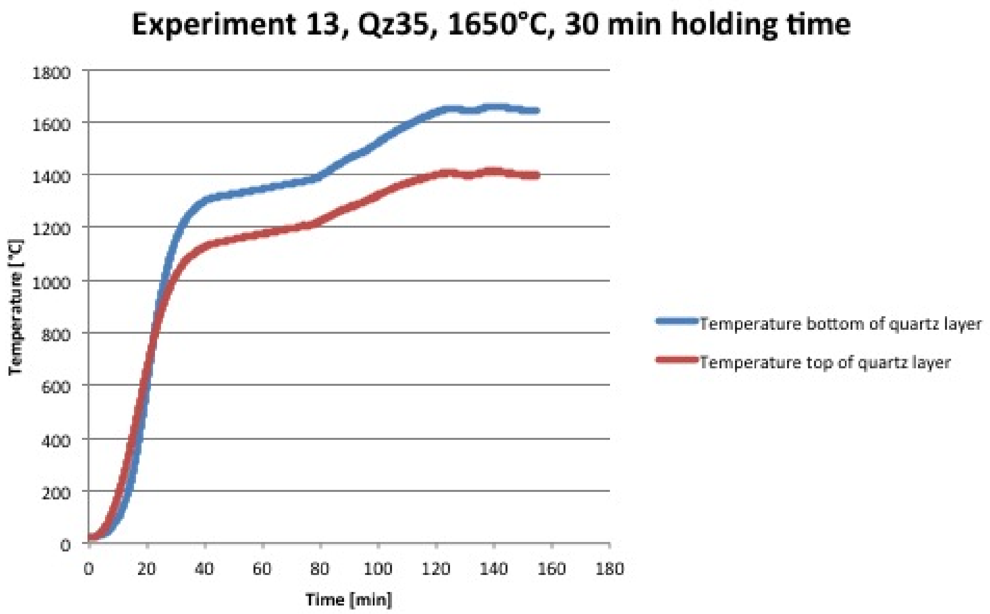
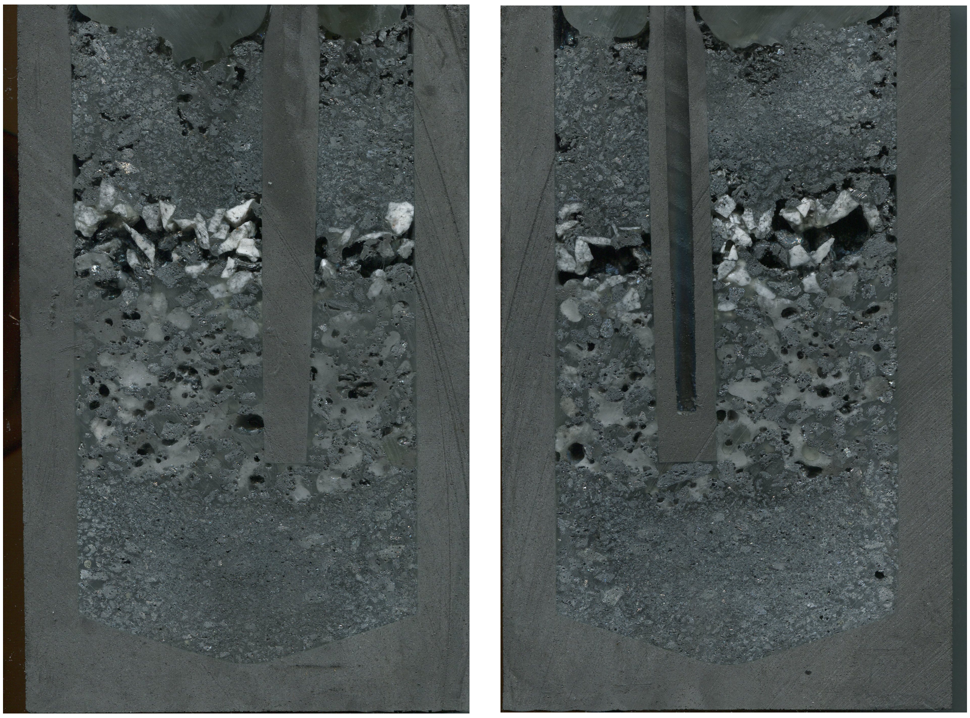


Figure 10: Heating rate for crucible 13, heated to maximum 1650 °C.

In figure 11 the surfaces of experiment 14 are shown. Maximum temperature was 1750 °C, quartz type was Qz35, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 12 shows the heating rate for crucible 14.



(a) 14a (b) 14b

Figure 11: Scanned surfaces from crucible 14.

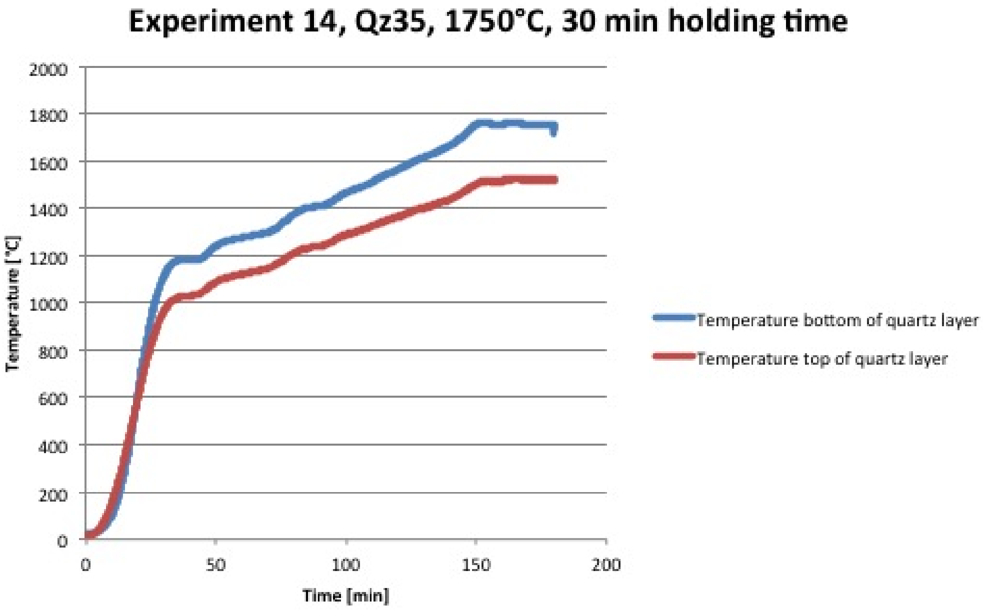
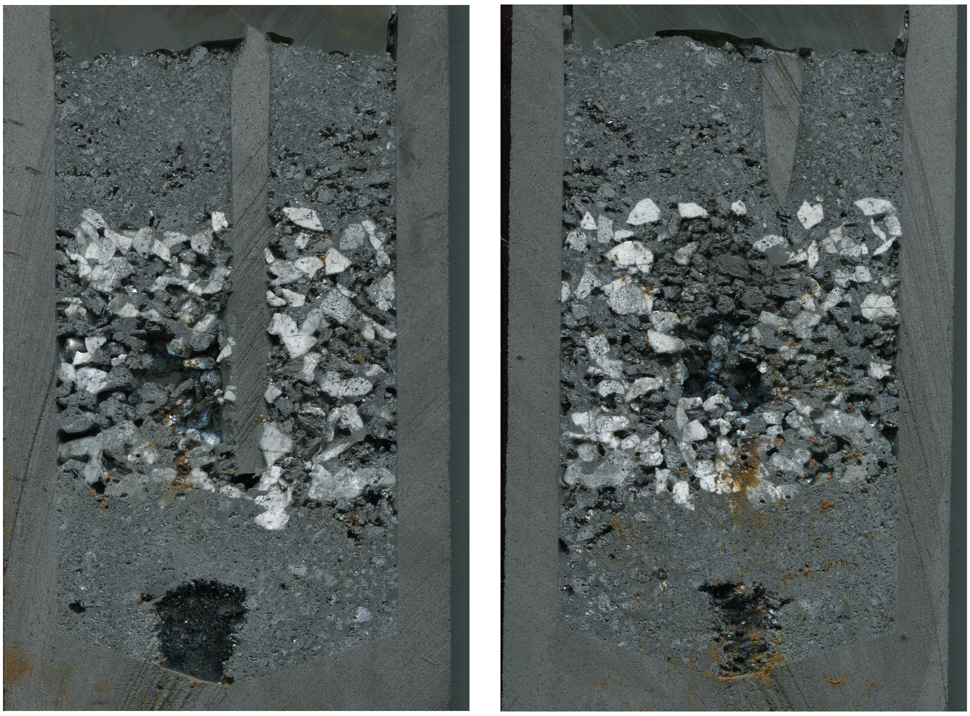


Figure 12: Heating rate for crucible 14, heated to maximum 1750 °C.

In figure 13 the surfaces of experiment 15 are shown. Maximum temperature was 1700 °C, quartz type was Qz35, heating rate was 5.5 °C/min and the particle size was 4.76-9.52 mm. Figure 14 shows the heating rate for crucible 15.



(a) 15a (b) 15b

Figure 13: Scanned surfaces from crucible 15.

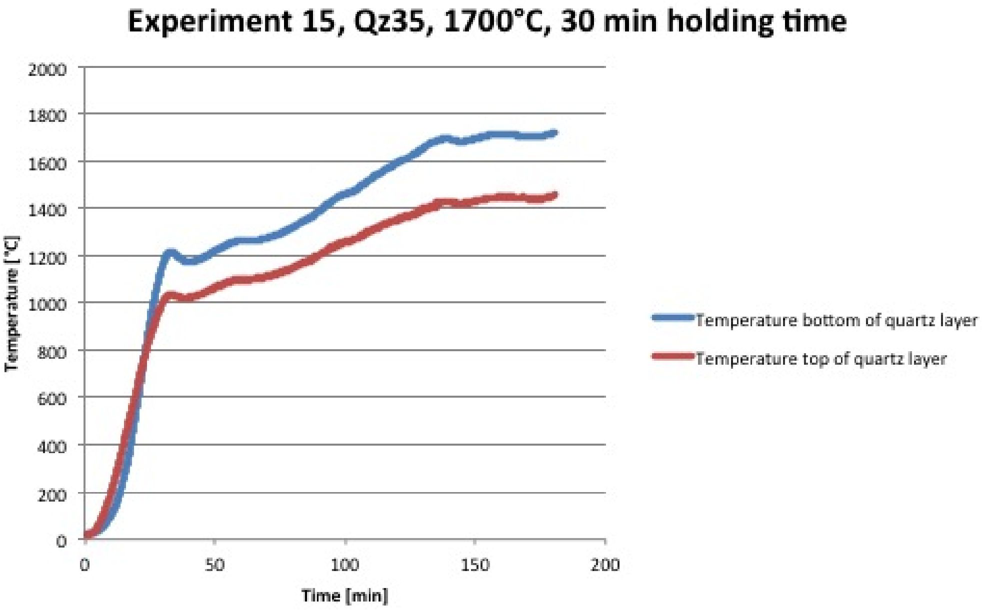
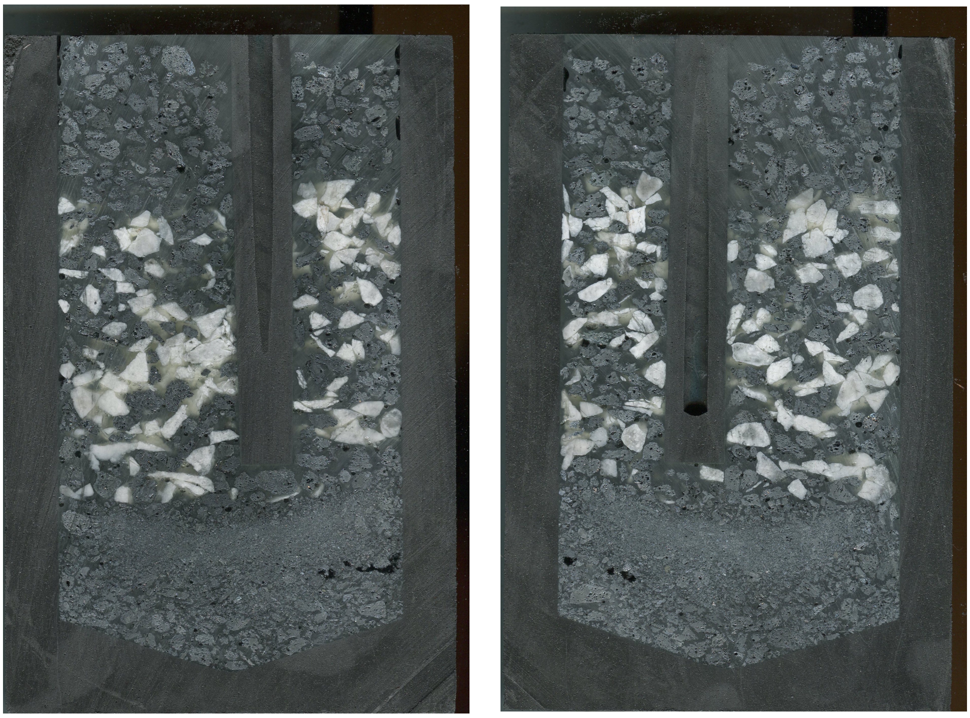


Figure 14: Heating rate for crucible 15, heated to maximum 1700 °C.

In figure 15 the surfaces of experiment 16 are shown. Maximum temperature was 1650 °C, quartz type was Qz27, heating rate was 11 °C/min and the particle size was 4.76-9.52 mm. Figure 16 shows the heating rate for crucible 16.



(a) 16a

(b) 16b

Figure 15: Scanned surfaces from crucible 16.

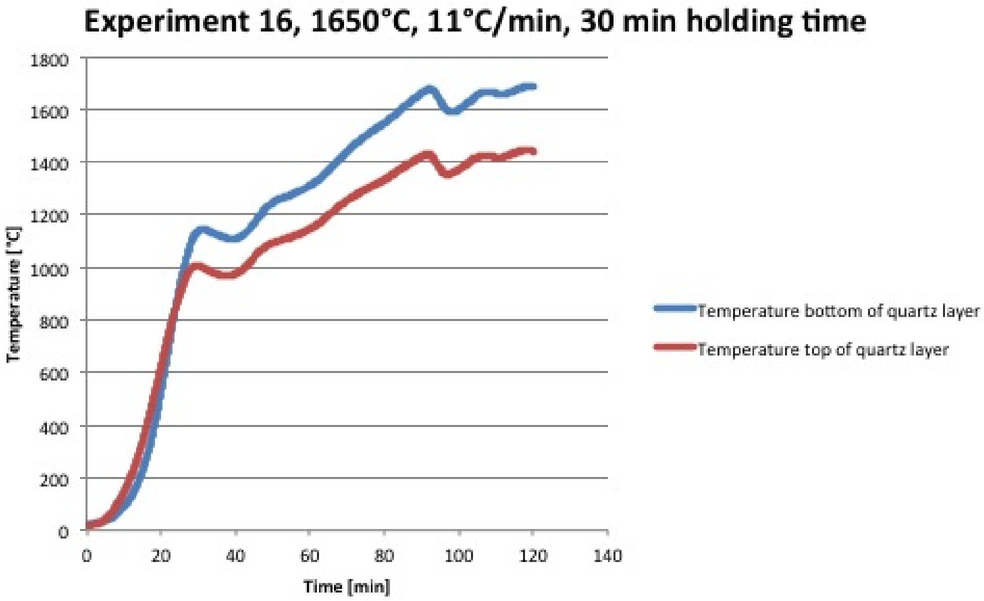


Figure 16: Heating rate for crucible 16, heated to maximum 1650 °C.

In figure 17 the surfaces of experiment 17 are shown. Maximum temperature was 1750 °C, quartz type was Qz27, heating rate was 11 °C/min and the particle size was 4.76-9.52 mm. Figure 18 shows the heating rate for crucible 17.

(a) 17a (b) 17b

Figure 17: Scanned surfaces from crucible 17.

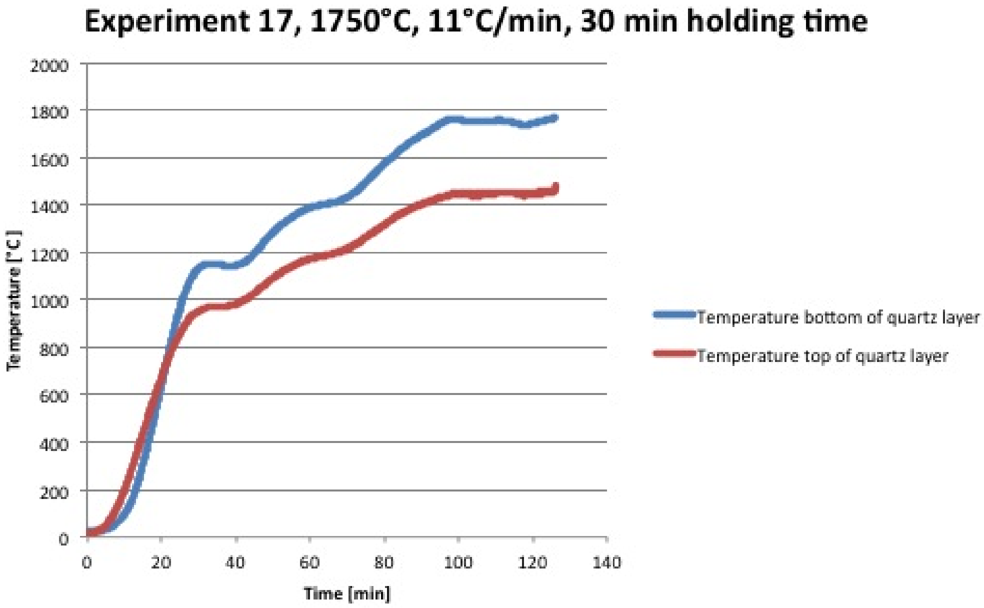
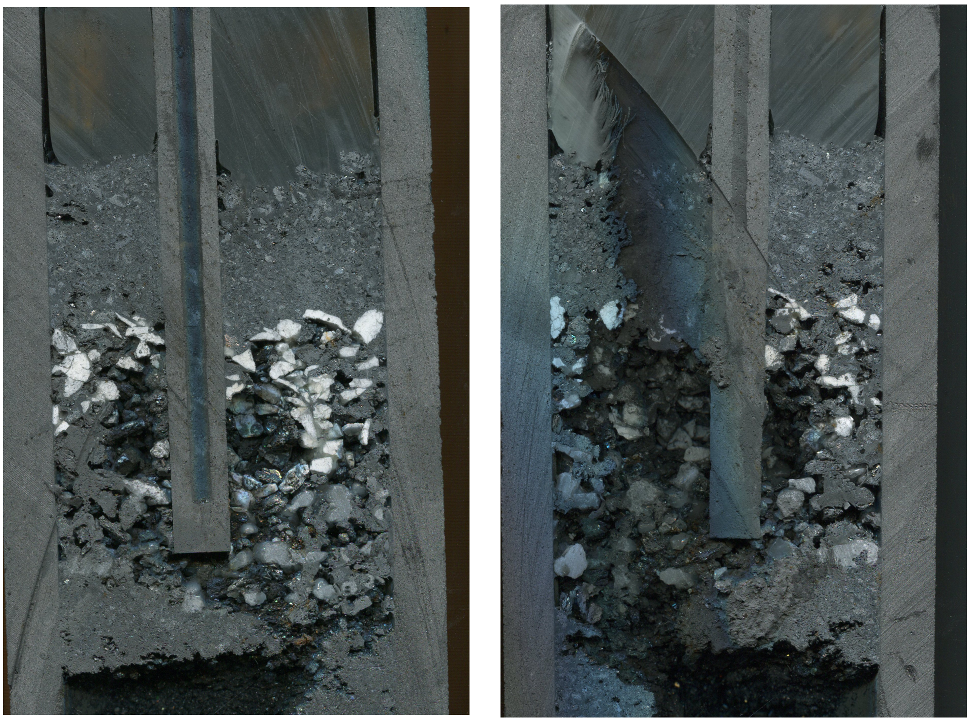


Figure 18: Heating rate for crucible 17, heated to maximum 1750 °C.

In figure 19 the surfaces of experiment 18 are shown. Maximum temperature was 1700 °C, quartz type was Qz27, heating rate was 11 °C/min and the particle size was 4.76-9.52 mm. Figure 20 shows the heating rate for crucible 18.



(a) 18a (b) 18b

Figure 19: Scanned surfaces from crucible 18.

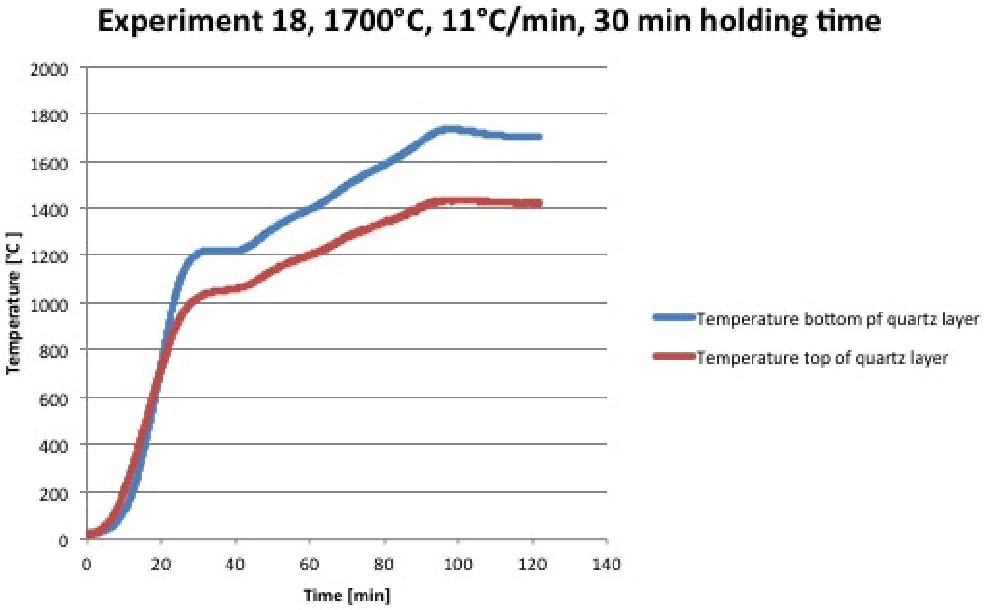


Figure 20: Heating rate for crucible 18, heated to maximum 1700 °C.

In figure 21 the surfaces of experiment 19 are shown. Maximum temperature was 1750 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 15-20 mm. Figure 22 shows the heating rate for crucible 19.

(a) 19a

(b) 19b

Figure 21: Scanned surfaces from crucible 1.

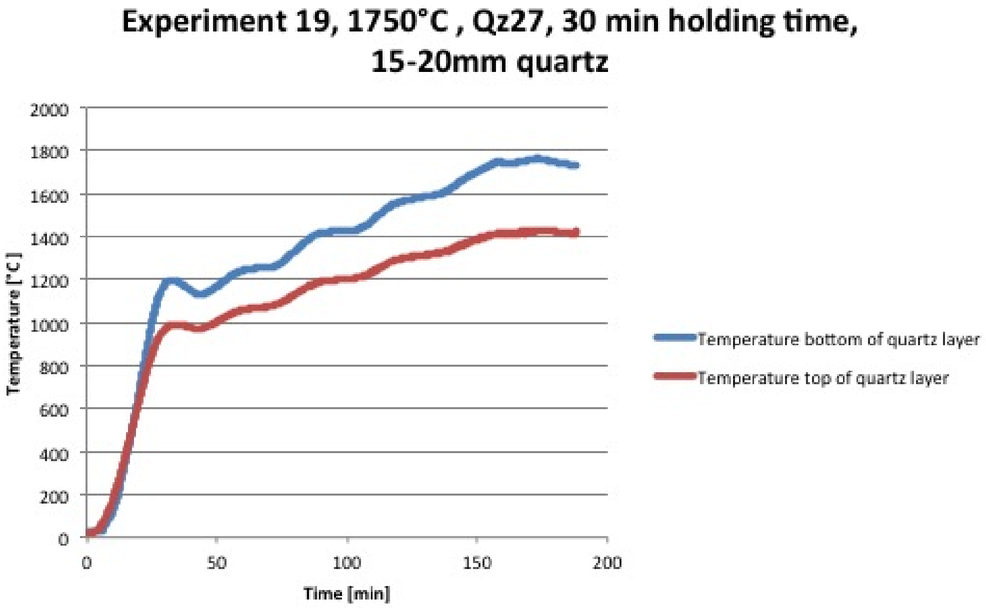
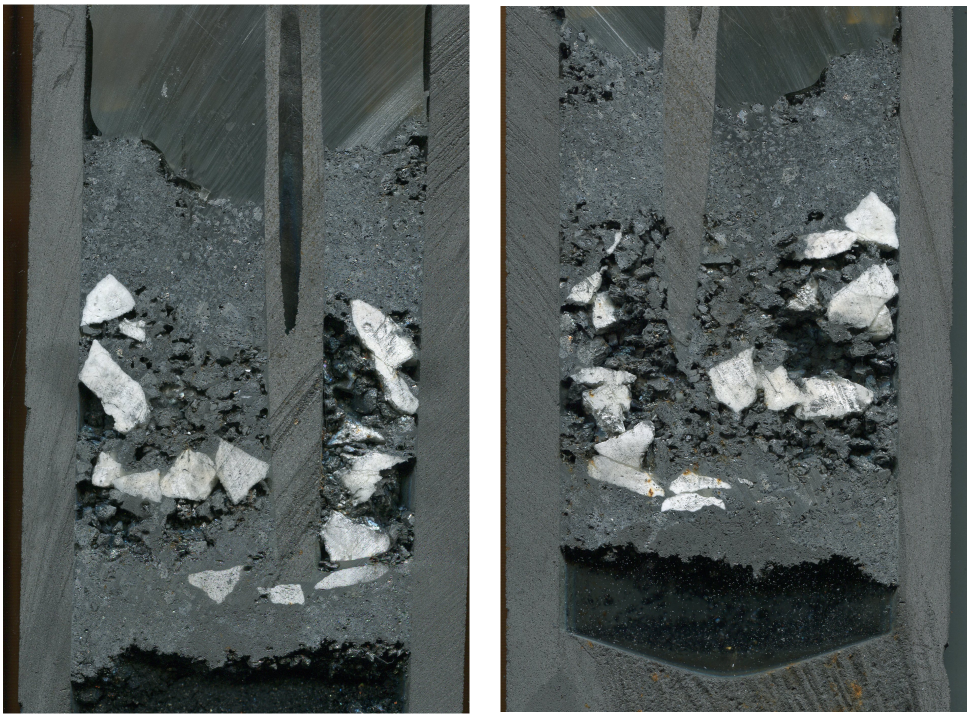


Figure 22: Heating rate for crucible 19, heated to maximum 1750 °C.

In figure 23 the surfaces of experiment 20 are shown. Maximum temperature was 1700 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 15-20. Figure 24 shows the heating rate for crucible 20.



(a) 20a (b) 20b

Figure 23: Scanned surfaces from crucible 20.

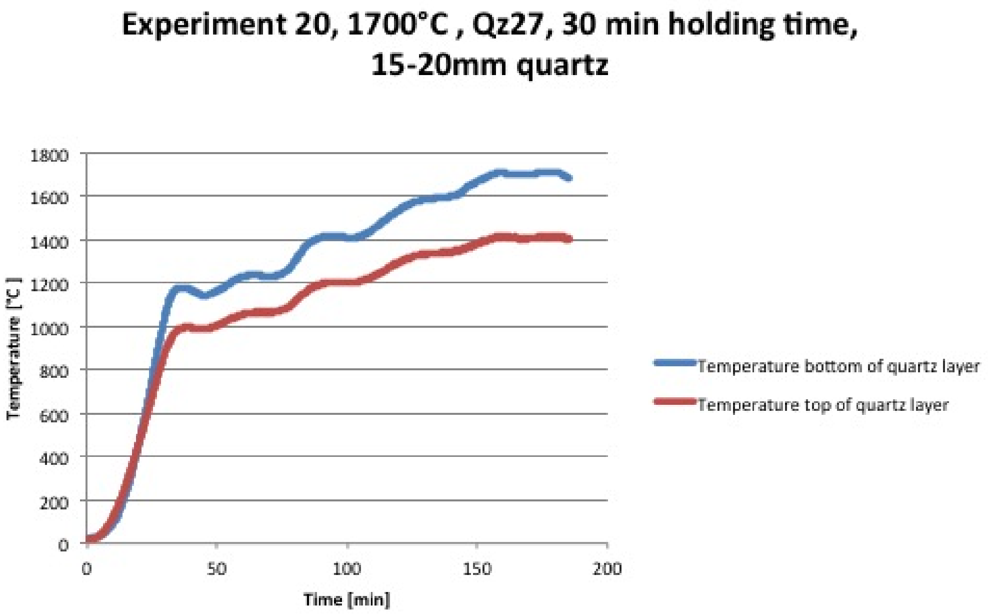
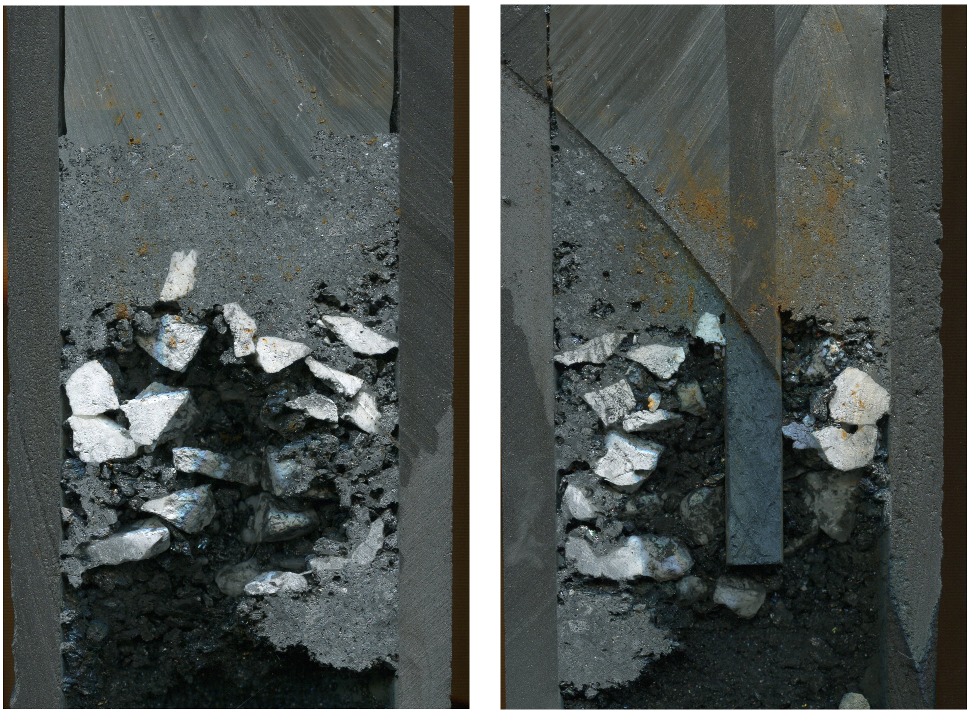


Figure 24: Heating rate for crucible 20, heated to maximum 1700 °C.

In figure 25 the surfaces of experiment 21 are shown. Maximum temperature was 1650 °C, quartz type was Qz27, heating rate was 5.5 °C/min and the particle size was 15-20. Figure 26 shows the heating rate for crucible 21.



(a) 21a (b) 21b

Figure 25: Scanned surfaces from crucible 21.

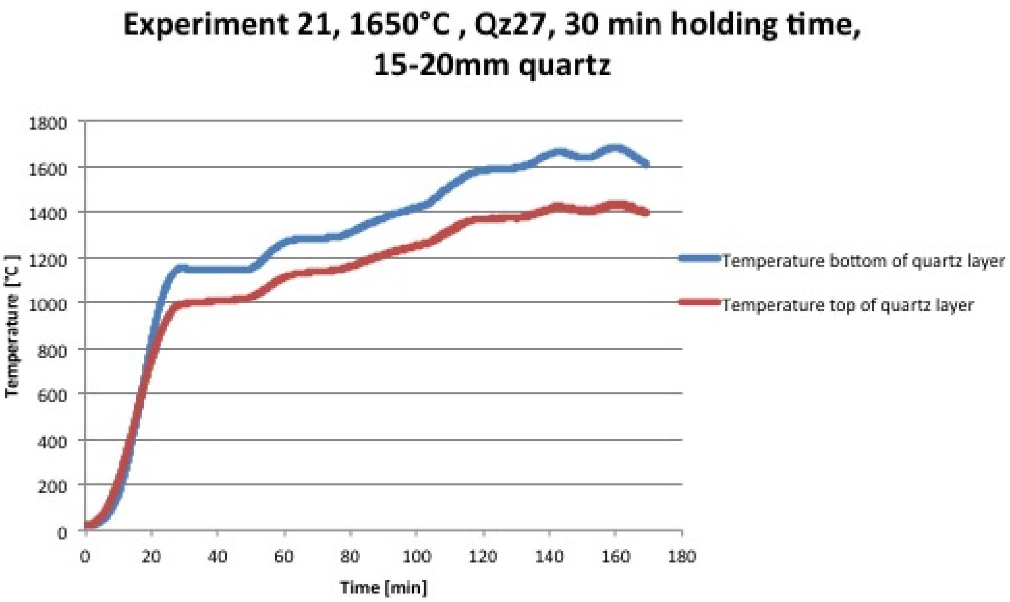


Figure 26: Heating rate for crucible 21, heated to maximum 1650 °C.