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## Influence of limestone grain size on glass homogeneity

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### Abstract

The lack of homogeneity in a glass is characterized by the occurrence of layers of different chemical compositions and densities. When starting materials relevant for the synthesis of soda-lime silicate glasses are melted in a crucible, silica- and calcium-enrichments are observed at the top and at the bottom of the melt respectively. This behaviour may be due to the occurrence of several reaction pathways. In this respect, an interesting observation is that the grain size of limestone is found to be an important parameter influencing the level of glass homogeneity. The reasons for this have been studied here using systematic differential thermal analysis and thermogravimetric analysis. The experiments showed that, in presence of limestone of small grain size (< 200 micrometers), sodium carbonate disappears before the temperature at which it is observed to interact with silica in the CaO - free system. We infer that this is most probably due to production of a mixed carbonate liquid, which subsequently reacts with silica to spontaneously yield a homogeneous silicate melt. A characteristic of this probable mixed carbonate (assumed to be close to the composition  $\text{CaNa}_2(\text{CO}_3)_2$ ) is its density of  $2.54\text{g/cm}^3$ , close to that of the silicates and of silica itself. On the contrary, coarse limestone decomposes to CaO (and  $\text{CO}_2$ ), which is slowly incorporated in the sodium silicate liquid formed when sodium carbonate interacts with silica. The much higher density of CaO ( $3.35\text{ g/cm}^3$ ) and of calcium silicates could explain the tendency for CaO concentrations to be greatest towards the base of melting crucibles.

### Introduction

The problem of striae caused by a lack of homogeneity delayed the development of optical glass in the nineteenth century. Indeed, the fabrication of lenses of good quality was not routinely possible until L. Guinand had the idea of mechanically stirring the liquid lead silicate as long as possible during the cooling process [1]. Even for the synthesis of simple soda-lime silicate "window" glasses, chemical heterogeneity is a well known problem, typically remedied by addition of a fining agent, such as sodium sulphate, which creates bubbles that stir and homogenise the liquid.

Despite its importance, the question of understanding and quantifying the heterogeneity of glass composition during synthesis has received relatively little attention in the scientific literature although several studies are worthy of note. For example, as early as 1944 – 1945, F.V. Tooley & R.L. Tiede [2 - 3] conducted melting experiments, crushed the resulting glass, mixed it with a high density organic liquid (mixture of tetrabromoethane and lower density isopropylsalicylate), then used a centrifuge to separate glass and liquid, following the experimental procedure proposed by Turnbull in 1941 [4]. The liquid used was chosen to have a density close to that of the glass, but with a significant temperature dependence. The density interval and distribution could thus be determined directly from measurement of the quantity of glass floating on the surface as a function of temperature. Chemical analyses of samples from different parts of the melting crucible [3] showed that there was a tendency for enrichment in  $\text{SiO}_2$  towards the top, and in CaO towards the bottom. This variability was attributed to the formation of eutectic or other low-temperature liquids, and their segregation from the more refractory components of the batch. The fact that low density liquids are observed at the top of the crucible and high density liquids at the base led the authors to

suggest that transiently produced silica – rich liquids migrate upwards and CaO-rich liquids downwards under the influence of gravity, although the details of generation of these liquids was not explicitly stated. The results also indicate that diffusion acts to eradicate chemical gradients caused by the segregation during melting, because the density spread is significantly and continuously decreased between 1 and 64 hours at 1400°C. An additional finding by the same authors is that grain size also has an influence on the degree of compositional heterogeneity (F.V. Tooley [5]), glass being more homogeneous when the raw materials are of smaller grain size.

Almost 20 years later, M. Cable & al. [6] reexamined the question of glass homogeneity, confirming that glasses melted in laboratory crucibles are highly heterogeneous on a large-scale, with a silica-enriched layer at the top, a lime-enriched layer at the bottom, and a fairly homogeneous glass at intermediate heights. Furthermore, the influence of grain size was confirmed, with decreasing grain size of sand and limestone found to considerably improve the homogeneity of the melt. A comparative study of different glass compositions showed that glass homogeneity is principally sensitive to the lime content, but no quantitative explanation of the complete data set of observed chemical variations has been proposed.

In this respect, we note that in the absence of an immiscibility field, there is no reason to expect spontaneous separation of a homogeneous liquid into compositionally distinct layers of different densities, leading to the conclusion that the different silicate compositions must be generated during the initial stages of the melting process. As mentioned above, locally produced liquids of variable density may lead to segregation, although an alternative proposition is that movement of unmolten solid grains is at the origin of the observed segregation. For example, unmolten grains of SiO<sub>2</sub> will be carried towards the upper surface of the crucible due to their low density and the presence of attached bubbles, while dense unmolten grains of CaO may sediment to the bottom of the crucible. In both cases dissolution of the solid grains will lead to a compositional gradient in the final liquid. The fact that solid-liquid separation velocities are a function of grain diameter (i.e. Stokes law) implies that this mechanism has the potential to explain a grain-size dependence of the extent of segregation. Alternatively, the relative movement of solid grains before melting begins, and/or an effect of the chemical reactions taking place during the earliest stage of melting may also potentially be of importance. In any case, at the present time no experimentally verified scenario has been proposed to take account of such large-scale segregation phenomena.

In this paper we present new results relevant to the generation of large-scale chemical heterogeneities during synthesis of soda-lime silica glasses. First of all, using starting materials of variable grain size, in particular CaCO<sub>3</sub>, we have quantified the extent of chemical heterogeneity as a function of height in laboratory crucibles. These new results and those of Cable et al. [6] are used to suggest that the simple segregation of unmelted solid grains separating because of density differences relative to the main liquid cannot fully account for the observed compositional profiles. In light of this fact, we have looked to explore the effects of chemical reactions taking place during carbonate breakdown, to assess to what extent such reactions may affect glass homogeneity and the observed effect of grain size. For this purpose we have performed systematic differential thermal analysis and thermogravimetric analysis of simple combinations of the relevant starting materials to quantify which reactions take place and at what temperatures.

## Experimental methods

### *Segregation experiments*

The chemical composition of the glasses is given in table 1 in wt% (impurities around 0.5%).

Industrial raw materials of mean grain size around 0.5 mm were used. Calcium carbonate was sieved to extract two ranges of grain size; less than 200 micrometers ("fine") and larger than 1 mm ("coarse").

The experiments were made in an electrically-heated furnace having a "hot zone" (volume in which temperature is constant) sufficiently large and well controlled that temperature gradients across the samples are largely insufficient to induce thermal convection, or diffusion due to the Soret effect. One kilogram of glass was prepared by heating well mixed (Turbula) starting products in a 1 litre platinum crucible approximately 12cm in diameter. The crucible was introduced directly at 1470°C, a temperature well above the liquidus temperature of the bulk composition (~950°C), then left for 90 minutes. The liquid was then cooled to 550°C and annealed at that temperature for 12 hours, before cooling to room temperature over a period of 48 hours. Samples were recovered from the crucibles by drilling a vertically oriented core which was then cut along section and polished. The chemical composition was measured from the top to the bottom of the crucible by electron microprobe analysis on this polished flat sample. Analysis conditions used were an accelerating voltage of 15kV and a beam current of 10nA

### ***Differential Thermal Analysis – Thermogravimetric analysis – Mass spectrometry***

DTA experiments were performed on samples of ~100mg, with a STA409 Netzsch apparatus equipped with mass spectrometry and thermogravimetric measurement. A 10K/min ramp was used.

## **Experimental results and discussion**

### ***Segregation experiments***

The compositional spread observed with coarse calcium carbonate (Figure 1) is consistent with the previous work referred to above [2-6]: silica is found in excess at the top of the crucible, while there is an enrichment in the concentration of CaO at the bottom. Although there is more Na<sub>2</sub>O than CaO on average in the silicate liquid, Na<sub>2</sub>O presents a much smaller gradient than CaO. It seems, therefore, that a depletion in SiO<sub>2</sub> is mostly compensated for by an enrichment in CaO, and vice-versa. On the contrary, the compositional spread is much smaller and close to analytical uncertainties when fine-grained limestone is used (Figure 2). Experiments were also performed using batches containing sodium sulphate and a reducing agent (coke), which are well-known for their positive influence on homogeneity due to mixing related to the generation of bubbles at high temperature (figures 3 and 4).

Samples formed from fine-grained limestone and sulphate are particularly homogenous (Figure 4), but even with a fining agent, the glass made with coarse limestone (Figure 3) is more heterogeneous than the glass made with fine limestone without fining agents (Figure 2). In other words, the presence of the fining agents is not sufficient to counteract the process at work when coarse limestone grains are used in the starting material. Figure 5 presents all the results expressed in terms of the compositional spread (standard deviation) of SiO<sub>2</sub>, Na<sub>2</sub>O and CaO contents obtained for segregation experiments with and without sulphate, illustrating these differences.

For samples made without fining agents, the anti-correlation of the profiles of SiO<sub>2</sub> and CaO and Na<sub>2</sub>O, and the correlation of the profiles of CaO and Na<sub>2</sub>O are at first glance consistent with the idea that silica moves towards the top of the crucible, probably in the form of unmolten sand grains. However, in detail the relative increase in CaO concentration is much greater than that of Na<sub>2</sub>O (Figure 1), implying that simple upward movement of silica grains is not the sole factor affecting the profile. To explain the enrichment in CaO at the bottom of

the crucible, one possibility is that CaO residual to decarbonation of limestone may form then sink, although no direct observation of lime grains has to our knowledge been described in the literature. To test that hypothesis we have therefore performed an additional experiment using a mixture containing coarse grained  $\text{CaCO}_3$ , but heated only to 1280°C with a 10K/min ramp (Figure 6). In this case, small scale compositional heterogeneities, as well as unmolten silica and unmolten CaO are observed, providing direct evidence for the potential sedimentation of lime. The feasibility for movement of unmolten grains to lead to compositional gradients may be assessed by calculation of the distance travelled assuming particles moving according to Stokes Law at their terminal velocity. Such calculations are hindered by the fact that grain size may evolve as a function of time due to dissolution, as well as the fact that bubbles attached to sand grains may have a significant effect on the density difference between "solid" and liquid. Despite these limits, distances travelled are calculated to be in the range 1-10 cm for grains of 200  $\mu\text{m}$  in diameter, and 10 to 100cm for grains 1mm in diameter. In other words, in all cases buoyancy effects should be capable of transporting solid grains along distances which are a significant fraction of the vertical dimension of our experimental samples (typically 5cm). However, despite this fact, several lines of evidence would argue against the relative movement of unmolten solid grains being the only mechanism controlling the existence and extent of large-scale compositional heterogeneity. For example, the excellent degree of homogeneity in the fine-grained experiment is not predicted by these calculations. Furthermore, the fact that the spatial extent of the silica-rich zone at the top of the crucible is significantly affected by a change in the size of initial  $\text{CaCO}_3$  grains (for the same size of  $\text{SiO}_2$ ) is a feature not predicted by simple buoyancy arguments. In addition, when the different compositions of figures 1 and 2 are plotted in a wt% CaO versus  $\text{SiO}_2$  wt% diagram (figure 7), the compositional spread in the case of starting materials containing coarse limestone is much more complex than that for the case of fine limestone, and this characteristic too requires some rational explanation.

In view of these data, there is a clear need to reconsider the mechanisms that may produce and/or impede formation and segregation of liquids of variable composition and density. In this respect our attention has focussed on the idea that chemical reactions associated with carbonate breakdown may be critical in the generation or absence of compositional gradients. With this idea in mind we have performed differential thermal analysis experiments on simplified carbonate-bearing mixtures containing fine and coarse limestone, in order to highlight the possible different reactional pathways.

### **Differential thermal analysis**

#### **Calcium carbonate decomposition**

First of all, the behaviour of limestone alone under heating was checked, in order to detect a possible delay in its decarbonation when of large grain size. No significant difference in the behaviour of coarse and fine-grained calcium carbonate was observed (Figure 8), although we note that the range of grain-size studied here is less than that considered in certain previous work which did find an effect of grain size [7]. In detail, the rate of decarbonation for both samples accelerates with increasing temperature, a feature predicted by the fact that the equilibrium vapour pressure of  $\text{CO}_2$  required to stabilise  $\text{CaCO}_3$  increases with increasing temperature [8].

#### **Binary mixtures of 50/50 calcium carbonate and sodium carbonate**

Secondly, when calcium carbonate is mixed with sodium carbonate, coarse limestone behaves in the same way as it does alone (Figure 9), the only difference being that the weight loss is proportional to its concentration in the mixture. On the other hand, the DTA for this binary

mixture is clearly more complex than for coarse limestone alone, with two successive phenomena, one at lower temperature corresponding most probably to the decarbonation of calcium carbonate and the other, a sharp endothermic phenomenon beginning at 860°C, but not accompanied by a weight loss, consistent with melting of sodium carbonate.

When the grain size of limestone is smaller than 200 micrometers (Figure 10), the observed weight loss is again divided into two successive steps: the first is very close to the curve for fine  $\text{CaCO}_3$  alone, suggesting that it corresponds to decarbonation of  $\text{CaCO}_3$ . This first stage stops around 800°C where an inflection is observed, implying that decarbonation almost stops. A second decarbonation stage begins at 810°C. The DTA curve shows several interesting features: a peak at 810°C (with a shoulder at 790°C), no precise peak at 860°C and a weak peak around 900°C. We note that the absence of a peak at 860°C indicates that when fine-grained limestone is used, no  $\text{Na}_2\text{CO}_3$  remains in the system at this temperature, in stark contrast to the case of coarse-grained  $\text{CaCO}_3$ .

Interpretation of these data requires an understanding of the possible interactions between sodium and calcium carbonates upon heating, a subject that has been treated in several papers [9-12]. From a practical point of view the  $\text{Na}_2\text{CO}_3$  -  $\text{CaCO}_3$  binary phase diagram of [9] (Figure 11) provides a simple framework in which our data may be rationalized. Two major features of the this phase diagram can be underlined: the existence of a mixed compound  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$  incongruently melting at 810°C, and the eutectic melting between this compound and sodium carbonate at 785°C. Another feature of the phase diagram that is of note is the formation of an additional mixed compound in the  $\text{CaCO}_3$ -poor part of the phase diagram, described as an “unknown compound” by F.W. Wilburn et al. [11], and as a solid solution by I. F. Poletaev & al. [9] and M. Cable [12]. The important feature of this compound is that its melting temperature is higher than that of pure sodium carbonate, the latter being at ~860°C.

In light of these considerations, one possible way to interpret our data is that when the limestone is of small grain size, the contacts between grains of the two carbonates are close enough and/or numerous enough, for the limestone and sodium carbonate to react. This could be either to form the double carbonate (at some unspecified temperature), to form a stable or metastable eutectic liquid (at a temperature of approximately 785°C), or even due to formation of a peritectic liquid produced by incongruently melting the double carbonate (at 810°C). In this respect we note that the synthesis conditions of the double carbonate reported by Johnson et al. [10] indicate that it is unlikely that the formation of the double carbonate is total in our experimental conditions, due to the relatively high heating rates used. In any case, formation of a new crystalline or liquid carbonate may be expected to interrupt the breakdown of limestone if the equilibrium  $\text{CO}_2$  vapour pressure required to stabilize the new phase is less than that required to stabilise crystalline  $\text{CaCO}_3$ , generating an inflection in the weight-loss curve. The fact that a TG plateau in our experiment with fine-grained limestone is observed at a temperature of approximately 800°C is most consistent with formation of a stable or metastable eutectic liquid formed by reaction of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  or  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ .

On the other hand, when limestone is coarse, our interpretation is that such eutectic melting does not take place, but that a small fraction of the calcium carbonate combines with sodium carbonate to produce the “unknown compound” of F.W. Wilburn which melts at 890°C.

## Conclusion

Our results demonstrate that the grain size of limestone has a significant influence on the way  $\text{CO}_2$  is lost during heating of  $\text{CaCO}_3$ - $\text{Na}_2\text{CO}_3$  mixtures, smaller grain size leading to an interruption of  $\text{CO}_2$  loss at a temperature of ~800°C. Taking into account the associated thermal consequences during heating we conclude that when grains of limestone are small

formation of a eutectic liquid is promoted. On the other hand, when grains of limestone are coarse, our interpretation is that interactions between carbonates are less frequent, such that little eutectic liquid is formed. In this case direct breakdown of limestone dominates, producing a significant amount of solid residual CaO. Nevertheless, even in this case we infer that a fraction of calcium carbonate reacts with  $\text{Na}_2\text{CO}_3$  to produce a crystalline solid solution close to pure  $\text{CaCO}_3$ , a compound which melts at temperature of  $\sim 890^\circ\text{C}$ .

Our conclusion that mixed carbonate liquids are formed when the grain-size of limestone is small may explain to some extent the relatively good degree of homogeneity of glasses produced from small-grained starting products, because such a liquid may significantly promote and accelerate reaction with silica at lower temperature. Indeed, M. Cable [12] even found that the reaction of sand with a mixture of carbonates is faster than the reaction with sodium carbonate alone, an observation which can be rationalized if one considers that reaction of unreacted silica with a carbonate *liquid* will be more efficient than reaction with solid sodium carbonate.

Alternatively, when limestone is of coarser grain size, heterogeneity is promoted because more reaction pathways are possible. For example, a degree of eutectic melting may occur where both carbonates are in contact, but simultaneously, elsewhere in the batch, other grains of  $\text{CaCO}_3$  may decarbonate directly to form CaO, or interact at higher temperature to form a Na-poor solid solution. CaO may later dissolve (or even recarbonate) during the reaction between sodium carbonate and silica, a scenario supported by SEM observations showing unmolten grains of sand as well as CaO floating in the silicate liquid at  $1300^\circ\text{C}$  (Figure 8). The initial carbonates or mixture of carbonate<sup>1</sup> and later, the calcium oxide and silicates have different densities, potentially leading to segregation and the formation of compositional gradients in the crucible

An unexpected consequence of the size of limestone may therefore be the number of unmolten grains present in the silicate liquid at the end of the decarbonation phase. If coarse limestone is used, our results tend to prove that (i) unmolten grains of CaO may be present, and (ii) less carbonate liquid is formed, that might in addition attack  $\text{SiO}_2$  less efficiently than a calcium-rich liquid [12], resulting in more unmolten grains of  $\text{SiO}_2$  that may be transported to the upper surface of the crucible.

When silica is present in the system, the possible reactions are more numerous and more complicated: reaction between silica and sodium carbonate could prevent interaction between the latter and limestone, especially as silica grains are far more abundant in a usual soda-lime silica glass than carbonates. More work is obviously needed before we understand perfectly the way glass “melts” and how it could be possible to do it more rationally. The study of reactions paths in the presence of silica will be the subject of future work.

Acknowledgments to Saint-Gobain Recherche for the experiments and characterizations, Elin Søndergård for various interesting discussions and Julien Grynberg for the batch sample photograph.

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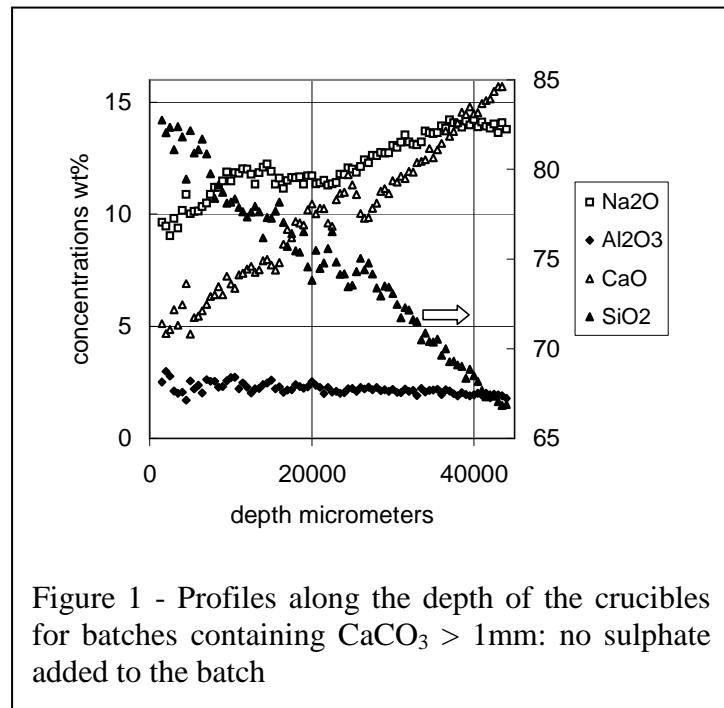
<sup>1</sup> The double carbonate has a density close to that of the final silicate, 2.54, whereas the initial carbonates are much denser; CaO - enriched silicates are denser than silica rich ones.

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$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{SO}_3\text{initial}$	$\text{Coke}_{\text{initial}}$	impurities
72.6	2.0	0.2	11.0	13.3	0.40*	0.04*	0.5

\* Initial content of the batch for 100 of glass when a fining agent was added.

Table 1- glass chemical composition



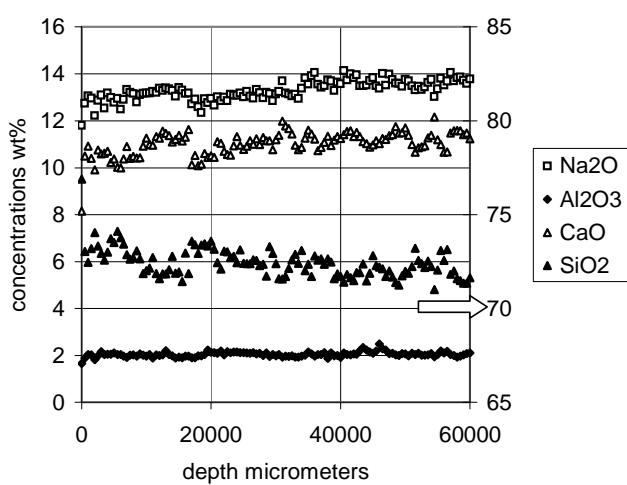


Figure 2 - Profiles along the depth of the crucibles for batches containing  $\text{CaCO}_3 < 0.2 \text{ mm}$  – No sulphate added to the batch

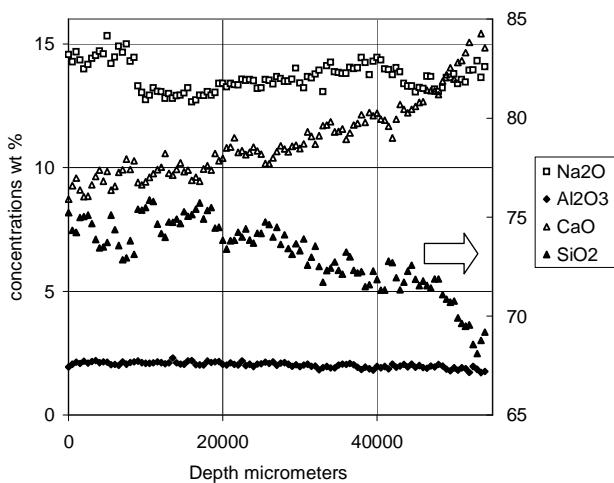


Figure 3 - Profiles along the depth of the crucibles for batches containing  $\text{CaCO}_3 > 1\text{mm}$ : sodium sulphate and coke added to the batch

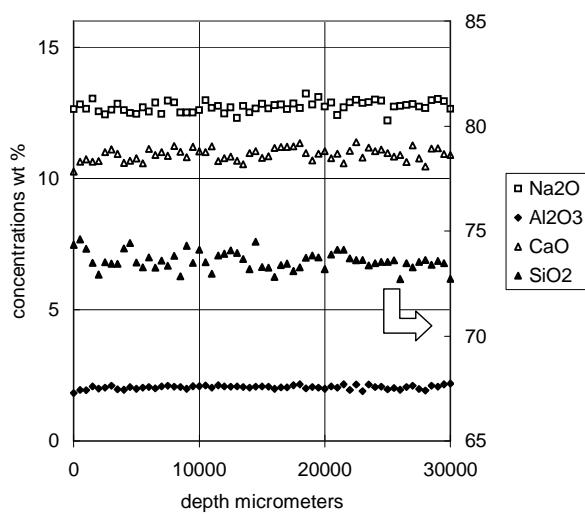


Figure 4 - Profiles along the depth of the crucibles for batches containing  $\text{CaCO}_3 < 0.2 \text{ mm}$ : sodium sulphate and coke added to the batch

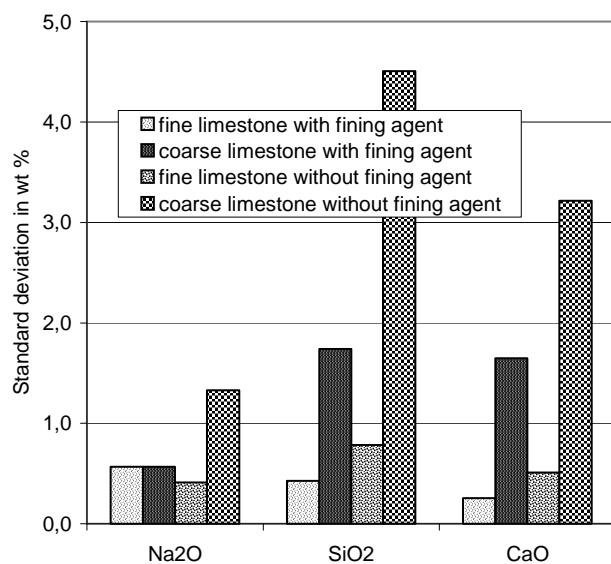


Figure 5 - Results of all the segregation experiments expressed as the compositional spread in  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$

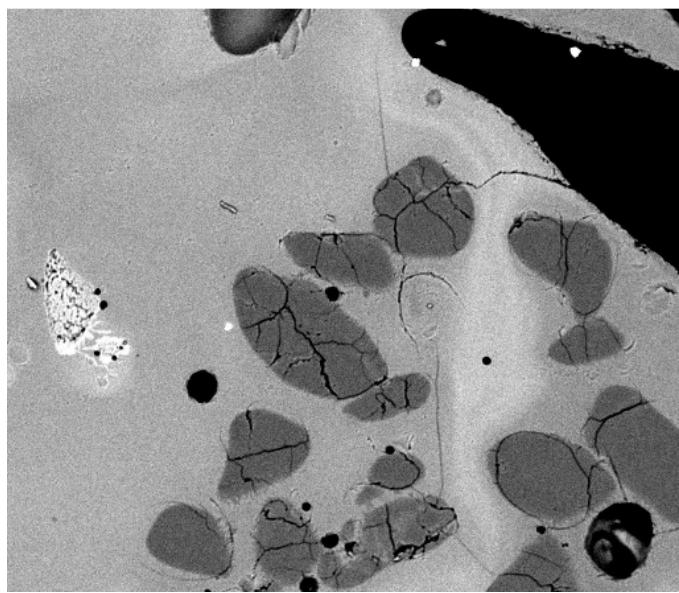


Figure 6 – SEM micrograph : black = holes, grey = silica grains, white = limestone

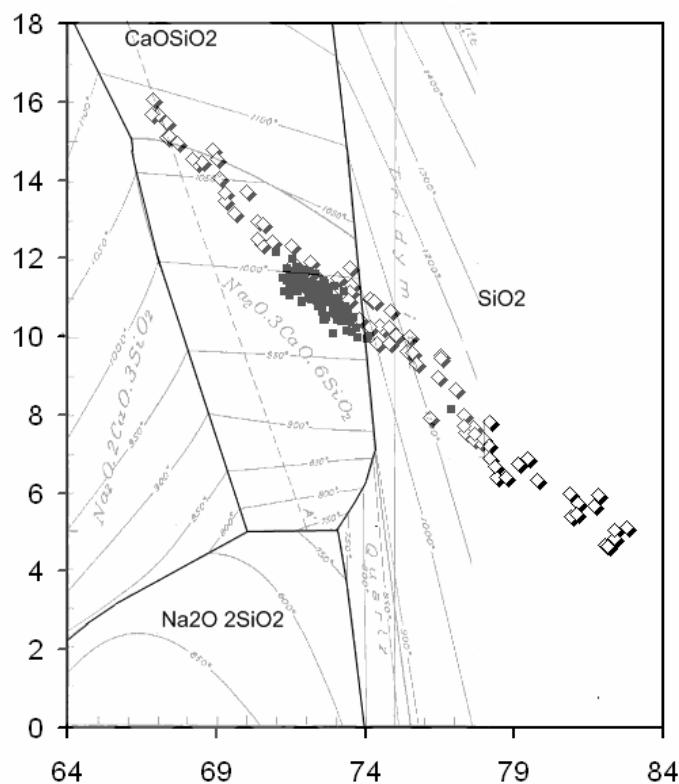


Figure 7 – CaO wt% vs SiO<sub>2</sub> wt % with coarse (white lozenges) or fine (black squares) CaCO<sub>3</sub>, superposed on Morey's orthogonal phase diagram (G.W. Morey, J. Amer. Ceram. Soc., 1930, 13(10), 683)

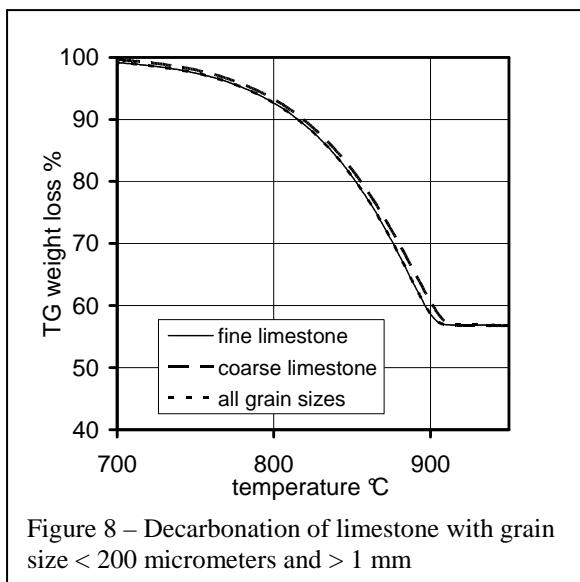


Figure 8 – Decarbonation of limestone with grain size < 200 micrometers and > 1 mm

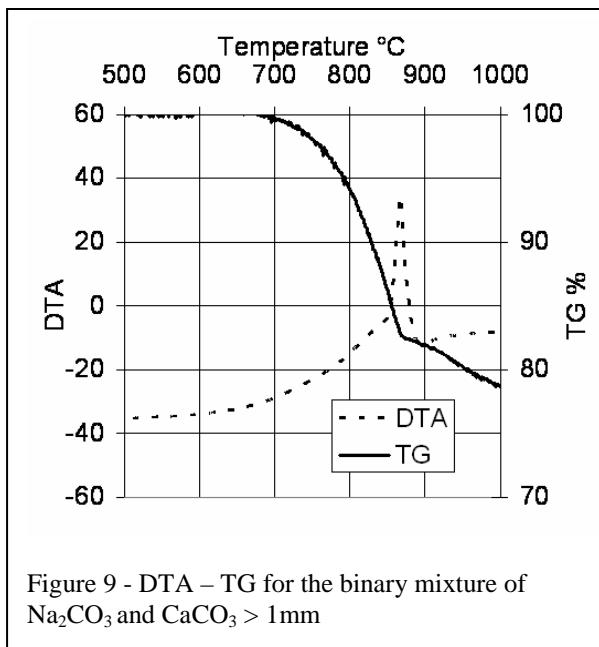


Figure 9 - DTA – TG for the binary mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  > 1mm

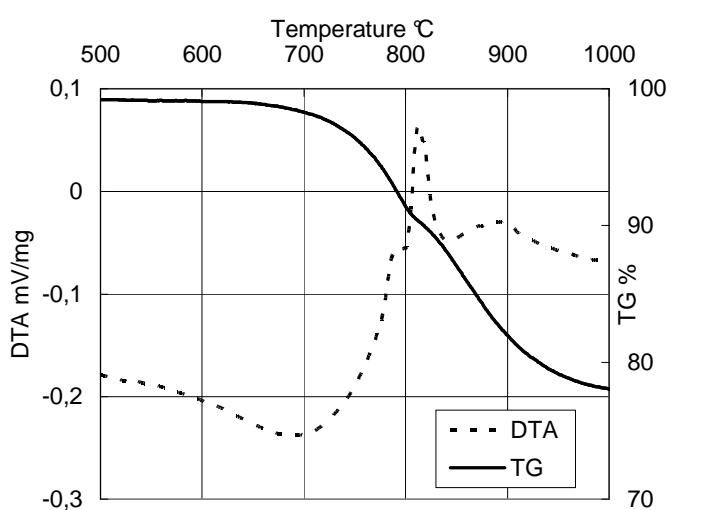


Figure 10 - DTA – TG for the binary mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3 < 0.2 \text{ mm}$

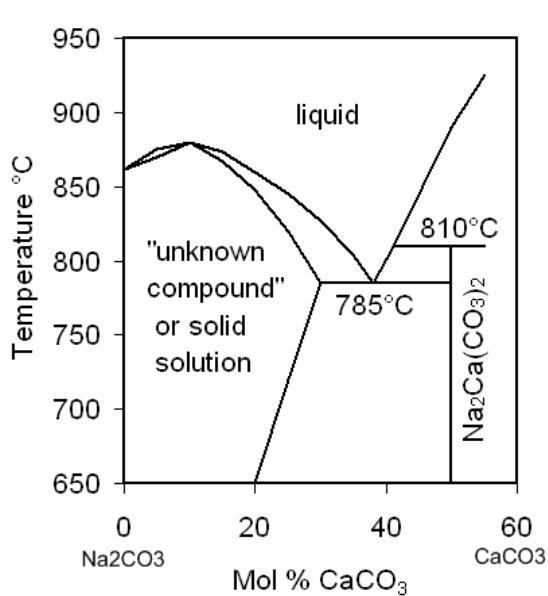


Figure 11 - Binary diagram  $\text{Na}_2\text{CO}_3$  –  $\text{CaCO}_3$  [6]  
Pressure of  $\text{CO}_2 = 1 \text{ atm}$