

PhD Proposal (2008-2011)

Making homogeneous glass from heterogeneous mixtures of oxides and carbonates: Physical and chemical processes during glass synthesis.

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Scientific context:

A constant concern in the glass-making industry is the ability to make large volumes of glass in which compositional variations are as small as possible. However, fabrication of homogeneous glasses from heterogeneous mixtures of raw materials (typically oxides and carbonates) is not a straightforward matter. This is because a wide range of complex physical and chemical processes takes place during heating of the starting products. From a chemical point of view these processes include the loss of CO₂ from the carbonates, local reactions between solid grains during the earliest stages of melting to form "metastable" liquid compositions, and subsequent dissolution of unreacted solids. From a physical point of view, the formation and elimination of bubbles (CO₂) and the potential relative movement of solids and liquids due to capillarity or gravity are important. Although "empirical" solutions to the problem of making inclusion-free, bubble-free glass of constant composition have been derived (with more or less success), detailed understanding of these processes, their consequences and their interplay is lacking. The aim of the PhD subject proposed here is to provide quantitative insights into these processes, with the ultimate goal of improving the quality of industrially produced glasses.

Proposed work:

The thesis will focus on "window glass" which, from a chemical perspective, may be represented by the ternary system Na₂O-CaO-SiO₂. Such glasses are made from mixtures of sodium carbonate, calcium carbonate and silica, and preliminary work shows that at a temperature of approximately 900°C decomposition of carbonates is complete. At this temperature the system would appear to consist of a metastable silicate liquid rich in sodium, residual solid grains, and gas. The liquid phase may have a complicated topology at this early stage, leading to complex interplay between dissolution of the residual solid grains, chemical diffusion in the liquid phase, and elimination of gas bubbles.

The work to be accomplished here concerns the evolution of this system upon heating to complete melting ($\sim 1100^{\circ}\text{C}$). It will involve synthesis of samples under controlled conditions using an experimental approach at high temperature, characterization of the experimentally produced samples (e.g. electron microscopy, electron microprobe, X-ray tomography), and numerical modelling of chemical diffusion and movement of solid, liquid and gaseous phases.

In detail, the initial phase of the project will involve experimental syntheses, the temperature-time path (e.g. rapid/slow heating) and the grain sizes of the starting materials being the principal experimental parameters. Once the experimentally produced materials are available, three complementary aspects of the problem will be treated:

A) The geometry of liquids, solids and gas: This aspect will involve characterisation of samples in 2D and 3D. For example, X-ray tomography (see figure 1 below) will be used to quantify the distribution of gas bubbles in 3D and may potentially be able to distinguish glassy and crystalline phases too. In addition, 2D polished sections will be prepared for observation on the scanning electron microscope (SEM) from which the relative proportions and distribution of liquid and solid phases can be quantified. In particular, the distribution of the liquid will be studied (wetted grains, capillary bridges, continuous nature of liquid and/or gas phases) as this information is essential for a complete understanding of the dissolution rate.

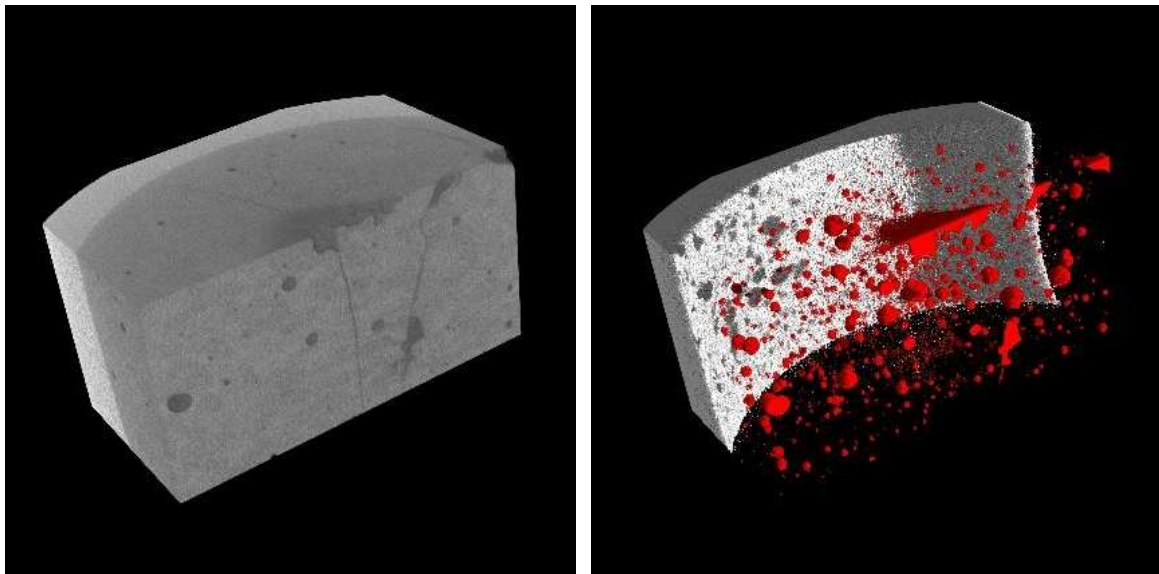


Fig. 1: Preliminary study of the feasibility of X-ray tomography to quantify the 3D distribution of gas bubbles. To the left is a block representation of the sample with several bubbles apparent on the cut exposed surface. To the right is a 3D reconstruction of the porosity (in red). The crucible is shown in white, behind.

B) Evolution of the chemical composition of liquids during heating: Once the locations of the glassy and crystalline phases have been identified, the electron microprobe will be used to quantify their composition. In particular, we wish to determine how the composition of the glassy phase evolves as a function of heating. As stated above there is reason to believe that

the first liquids formed are rich in sodium, poor in silica and poor in calcium relative to the bulk composition (red dot on figure 2). However, the homogeneity of such liquid compositions is unknown. Furthermore, with increasing temperature, liquid composition must necessarily evolve towards that of the bulk system (green square on figure 2), but the path taken is also unknown. We are particularly interested to measure how liquid compositions vary within the phase diagram (i.e. do liquid compositions follow an isotherm?; Fig. 2).

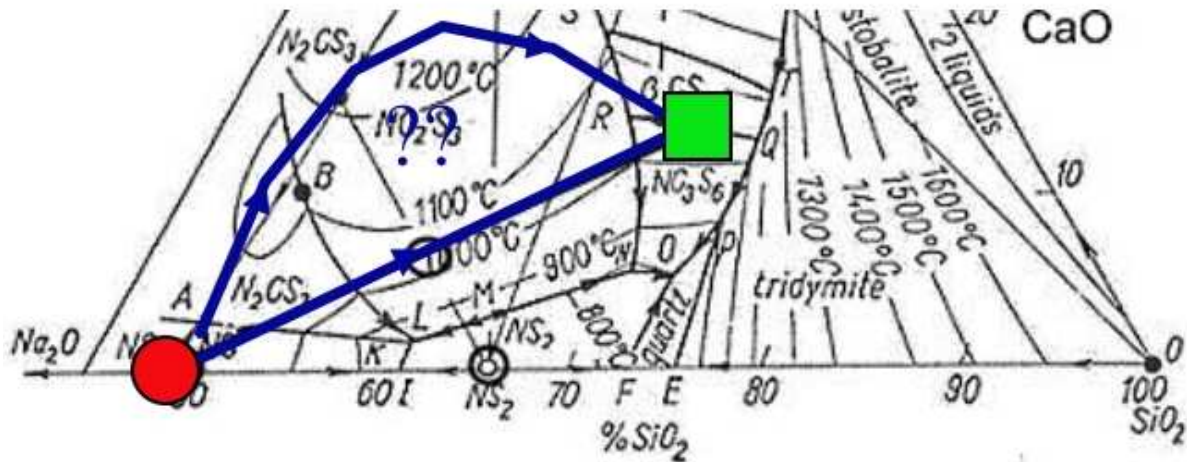


Fig. 2: Silica-rich portion of the phase diagram CaO-Na₂O-SiO₂. The first formed liquids are likely to be sodium-rich due to reaction of sodium carbonate and silica (red dot). On the other hand, the subsequent path taken to the final (bulk) composition (green square) is unknown (blue lines).

C] Understanding the observations and prediction/optimisation of the behaviour of industrial systems: Rationalisation of these results will require numerical modelling of the dissolution process and a significant effort concerning this aspect will be expected. For example, continuous dissolution of "residual" grains of silica can be modelled assuming that diffusion of SiO₂ in the existing liquid is the rate-limiting process. However, such calculations also require definition of the relative proportions and geometry of the solid and liquid phases (choices here will be guided by the observations obtained in the experiments) in addition to the notion of the degree of thermodynamic undersaturation of the liquid in SiO₂. Theoretical approaches to modelling such systems exist in the literature, but application of such models is generally crude. For example, diffusivity is considered to be independent of local liquid composition, an assumption known to be incorrect.

Furthermore, an attempt to transpose results obtained on samples at the laboratory scale (typically millimetres to centimetres) to those relevant to an industrial process (typically metres) will be attempted using numerical approaches to simulate the mobility of solids and liquids. Model experiments with "simple" geometries (e.g. flat samples where gravity should not play a dominant role) will be necessary to validate the models.