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Melting path-ways of medieval glass from Certosa di Pavia (Italy)

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Abstract

The melt of silicate system and the compositional evolution of glass-melt can be modelled by the K_2O-SiO_2-CaO system. Furthermore, in this way we achieve useful information about solid phases in the batch related to the melt glass. The case of study is taken from the chemical analyses of stained glass windows of Certosa di Pavia (Carthusian Monastry) XVth century AD and it demonstrates how the chemical compositions of different kind of glass are clustered in a narrow region of the plot. This suggests a common recipe and a total batch melting-model followed by all glass typologies.
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1. Introduction

Nowadays, the research on glass gives us information about its structure and its composition to better understand its properties; nevertheless, several attempts have also been done in the game of “postdict” ancient glass recipes and processes.

Starting from analytical studies of ancient artefacts, the unravelling of glass recipe and processing, represents an uneasy task; actually, a great sequence of operation can be performed to have glass artefacts, starting from raw materials. Scientific studies are exhaustive [1–5] and allow us to reconstruct the aspect of glass production and they provide an insight into the pre-industrial processes related to the so-called firing technology. One of the main problems addressed in studying ancient glass production is the composition of the batch in term of raw materials and consequently the glass recipe. Glass bears a complex melting process that usually implies two subsequent steps: fritting and melting. Once the frit has been crushed and poured in crucible, the melting starts.

Rehren [6,7] and Shugar and Rehren [7] proposes two melting typologies to be considered to create a model of glass melting: the *partial* and the *total-batch melting model*. In particular, the first model was used to explain the tight compositional clustering of some ancient Na–Ca glasses.

In the glass history [8,9], two compositionally different glass productions succeeded. Until the Carolingian times, glass making in the Mediterranean and Central Europe was dominated by Na–Ca glass [10]. Towards the end of the first millennium K–Ca glass came in use in Europe. During the Middle Ages the K–Ca glass provide flat glass to performed stained glass windows of most of European cathedrals in Europe.

Our previous paper [11] reports preliminary results on major and selected trace element abundances on 11 glass samples from stained glass windows of Certosa di Pavia from the XV^{th} century, in order to define the compositional variability among samples, in terms of vitrifying, stabilising and flushing component percentage. The chemical composition of Certosa’s glass results similar to medieval glass [4] and closely matches late wood-ash glass.

This paper aims to present some thermodynamic aspects that characterize the production technology of stained glass windows in Certosa di Pavia, and it tries to modelize the melting path-way using a simplified chemical system. The presence of minor components, such as Al_2O_3, MgO, Na_2O,

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vicariant of SiO_2, CaO and K_2O, respectively, is not considered in modelling, even if they produce a shifting of eutectic and peritectic points as well as of cotectic curves. The low concentration of these elements can cause changes in intrinsic glass properties (viscosity, workability, etc.) but do not widely influence the melting path, defined by the system $K_2O{-}CaO{-}SiO_2$.

We consider for the modelling a simplified system defined by the three main components of the glass, which represent more than 80% of the glass composition.

2. The system $K_2O{-}CaO{-}SiO_2$

The system allows describing the composition of K-glass in terms of vitrifying (SiO_2), flushing (K_2O) and stabilising (CaO) components [12]. The Fig. 1A is a portion of the $K_2O{-}SiO_2{-}CaO$ diagrams, and it is relevant to K-glass compositions. It displays the liquidus surface contoured with lines, which represent constant temperature (isotherms) and the extensions of the binary eutectics, called cotectic curves; arrows indicate the down-temperature direction to the ternary eutectic minimum. At the ternary eutectic composition, a congruent reaction could be

$$\text{solid}(1) + \text{solid}(2) + \text{solid}(3) = \text{melt}(\text{eutectic}) \qquad (1)$$

Besides there are other inflection point in the system called peritectic points. A solid phase at a fixed temperature reacts giving a peritectic melt with a new solid phase. A typical example of this incongruent melting is the reaction

$$\text{solid}(1) = \text{solid}(4) + \text{melt}(\text{peritectic}) \qquad (2)$$

The figure also shows the compositional plan of the system as though the observer is looking down the temperature axis. Straight segments, which represent divariant mineral assemblages, compatible with the different bulk compositions, subdivide the compositional plan in triangles. Eutectic points are at converging of three cotectic lines and represents the minimum temperature. Peritectic points are at converging of three cotectic lines and are inflection points. The Alkemade lines are a subset of binary lines, which connect the primary compositions of two-phase fields that share a common boundary. The lines also divide the phase diagram in compatibility triangles. The cotectic curves separate the liquidus surface in different areas, corresponding to liquidus coexisting with a different solid.

3. Bulk composition of glass from stained windows of Certosa di Pavia

Micro-analyses were performed on a JEOL JXA 840A electron analyser equipped with three wavelength-dispersive spectrometers (WDS) (TAP, TAP,LIF, analysing crystals and one Si (Li) energy-dispersive spectrometer (Be-window).

Analytical conditions were 20 kV accelerating voltage and 20 nA. Spot size was 5 μm^2. Counting time was 20 s for all elements except Mn and Fe (40 s), data collected by the WDS were processed with the TASK correction program that calculate oxides composition starting from the elemental ones. Mineral phases were used as standards. Estimated precision was about 3% for major and 10% for minor elements, respectively. The compositional variability of glass [11] was

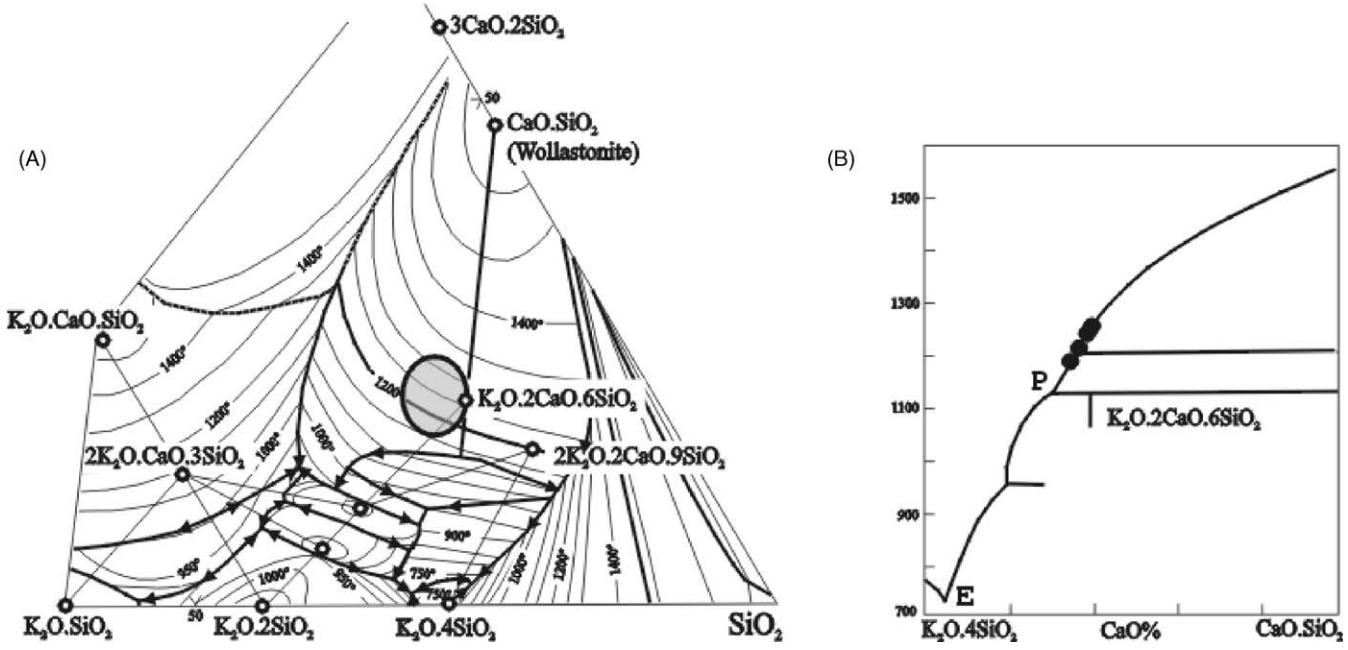

Fig. 1. (A) Ternary phase diagram displaying the liquidus surface (encountered by isotherms and cotectic lines). A grey area displays the composition values for blue, yellow, red and green glass. (B) Sections of $K_2O{-}CaO{-}SiO_2$ system. The $K_2O{-}Al_2O_3{-}6SiO_2$ phase have incongruent melting at peritectic temperature (P); (E) = binary eutectic point.

Table 1
A selection of chemical composition used in modelling

Blue			Red			Yellow			Green		
CaO	K_2O	SiO_2	CaO	K_2O	SiO_2	CaO	K_2O	SiO_2	CaO	K_2O	SiO_2
18.86	12.66	52.64	15.39	14.74	55.28	24.18	4.67	58.07	13.63	16.75	49.73
19.06	13.00	51.23	15.27	14.64	55.01	24.10	4.62	58.01	12.91	15.89	52.87
16.72	13.16	47.59	14.98	14.51	55.03	23.63	4.51	58.24	11.73	14.59	50.21
19.03	12.84	51.39	13.83	16.88	50.15	13.77	16.52	51.72	13.67	17.10	49.55
19.04	12.90	51.07	13.89	16.83	51.13	13.93	16.37	51.62	13.35	16.51	49.64
15.80	15.29	51.50	15.62	14.80	52.63	13.61	15.61	53.23	13.77	17.28	54.00
15.83	15.24	51.78	13.02	14.88	56.34	13.17	14.95	53.69	13.40	16.60	53.49
			13.77	16.79	52.30	13.81	15.05	53.08	12.55	15.57	52.56
			14.83	17.69	50.80	17.86	14.21	51.57	18.56	12.50	56.78
			14.23	16.70	52.08	18.13	14.55	51.22	17.76	13.10	52.55
			14.79	17.37	48.70	18.56	14.87	50.61	13.48	16.32	54.50
			13.71	15.95	51.85	18.35	14.78	50.86	13.50	16.39	54.48
			14.09	16.37	52.02	18.29	14.48	51.19	13.62	16.66	54.47
			14.71	17.17	50.60	18.04	14.23	51.69			
						18.05	14.49	51.36			
						17.75	14.10	51.81			
						17.68	13.96	51.74			

ascertained by 51 analyses of 14 major chemical components. SiO_2 varies around 50 wt.% and Al_2O_3 is always lower than 3.1 wt.%. Na_2O never exceeds 3.5 wt.%, confirming the K-character of glass (K_2O up to 17.69 wt.%) CaO varies widely from 11.7 to 24.2 wt.% and MgO never exceeds 6.4 wt.%. All glass samples are quite rich in phosphorous, up to 5.4 wt.%. CuO and MnO abundances are closely related to colour attribute, and in some samples they reach the very high values of 4.4 and 6.7 wt.%, respectively. Iron and chromium contents may be considered below detection limit of microprobe; using EDS detector, with a "dead-time" higher than 100s, any appreciable counting is obtained on peak positions. Table 1 only reports values of SiO_2, K_2O and CaO, which define the simplified system used in modelling. It is worth to note that the glass composition (as mean as value) closely matches the phase $K_2O–2CaO–6SiO_2$ that has incongruent melting, according to the reaction

$$K_2O\text{–}2CaO\text{–}6SiO_2 = \text{melt(P)} + CaO\text{–}SiO_2\text{(wollastonite)} \tag{3}$$

4. Discussion

The model for K–Ca-glass melting is illustrated on the $K_2O–CaO–SiO_2$ phase diagram (Fig. 1B); the process develops into two stages: at first eutectic and then peritectic glass melting in presence of a solid phase. The following model considers actual K–Ca glass composition of the stained glass windows [11]. The melting starts at the ternary eutectic point in which mainly K_2O and SiO_2 components participate. The eutectic has a fixed proportion between the three components: K_2O (24%)–CaO (2%)–SiO_2 (74%). It is worth to note that the eutectic composition closely matches the recipe proposed by Piccolpasso [13]: a proportion of K-flushing (wine dregs ash) and quartz sand of about 1:3. Once the eutectic liquid formed, the melting process moves towards an increasing of $CaO{\cdot}SiO_2$ and K_2O content rise with a constant ratio.

The model proposed here is rooted in the petrologic model for the formation of silicate melt by equilibrium melting: the crystalline material from the batch works as a buffer and it is the reservoir material from which the melt forms. Fractional melting is common melting process that work to produce different batch of natural magma, within the Earth lithosphere, thus it generates the variability of the parental magma.

5. Conclusions

In glass making, *partial-batch melting model* can describe glass composition variability during the melting process. In this model, in fact, only three melt-types bear a fixed composition and they correspond to invariant points on the diagram: (i) eutectic, (ii) peritectic and (iii) the melt derived from the full melting of the batch. The eutectic melting occurs at lower temperature in a compositional zone of the diagram where glass is very poor in stabilising component. Peritectic melt, even if it bears suitable composition for working, suffers from the reaction mechanism consequence by reaction (2): melt is in equilibrium with crystalline phases produced by the melt itself. In this case worked glass could contain solid phases, as defects. The "*total batch-melting model*" produces the best glass and this occurs at temperature values exceeding the peritectic point, as indicate by Fig. 1B. Compositions of glass from stained windows of Certosa di Pavia are clustered in a narrow region of the plot at temperature slightly exceeding the peritectic point conditions and this suggests a common recipe and a "*total batch-melting model*" attained by all glass typologies.

Moreover, the *“partial batch-melting model”* implies that chemical composition of archaeological glasses does not reflect chemical composition of the entire batch and this, consequently, conflicts with the possibility to reconstruct the ancient glass recipes by glass-artefacts analyses.

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