SODIUM SOLUBILITY IN MOLTEN SILICATES

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ABSTRACT

A new thermochemical reactor have been designed to control alkali-metal oxide activity simultaneously in several molten silicates at temperature up to 1400°C. The method consists in imposing a Na vapour pressure in a closed system by $Na_{(g)}$ *evaporation from* Na_2O*-x*SiO_2 *melt and equilibrating this vapour with the molten silicate samples. This device has been applied to determine* Na_2O *activity and* Na_2O*-solubility data in molten silicates of the CaO-MgO-*Al_2O_3*-*SiO_2 *system, at 1400°C, at fixed Na-partial pressure (*P_{Na}*) and at fixed oxygen fugacity (*P_{O2}*). The compositional effect on solubility will be described in particular the effects of Si and Mg, with application in metallurgy process and geological interests.*

INTRODUCTION

By comparison with others major silicate melt components (Ca, Al, Si, Mg, Fe), thermodynamic properties of alkali metals, mainly Na and K [1, 2, 3], are poorly documented, despite their ubiquitous presence in molten silicate and magmas. Indeed alkalis are often used in industry as fluxes in molten silicates or slags [4, 5], while on earth, alkali metals occurs in common rock-forming minerals [1], leading by partial melting to aluminosilicate magmas of which some are significantly enriched in sodium and potassium (up to $Na_2O + K_2O \approx 15$ wt%). Even at minor concentration levels, alkalis act either as network modifying cations and/or as charge compensating cations, explaining their drastic influence on the physicochemical properties of silicate melts, including solubility, diffusion, viscosity, etc. Despite this critical role, there is only few data describing their activity/composition relationships in molten silicates, mainly due to difficulty of performing experiments since alkalis become highly volatile at high temperature and/or at reducing redox conditions. To tackle this issue, we have developed a new device to control alkali-metal oxide activity in molten silicates (aNa_2O) by equilibration of melts with gaseous environment of known Na partial pressure (PNa) at high temperature and fixed oxygen fugacity (PO_2). Here we show that this design allows to establish a consistent database of Na_2O activity and Na_2O solubility in CaO-MgO-SiO_2 and CaO-Al_2O_3-SiO_2 silicate melts that helps to understand how melt composition and melt structure control the sodium solubility in molten silicates.

METHODOLOGY

The more frequent technique consists in equilibrating at high temperature molten silicates with alkali metal vapor pressure established by a reference system composed of simple alkali-silica binary melts or salts. For instance, Lewis *et al.* [6] used NaCl as a carrier to produce Na vapors, George et al. [7] fixed constant K vapor pressure by using a mixture of K_2CO_3 and graphite, Limpt *et al.* [8] used the evaporation of NaOH of the molten sodium-disilicate glasses, while other workers operate with Na_2O-SiO_2 [3, 9, 10] or K_2O-SiO_2 [11, 12] melts for fixing a Na or K metal vapor pressure. In the later designs, alkali evaporates from the source according to:

$$MeO1/2^{(source)} \rightarrow Me_{(g)} + 1/4\ O_2 \qquad \text{with Me} = (\text{Na, K}) \tag{1}$$

bathing the samples in alkali vapor, which dissolves in the molten silicate samples in agreement with

$$Me_{(g)} + 1/4\ O_2 \rightarrow MeO_{1/2}{}^{(sample)} \tag{2}$$

Because at equilibrium conditions, the alkali metal oxide activity in molten samples is fixed by the source according to

$$aMeO_{1/2}(sample) = aMeO_{1/2}{}^{(source)} \tag{3}$$

we used this procedure for controlling alkali metal oxide activity in molten silicates. Our experimental strategy was lead by developing a very simple method for controlling alkali metal oxide activity in molten silicates, easy to implement and able to control several parameters independently, i.e., melt sample composition, $aNaO_{1/2}$, fO_2, T. For these reasons, this method consists in imposing an alkali metal vapor pressure in a closed system by controlled evaporation of Na_2O-xSiO_2 melt reservoir and equilibrating this vapor with the molten silicate samples of interest.

EXPERIMENTAL

The cell (Figure 1) is a sealed silica tube of around 25-30 cm^3 (Ø ext = 22 mm, h ≈ 120 mm) containing several components that fix the thermochemical parameters of the system. The Na vapor partial pressure is imposed by two grams of a Na_2O-2SiO_2 source melt of known $aNaO_{1/2}$ located in a platinum crucible (Ø = 16 mm, h = 20 mm), shut by a platinum lid. The glass samples to be studied are suspended in the reactor from the lid using the Pt wire loop technique (Figure 1). Depending on the experimental purpose, several glass bead samples can be suspended simultaneously above the reference melt. The Pt crucible hosting the source and the sample constitute the reactor of the cell. The oxygen fugacity in the device is controlled by a solid M/M_xO_y buffer (M = Metallic element; Ni/NiO in this study) incorporated below the reference reservoir either at the bottom of the silica tube or in an alumina crucible to prevent reactions with the silica tube and to avoid alloying between the solid buffer with the platinum crucible (Figure 1). This silica tube is then evacuated and directly sealed under vacuum and sealed.

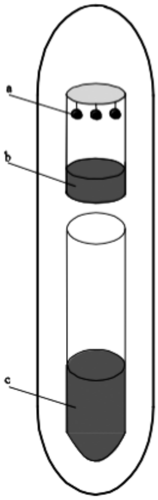

Figure 1: Scheme of the thermochemical cell. (a) Glass samples to be studied, suspended at the platinum lid of the reactor by the wire loop techniques, (b) Semi-closed Pt crucible containing 2g of Na_2O-2SiO_2 reference melt (source) and constituting the reactor, (c) Silica crucible containing around 5g of solid Ni/NiO oxygen buffer. See text for further explanations.

RESULTS

With the above design [13], sodium solubility have been investigated at 1400°C and 1 atm total pressure in molten silicates belonging to the CaO-MgO-SiO_2 (CMS) and CaO-Al_2O_3-SiO_2 (CAS) system and covering a large range of compositions (0< CaO and MgO <40; 0< Al_2O_3 <45; 15 < SiO_2 < 85; in wt%) with bulk polymerization, i.e., NBO/T [1], varying from 0 to 3. A Na_2O-2SiO_2 source [2, 13, 14] was used to impose, at 1400°C, a Na partial pressure at around 10^{-4} atm. At equilibrium (see discussion in [13]), the solubility of sodium is determined using electron microprobe for Na_2O concentration and the sodium oxide activity coefficient is calculated using data of [15] according to

$$\gamma NaO_{1/2}^{(sample)} = aNaO_{1/2}^{(source)} / XNaO_{1/2}^{(sample)} \tag{4}$$

From this set of experiments [this work, 14], the liquidus at 1400°C and a $P_{Na}=10^{-4}$ atm has been evaluated and reported in Figure 2. The iso-solubility curves were then determined by triangulation using the measured solubilities, and drawn in the corresponding part of the CMS system (Figure 2). From these results, one can see that changes in the melt compositions in the CMS system result in drastic changes in the Na_2O-solubility. Two main effects can be outlined: i) an increase in the melt polymerization clearly results in a net increase in the Na_2O-solubility in the CMS melt (by almost an order of magnitude, see Figure 2), reaching the maximum value at 32.7 wt% for a pure SiO_2 melt (i.e., NBO/T = 0), and ii) the substitution of Ca by Mg favors significantly the solubility of Na in the melt, irrespective of its polymerization; for instance the full substitution of Ca by Mg along meta-silicate melt compositions (i.e., NBO/T = 2) results in a change of the Na content by close to 10 wt% (Figure 2). Owing to these experiments and in agreement with Equations 3 and 4, it is also possible to calculate and represent the iso-activity coefficient curves in the CMS system (Figure 3). First of all, the extremely large negative deviation from Raoult's law for dissolution of sodium in CMS silicate melts is noticeable. As expected from equation 3, the activity coefficients of $NaO_{1/2}$ in the CMS melts show a reverse variation, with a drastic decrease towards the silica rich end-member, an increase towards Ca- and Mg-rich compositions, and the effect of the Ca/Mg exchange.

Preliminary experiments were also carried out in the CAS system in order to resolve the specific effect of Al_2O_3 on the solubility of sodium in molten silicates. The results, summarized in the figure 4, show that if the enrichment of silica increases also the Na solubility in aluminous-rich melts. In contrast, one can see that the addition of Al_2O_3 (up to tens wt%) does not have any significant effect on Na solubility, confirming the work of Rego *et a.l* [10] and O'Neill [3].

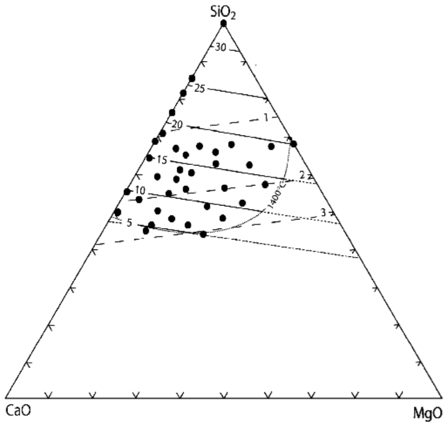

Figure 2: Na_2O-solubility (in wt%) in the CaO-MgO-SiO_2 system at 1400°C and $PNa=10^{-4}$ atm. Dots represent the experimented CMS glass compositions. The dotted line represents the liquidus curve at a $PNa=10^{-4}$ atm and 1400°C [14]. Solid lines correspond to the iso-Na_2O solubility curves in the liquid domain and their prolongation (dashed) in the sub-liquidus domain. Dashed lines represent the degree of bulk polymerization of the Na-free melt (i.e., NBO/T see [1]).

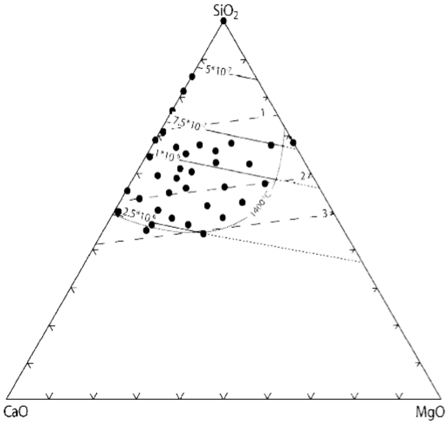

Figure 3: Sodium oxide activity coefficients in CaO-MgO-SiO_2 system at 1400°C and P_{Na}=10^{-4} atm. Solid lines represent the Na_2O-activity coefficients determined by our method; other symbols as in Figure 2. See discussion in the text

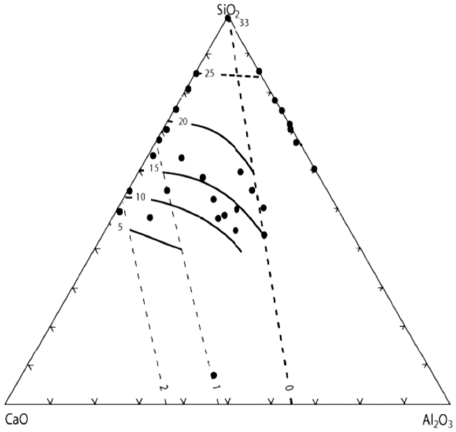

Figure 4: Preliminary results of Na_2O-solubility (in wt%) in CaO-Al_2O_3-SiO_2 system at 1400°C and P_{Na}=10^{-4} atm. Dots represent the experimented CAS glass compositions. Solid lines correspond to the iso-Na_2O solubility curves in the liquid domain. Dashed lines represent the degree of bulk polymerization of the Na-free melt (i.e., NBO/T see [1]).

DISCUSSION

These new results give some insights on how melt compositions and their structures control the solubility of Na atoms in the CMS and CAS silicate melts. The strong positive correlation between the Na solubility and the silica content of the melt (Figure 2 and 4) confirms that the degree of polymerization of melts is one of the key parameters controlling the sodium solubility in molten silicates, with an increase in solubility by increasing the polymerization of melt. This suggest that Na solubility, in a similar manner as rare gases, is highly sensitive to a steric effect, in which Na atoms seems to have a high preference for the free space between interconnected tetrahedra as the number of network-forming cations (i.e., Si or Al) increase in the silicate melt lattice. In contrast with rare gases, which dissolve in silicates melts with an ideal behavior, Na will interact with the structure. This strong Na-Si interaction can be evaluated in the light of the negative relationship between the $NaO_{1/2}$ activity coefficient and the melt silica content (Figure 3) and of the strong non ideality of Na solubility in these CMS and CAS melts. This is not unexpected given the extraordinarily large interactions between $NaO_{1/2}$ and SiO_2 in melts in the system Na_2O-SiO_2 [2]. More surprising however is the fact that addition of Al_2O_3 in the CS melt (Figure 4) don't have any appreciable effect on the Na solubility, even at high Al_2O_3 dilution. No significant decrease in the $NaO_{1/2}$ activity coefficients are neither observable as the Al_2O_3 content in the melt increases, suggesting the lack of Na-Al interactions. This latter behavior is important and inconsistent with *quasi-crystalline* models of melt thermodynamics that hypothesize coupled Na-Al components. Whether this Na-Al species are real or not should be readily testable with the present method.

Finally, it is worth to notice that increasing the proportion of network-modifying cations (i.e., Ca^{2+}, Mg^{2+}) in the melt results in a significant decrease in the sodium solubility (Figure 2 and 3), consistent with the depolymerization of the melt and the correlative decrease of the available volume to allocate the Na atoms. From NMR and Raman spectrometry data [17, 18, 19], the higher field strength of the Mg cations with respect to Ca favors disproportionation in the Q speciation of liquids, i.e., $2Q^n = Q^{n-1} + Q^{n+1}$; $K_n = [Q^{n-1}].[Q^{n+1}]/[Q^n]^2$. Therefore, the significant increase of Na solubility in CMS melts with Mg-content at fixed polymerization hints that Na prefers higher disorder local structures. These results provide a rational explanation to the use of addition of dunite (olivine-rich rocks) to increase the alkali (Na and K) solubility in blast furnace slags [4, 5, 11].

CONCLUSIONS

The proposed thermochemical cell method allows to impose a sodium-metal oxide activity in molten silicates and to determine sodium solubility up to 1400°C if silica tubes are used as confining media. This method allows controlling sodium-metal oxide activity simultaneously in several different molten silicates and will be very easy to implement to other alkali elements. This method is particularly suitable for establishing a consistent thermodynamic data base for alkali solubility in complex molten silicates.

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