Chemical Geology 346 (2013) 57–71

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Effect of the Na/K mixing on the structure and the rheology of tectosilicate silica-rich melts

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ARTICLE INFO

Article history:
Accepted 5 September 2012
Available online 11 September 2012

Keywords:
Raman spectroscopy
Aluminosilicate melts
Mixed alkali effect
Viscosity
Glasses
Structure of glasses and melts

ABSTRACT

Viscosity and structure of Na/K tectosilicate glasses containing 75 and 83 mol% of SiO_2 have been investigated. Viscosity increases non-linearly when K^+ ions substitute Na^+ ions in these melts. The viscosity variations depending on chemical composition cannot be reproduced using an ideal mixing model of the configurational entropy. Consequently, it appears that Na and K elements do not mix randomly in the studied aluminosilicate melts. Raman spectra of glasses show that, during the Na/K substitution, evolutions of both the ring distribution and the T-O-T mean angle, or force constant, occur. The proportion of small-membered (three, four) rings, compared to large-membered rings, is higher in K-rich glasses than in Na-rich glasses. Moreover, Raman spectra features suggest that two different TO_2 environments exist and cohabit into the glass. They could represent two populations of six-membered rings differing by their force constant or their T-O-T angles. One of these environments evolves when K substitutes for Na, showing an increase of its mean T-O-T angle and force constant. The other environment remains unchanged. From the observations, we propose that Na/K mixed tectosilicate glasses contained two sub-networks: one composed of the Si, Al, O and K atoms, and another of the Si, Al, O and Na. We suggest that the different size of alkali elements combined to the charge balancing needs of Al^{3+} ions can be the source of the different clustering of alkali cations into different sub-networks. Furthermore, and as previously inferred by older studies, potassic tectosilicate glasses could present silica-like and leucite-rich regions, explaining notably the incongruent crystallization of the orthoclase liquid.

1. Introduction

Quantitative structural data at magmatic temperatures are available at 1 atm for some compositions in the systems $K_2O–Al_2O_3–SiO_2$ and $Na_2O–Al_2O_3–SiO_2$ (Mysen and Frantz, 1992, 1993, 1994a, 1994b; Neuville and Mysen, 1996). Moreover, several studies have investigated the thermodynamic and rheological properties of glasses and melts in the $Na_2O–Al_2O_3–SiO_2$ ternary (Schairer and Bowen, 1956; Riebling, 1966; Taylor and Rindone, 1970; Urbain et al., 1982; Richet 1984; Toplis et al., 1997a,b; Neuville, 2006; Neuville et al., 2010; see also the compilation of Mazurin et al., 1987). However, data in the $K_2O–Al_2O_3–SiO_2$ system are scarce because of the high temperature of liquidus (Schairer, 1950; Schairer and Bowen, 1955), and few data have been acquired on the Na/K mixing effect affecting aluminosilicate melts.

This mixed alkali effect can play an important role for Material Sciences as well as for Earth Sciences. Indeed, many volcanoes displaying a high statistical recurrence of explosive activity have erupted differentiated, alkali-rich lavas such as phonolite, trachy-andesite, trachyte or rhyolite. For example, plinian to ultraplinian eruptions of the Krakatau and the Tambora (Indonesia), the Mont Dore (France) and the Vesuvius (Italy) have emitted lavas containing more than 7 wt.% of Na_2O+K_2O (Brousse and Lefèvre, 1966; Carey and Sigurdsson, 1987; Sigurdsson and Carey, 1989; Mandeville et al., 1996). A high Na_2O+K_2O concentration indicates differentiated melts, potentially rich in silica and highly viscous. In the case of Mont Dore, its 3.1 Ma eruption emitted several pumices flows that have built the “Grande Nappe” ignimbrite formation (Brousse and Lefèvre, 1966; Pastre and Cantagrel, 2001 and references therein). The “Grande Nappe” covers an area of 350 km^2 with a maximum thickness of 20 m, representing a total volume of 7 km^3. This major event was associated with the formation of a 5 km-diameter and 250 m-deep caldera. Chemical analysis of pumices reveals that the emitted melt was a nearly pure Na/K-mixed aluminosilicate melt, with a silica concentration typical of rhyolite (Table 1). Its viscosity at 900 °C is $10^{10.80}$ Pa.s, close to that of mixed albite and orthoclase melts (Fig. 1). This melt therefore deals with the Qz–Ab–Or system (Quartz–Albite–Orthoclase), which is of prime importance for the understanding of the formation and evolution of rhyolitic and granitic rocks (Tuttle and Bowen, 1958). Furthermore, and as it has been highlighted previously, the study of the quaternary $Na_2O–K_2O–Al_2O_3–SiO_2$ system is not only pertinent for the Qz–Ab–Or system, but is also fundamental for the understanding of rheological properties of all other alkali-rich melts.

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http://dx.doi.org/10.1016/j.chemgeo.2012.09.009

Table 1
Chemical composition of NAK products in mol%, measured with a Cameca SX50 microprobe. All results have been converted from wt.% to mol%. Relative density error is 0.001. **Others* refer to other elements present only in the natural Mt Dore glass: CaO = 0.45 (0.10), MgO = 0.10 (0.06), TiO_2 = 0.08 (0.08) and FeO = 0.71 (0.04).

NAK:	75.12.0	75.12.2	75.12.5	75.12.6	75.12.7	75.12.10	75.12.12
SiO_2	*74.97*	*75.36*	*75.33*	*75.15*	*75.53*	*75.14*	*75.13*
	(0.50)	*(0.32)*	*(0.30)*	*(0.25)*	*(0.80)*	*(0.11)*	*(0.42)*
Al_2O_3	*12.53*	*12.51*	*12.44*	*12.50*	*12.30*	*12.43*	*12.76*
	(0.14)	*(0.12)*	*(0.19)*	*(0.22)*	*(0.42)*	*(0.11)*	*(0.27)*
K_2O	*0.00*	*2.37*	*4.80*	*6.19*	*7.15*	*9.76*	*12.11*
	(0.06)	*(0.09)*	*(0.11)*	*(0.23)*	*(0.33)*	*(0.19)*	*(0.36)*
Na_2O	*12.49*	*9.76*	*7.43*	*6.15*	*5.02*	*2.67*	*0.00*
	(0.21)	*(0.25)*	*(0.24)*	*(0.34)*	*(0.14)*	*(0.10)*	*(0.05)*
Relative density	*2.369*	*2.374*	*2.368*	*2.371*	*2.372*	*2.370*	*2.357*
NAK:	83.8.0	83.8.2	83.8.4	83.8.6	83.8.8	Mt Dore:	Bulk glass
SiO_2	*83.90*	*83.40*	*83.23*	*83.27*	*83.10*	SiO_2	*83.19*
	(0.12)	*(0.62)*	*(0.20)*	*(0.24)*	*(0.20)*		*(0.33)*
Al_2O_3	*8.74*	*8.33*	*8.42*	*8.48*	*8.60*	Al_2O_3	*8.32*
	(0.13)	*(0.08)*	*(0.16)*	*(0.08)*	*(0.17)*		*(0.1)*
K_2O	*0.00*	*2.06*	*4.14*	*6.06*	*8.18*	K_2O	*3.77*
	(0.02)	*(0.08*	*(0.11)*	*(0.06)*	*(0.11)*		*(0.25)*
Na_2O	*7.35*	*6.21*	*4.21*	*2.19*	*0.12*	Na_2O	*3.38*
	(0.18)	*(0.17)*	*(0.19)*	*(0.12)*	*(0.04)*		*(0.21)*
Relative density	*2.317*	*2.318*	*2.317*	*2.323*	*2.313*	*Others**	*1.34*
							(0.28)
						Relative density	*2.328*

Mixing alkali elements in silicate ($M_xSi_yO_z$ compositions, with M an alkali) melts and glasses produces important deviations of their properties from the linearity (see the reviews of Isard (1969) and Day (1976)). This effect is called the *mixed alkali effect*, and affects the electrical conductivity and dielectric loss, the alkali diffusion coefficients, and the chemical durability of alkali silicate glasses. For example, mixing K and Na elements in silicate glasses produces an increase of their resistivity, which reaches a maximum when the Na/(K + Na) ratio is equal to 0.5 (Isard, 1969). More generally, with M and M′ two alkali elements, crossing the ratio $M_2O/(M_2O + M'_2O) = 0.5$ induces an extremum (maximum or minimum) in the observed property (Poole, 1949; Isard, 1969; Day, 1976; Richet, 1984).

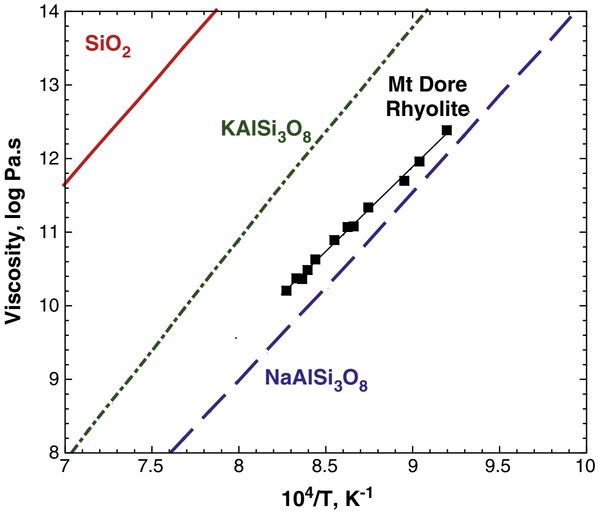

Fig. 1. Viscosity (in log Pa.s) as a function of the temperature (1/K) of SiO_2, Albite, Orthoclase melts, and of the Mont Dore bulk rock (see Table 1 for the chemical composition). Viscosities of SiO_2, Albite and Orthoclase came from Urbain et al. (1982). Viscosity of the Mont Dore sample was measured following the protocol described in Section 2.2.

Also, viscosity near the glass transition temperature *Tg* exhibits a similar behavior (Poole, 1949). Indeed, when the Na/(K + Na) ratio in a silicate melt is equal to 0.5, viscosity decreases and reaches a minimum (Poole, 1949). This effect is less visible at high temperature (Bockris et al., 1955). These viscosity variations can be modeled using the configurational entropy theory (Richet, 1984), which is based on Adam and Gibbs' theory of relaxation processes (1965). It relates the viscosity of a melt to its configurational entropy, $S^{conf}(T)$, following:

$$log\eta = A_e + B_e/TS^{conf}(T), \tag{1}$$

where A_e is a pre-exponential term, B_e a constant proportional to the potential barrier opposed to the cooperative rearrangement of the liquid structure, η the viscosity in Pa.s and *T* the temperature in K (Richet, 1984; Neuville and Richet, 1991). In this model, matter transport in a viscous melt needs a cooperative rearrangement of the melt configuration. Thus, the temperature dependence of the viscosity arises from more configurations available for the elements at high temperature than at low temperature. Moreover, the configurational entropy reflects the configurational state of a glass, providing an image of the atomic disorder. It has two contributions: i) a topological part, which is mainly due to the various distributions of bond angles, interatomic distances and coordination numbers, and ii) a chemical part, induced by the mixing of different elements in equivalent sites (Neuville and Richet, 1991). The configurational entropy at the temperature *T* can be expressed as

$$S^{conf}(T) = S^{conf}(Tg) + \int_{T_g}^{T} Cp^{conf}/TdT, \tag{2}$$

with

$$Cp^{conf} = C_{pl}(T)–C_{pg}(Tg), \tag{3}$$

$S^{conf}(Tg)$ is the configurational entropy of the melt at *Tg*, and is equal to the residual entropy of the corresponding glass at 0 K, $C_{pl}(T)$ is the heat capacity of the liquid at the temperature *T* and $C_{pg}(Tg)$ is the heat capacity of the glass at *Tg*. Near the *Tg*, the $S^{conf}(Tg)$ term is predominant and drives viscosity variations. At high temperature, the configurational heat capacity of the melt is governed by the variation of the heat capacity of the liquid, which, most of the time, varies linearly following chemical changes. This also explains why the low viscosity variations of mixed alkali silicate melts at high temperature are generally linear (Bockris et al., 1955; Richet, 1984).

For Na/K silicate melts, the configurational entropy at *Tg* can be calculated by simply using an ideal mixing model:

$$S^{conf}(Tg) = \sum x_i S_i^{conf}(Tg)–nR\sum x_i \ln x_i, \tag{4}$$

with x_i the mol fraction of K, i.e. K/(K + Na), or Na, i.e. Na/(K + Na), $S_i^{conf}(Tg)$ the configurational entropy of the end-members *i* (the pure K and Na silicate melts), *n* the number of exchanged atoms, and *R* the gas constant (Richet, 1984). This thermodynamic ideal mixing model also implies a structural random mixing between the exchanged elements.

These equations and theory can be also used for other chemical systems. In particular, Eq. (4) allows one to reproduce well the viscosity variations of (Mg, Ca) silicate and aluminosilicate melts (Neuville and Richet, 1991). On the other hand, viscosity variations between Na/Sr and Na/Ca silicate melts (Neuville, 2005, 2006) do not follow an ideal mixing, therefore implying a non-random distribution of these elements. This has been also pointed out by NMR spectroscopy studies on Na/Ca, Ba/Mg or Ba/Na elements in silicate glasses (Lee and Stebbins, 2003a; Lee et al., 2003). Furthermore, quasielastic neutron scattering experiments suggest that Na^+ and K^+ ions could be