Structure and configurational properties of felsic magmatic liquids at magmatic temperatures

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Magmatic processes, including partial melting, melt aggregation, magma ascent, and crystallization are governed by transport and thermodynamic properties of the melts and minerals in the processes. Examination of relevant melt compositions with the aim to relate structure to configurational properties of the melts have been carried out.

A total of 211 anionic speciation data points in the system Na_2O-Al_2O_3-SiO_2 were determined and combined with published data in other alkali aluminosilicate melt systems (Mysen, 1995, 1996, 1997; Mysen and Frantz, 1994a). Numerical description of the relationship between abundance of structural units, temperature, and bulk composition was derived by stepwise regression of expressions such as:

$$X_{Qi} = a + b\cdot(NBO/T) + c\cdot T + d/T + e\cdot[\mathrm{Al/(Al{+}Si)}] + f\cdot[\mathrm{Al/(Al{+}Si)}]^2$$

The equilibrium constants, K, for the two relevant anionic equilibria, $2Q^3 \rightleftharpoons Q^2{+}Q^4$, and $2Q^2 \rightleftharpoons Q^1{+}Q^3$, were determined at temperatures above the glass transition. The K-values were fitted via stepwise regression to expressions of the form;

$$\ln K_1 = a + b/T + c\cdot[\mathrm{Al/(Al{+}Si)}] + d\cdot[\mathrm{Al/(Al{+}Si)}]^2 + e\cdot(NBO/T)$$

The enthalpy of reaction for the anionic equilibria was extracted from the linear relationships, $\ln K = a{+}b/T$. These are in the range $-30{-}70$ kJ/mol. The values are systematic functions of bulk composition generally increasing with increasing Al/(Al+Si) and with increasing ionization potential of the metal cation. The enthalpy is not sensitive to bulk melt polymerization.

The configurational heat capacity of individual species were derived by combining speciation data in metal oxide silicate melts with published thermodynamic data (Richet and Neuville, 1992). The configurational heat capacity, C_p^{conf}, of individual Q^i-species in simple binary alkali silicate melts was extracted from the data of Richet and Neuville (1992) and combined with speciation data of Mysen and Frantz (1994b) for the system Na_2O-SiO_2. A of set of linear equations;

$$\sum_{i=1}^{i} X_Q^i C_p^{config}(Q^i) = C_p^{config}$$

was employed to compute the configurational heat capacity of the individual structural units. The resultant values are $C_p^{config}(Q^4)$=7.8 J/mol K, $C_p^{config}(Q^3)$ = 13.9 J/mol K, and $C_p^{config}(Q^2)$ = 16.8 J/mol K. Absent melt structure data for compositions where Q^1 species are significantly abundant, it is assumed that $C_p^{config}(Q^1) \sim C_p^{config}(Q^2)$. The X_{Q1} is so low (< mol%) that this assumption does not introduce a large error. From stepwise regression against temperature and compositional variables, in the Na_2O-Al_2O_3-SiO_2, system (221 data points), these relations are:

$$C_p^{config} = 5.8\pm0.6 - 0.002\pm0.001 \times T + 5.7\pm3.3 \times 10^{-7} \times T^2 - 5.9\pm0.9 \times \frac{\mathrm{Al}}{\mathrm{Al{+}Si}} + 12.2\pm2.7 \times \left(\frac{\mathrm{Al}}{\mathrm{Al{+}Si}}\right)^2 + 18.2\pm1.4\,\frac{NBO}{T} - 10.4\pm0.9\left(\frac{NBO}{T}\right)^2$$

The changes in configurational entropy with temperature, is extracted from the heat capacity data:

$$\Delta S^{config} = \frac{C_p^{config}}{\ln\frac{T}{T_0}}$$

where T (Kelvin) is the temperature of interest and T_0 is the reference temperature (the glass transition temperature is used). The ΔS^{config} thus obtained (Fig. 1) show a strong positive and nonlinear function of temperature similar to that observed by direct measurements for other compositions (e.g. Neuville and Richet, 1991), The ΔS^{config} is subtly dependent on Al/(Al+Si) and also on the NBO/T of the melt.

The results (Fig. 1) were combined with the structural data to separate the topological and mixing contributions S^{config} from

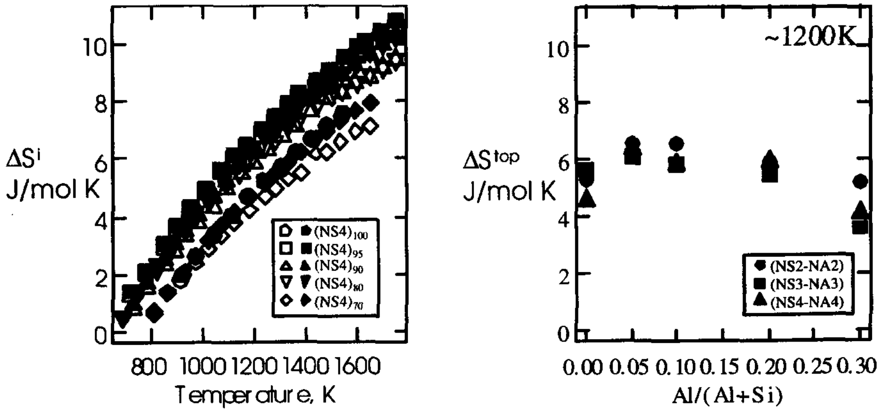

FIG. 1. Changes in configurational (closed symbols) and topological (open symbols) entropy, ΔS^i, the glass transition in the system Na_2O-Al_2O_3-SiO_2 for compositions as indicated and as a function of Al/(Al+Si) at ~1200K. $(NS4)_x$ etc. denotes $Na_2Si_4O_9$ (NS4)–$Na_2(NaAl)_4O_9$ (NA4) melts where x represents mol % NA4 component. NS2-NA2 and NS3-NA2 denote compositions on the joins $Na_2Si_2O_5$-$Na_2(NaAl)_2O_5$, and $Na_2Si_3O_7$-$Na_2(NaAl)_3O_7$, respectively.

$$S^{config} = S^{top} + S^{mix}$$

and

$$S^{mix} = -nR\sum_{i=1}^{i} X_{Q^i} \ln X_{Q^i}$$

The change in topological entropy, ΔS^{top}, is shown as open symbols in Fig. 1. The values of ΔS^{config} and ΔS^{top} are only subtly different. The contribution to the configurational entropy from the mixing of the structural units in the melts is, therefore, nearly insignificant (representing <10% of the total value) an observation similar to that noted for the mixing behaviour of Al-free Li-, Na-, and K-silicate melts (Mysen, 1995).

References

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