The effect of P₂O₅ on the viscosity of haplogranitic liquid.

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Abstract : The effect of P_2O_5 on the viscosity of a haplogranitic (K_2O-Na_2O-Al_2O_3-SiO_2) liquid has been determined at 1 atm pressure in the temperature interval of 700 - 1650°C. Viscosity measurements of a haplogranite, haplogranite + 5.1 wt.% P_2O_5 and haplogranite + 9.5 wt.% P_2O_5 have been performed using the concentric cylinder and micropenetration methods.

The viscosity of haplogranite liquid decreases with the addition of P_2O_5 at all temperatures investigated. The viscosity decrease is nonlinear, with the strongest decrease exhibited at low P_2O_5 concentration. The temperature-dependence of the viscosity of all the investigated liquids is Arrhenian, as is the case for P_2O_5 liquid. The Arrhenian activation energy is slightly lower in the P_2O_5-bearing liquids than in the P_2O_5-free haplogranite with the result that the effect of P_2O_5 on viscosity is a (weak) function of temperature. At temperatures corresponding to the crystallization of phosphorus-rich granitic and pegmatitic systems the addition of 1 wt.% of P_2O_5 decreases the viscosity 0.2 $\log_{10}$ units.

The effect of P_2O_5 on haplogranitic melt viscosity is much less than that for B_2O_3, F_2O_{-1} on the same melt composition (Dingwell *et al.*, 1992 and this study). This implies that P_2O_5 concentration gradients in high-silica melts during, for example, phosphate mineral growth or dissolution in granitic magmas, will not significantly influence melt viscosity.

Keywords : silicate melt, viscosity, micropenetration, concentric cylinder, granite, phosphorus.

1. Introduction

The remarkable phosphate mineralogy of pegmatite fields (Moore, 1982) and the significant phosphorus contents of nominally phosphorus-free minerals (London *et al.*, 1990a) may result in part from extreme enrichment of phosphorus at the magmatohydrothermal stage of pegmatite evolution. Certain rare-element granitic pegmatites are estimated to contain up to 1 wt.% of P_2O_5 (London *et al.*, 1990a ; Černý, 1991) and the glassy eruptive macusanites of SE Peru contain 0.5 to 1.0 wt.% P_2O_5 (Pichavant *et al.*, 1987). There is no reason to doubt that even higher concentrations may be attained in certain extreme pegmatitic differentiates (Černý *et al.*, 1985). Such enrichments may well occur at the magmatohydrothermal stage and thus the properties of P_2O_5-rich magmas, both chemical and physical, are of geological relevance.

Several experimental hydrothermal investigations of phosphate - melt equilibria exist. Wyllie & Tuttle (1964) demonstrated that the addition of P_2O_5 to granitic and albitic melts strongly reduces the melting temperature under 2.75 kbar pH₂O. Studies of apatite and monazite solubility in peralkaline and metaluminous compositions indicate moderate melt P_2O_5 contents (0.1-0.4 wt.%, Watson, 1979, 1980 ; Rapp & Watson, 1987). Peraluminosity, however, has been demonstrated to enhance P_2O_5 solubility up to several weight percent (Montel, 1986).

In a different but equally important context, the rich diversity of phosphate mineralogy is matched by a large glassforming range of composition in silicophosphate and phosphate glasses (Scholze, 1988), and indeed P_2O_5 itself is glassforming. As a result the properties of phosphate glasses and liquids have been investigated (Bansal & Doremus, 1986).

Table 1. Haplogranite analyses (wt%).

Composition	Na$_2$O	K$_2$O	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	total
HPG8	4.53	4.17	11.89	77.90	-	98.48
	4.60	4.23	12.07	79.1	-	100.00
HPG8P5	4.26(6)	3.92(5)	11.50(7)	74.5(2)	5.1(1)	99.31
	4.52	4.16	12.21	79.1	-	100.00
HPG8P10	3.76(5)	3.74(5)	11.29(7)	71.1(4)	9.5(2)	99.36
	4.18	4.16	12.56	79.1	-	100.00

Analysis by electron microprobe, Cameca SX-50 in wavelength dispersive mode. Operating conditions of 15 kV, 15 nA on brass, a 10μm defocussed beam and 20 s count times. Standards were albite (Na, Al, Si), orthoclase (K) and apatite (P).

The structural role of phosphorus in silicate melts has been the subject of a large number of spectroscopic measurements (see Mysen, 1988, for a review) and it has been demonstrated that phosphorus additions can produce octahedrally coordinated Si in silicophosphate glasses at 1 atm (Sekiya et al., 1988). Equally important with respect to the structural role are the contributions based on crystal-melt equilibria. P$_2$O$_5$ strongly shifts the pseudowollastonite - silica eutectic composition towards lower SiO$_2$ contents (Kushiro, 1975). Based partially on such data, Ryerson & Hess (1980) have argued for a dual role of phosphorus in silicate melts involving phosphate tetrahedra participating in the silicate network of SiO$_2$ but also metal phosphate groups that increase the activity of SiO$_2$ in metal oxide - silica melts. More recently, in the haplogranite-H$_2$O system at 2 kbar pH$_2$O, London et al. (1990b) have observed a shift of the quartz-albite-orthoclase eutectic towards the albite apex with increasing P$_2$O$_5$ content.

Due to the complexity of P$_2$O$_5$ solution in silicate melts, extrapolations of the effects of P$_2$O$_5$ on the physical properties of industrial melt compositions must be treated with caution. With this in mind we have begun an evaluation of the effects of P$_2$O$_5$ on the macroscopic properties of haplogranitic melts at magmatic temperatures. In the present study we have determined the effect of P$_2$O$_5$ on the viscosity of a haplogranitic composition (which lies near the 1 kbar pH$_2$O cotectic minimum) at temperatures down to 798°C.

2. Methods

Starting materials for the preparation of phosphorus-bearing samples were Na$_2$CO$_3$, K$_2$CO$_3$,

Al$_2$O$_3$, SiO$_2$ and NH$_4$PO$_3$. The powders of the starting reagents were dried at 120°C overnight prior to weighing except for the NH$_4$PO$_3$ which was weighed immediately after opening the airtight seal on the original packing. One hundred gram (decarbonated, dehydrated equivalent) batches of the powders were weighed directly into plastic bottles and mixed by agitation for 5-10 minutes. The starting compositions were chosen to represent 5 and 10 wt.% additions of P$_2$O$_5$ to a haplogranite composition (designated HPG8), near the 1 kbar (pH$_2$O) ternary minimum composition in the system SiO$_2$-NaAlSi$_3$O$_8$-KAlSi$_3$O$_8$-H$_2$O. The HPG8 glass is taken from Holtz et al. (1992). The phosphorus-bearing haplogranitic compositions were fused directly for several hours at 1650°C in 75 cm^3 thinwalled platinum crucibles using a MoSi$_2$ box furnace. The products of these fusions were bubble-rich. To eliminate the bubbles and promote full reaction and homogenization of the samples, the crucibles were transferred to a second MoSi$_2$ box furnace equipped with a concentric cylinder viscometer. The samples were heated to 1650°C and stirred at 20 rpm using a Pt$_{80}$Rh$_{20}$ spindle. The sample was inspected periodically by remov-

Table 2a. Viscosities (log$_{10}$ dPa s) by concentric cylinder.

Temperature (°C)	HPG8	HPG8P5	HPG8P10
1348	-	5.89	5.69
1397	5.90	5.51	5.32
1446	5.53	5.19	5.00
1495	5.15	4.90	4.71
1544	4.81	4.63	4.45
1594	4.58	4.35	4.19
1643	4.24	4.10	3.94

Table 2b. Viscosities (log$_{10}$ dPa s) by micropenetration.

	HPG8	HPG8P5	HPG8P10	HPG8F5	HPG8F10
844.2	12.50	-	-	-	-
903.3	11.90	-	-	-	-
969.2	10.77	-	-	-	-
826.6	-	11.97	-	-	-
854.6	-	11.56	-	-	-
882.6	-	11.05	-	-	-
908.6	-	10.69	-	-	-
936.6	-	10.33	-	-	-
798.8	-	-	11.91	-	-
825.8	-	-	11.39	-	-
853.7	-	-	10.97	-	-
882.2	-	-	10.55	-	-
908.6	-	-	10.20	-	-
599.9	-	-	-	12.15	-
621.1	-	-	-	11.73	-
630.9	-	-	-	11.61	-
641.0	-	-	-	11.32	-
658.1	-	-	-	11.02	-
674.6	-	-	-	10.69	-
687.2	-	-	-	10.42	-
602.8	-	-	-	-	12.07
622.5	-	-	-	-	11.64
641.8	-	-	-	-	11.22
661.0	-	-	-	-	10.75
680.4	-	-	-	-	10.32

Table 3. Fit parameters.

Composition	a	b (x 10^4)	E (kJ mol^{-1})	n
HPG8	-7.69(12)	2.28(3)	436	9
HPGP5	-6.70(6)	2.05(1)	392	12
HPG8P10	-6.25(4)	1.941(6)	372	12

n = number of data points

ing the spindle and checking the adhered melt. The bubble- and crystal-free products of this process were cooled slowly in the viscometry furnace to less than 400°C and removed to cool to room temperature. Cylinders (8 mm diameter) of the glasses were cored from the thinwalled crucibles. Some of these cylinders were sawn into disks 3-4 mm long and polished on both ends. The polished disks were stored in a desiccator until use in the micropenetration experiments. The remainder of the samples were broken from the crucibles with a hammer and stored until use in concentric cylinder experiments.

Samples of the glasses were analyzed by electron microprobe methods. The results of the analyses are presented in Table 1. The analyzed P$_2$O$_5$ contents, cast into the haplogranite - P$_2$O$_5$ system, are the basis for discussion of the results.

Low-temperature viscosities were determined using a micropenetration technique. This involves determining the rate at which a sphere under a fixed load moves into the melt surface. These measurements were performed in a Netzsch TMA 402® vertical silica glass push rod dilatometer. The sample is placed at the bottom of the sample holder with the indent sphere being held in place by a rod of SiO$_2$ which is attached to a weight pan. The metal connection between the silica glass rod and the weight pan acts as the core of a calibrated LVDT. The movement of this metal core as the sphere is pushed into the melt is translated into the displacement. The present system uses 3 mm diameter precision spheres of alumina (Frialit-Degussit®), and a force of 1 N. The absolute shear viscosity is determined from

$$\eta = \frac{0.1875 \, P \, t}{r^{0.5} \, \alpha^{1.5}} \qquad (1)$$

(Pocklington, 1940 ; Tobolsky & Taylor, 1963) for the radius of the sphere r, the applied force P, indent distance α, and time t (t = 0 and α = 0 upon application of the force).

The glass samples used are cylinders of 8 mm diameter which are at least 3 mm thick. The measurements are performed over indentation distances less than 100 μm as Eqn. 1 is derived on the assumption that the indentation distance is much less than the radius of the indent sphere ($\alpha \ll r$). The viscosity of NBS711 lead-silica glass was determined with an accuracy of ± 0.1 log$_{10}$ unit using this technique over a viscosity range of 10-12 log$_{10}$ dPa s. With 3 mm thick sample
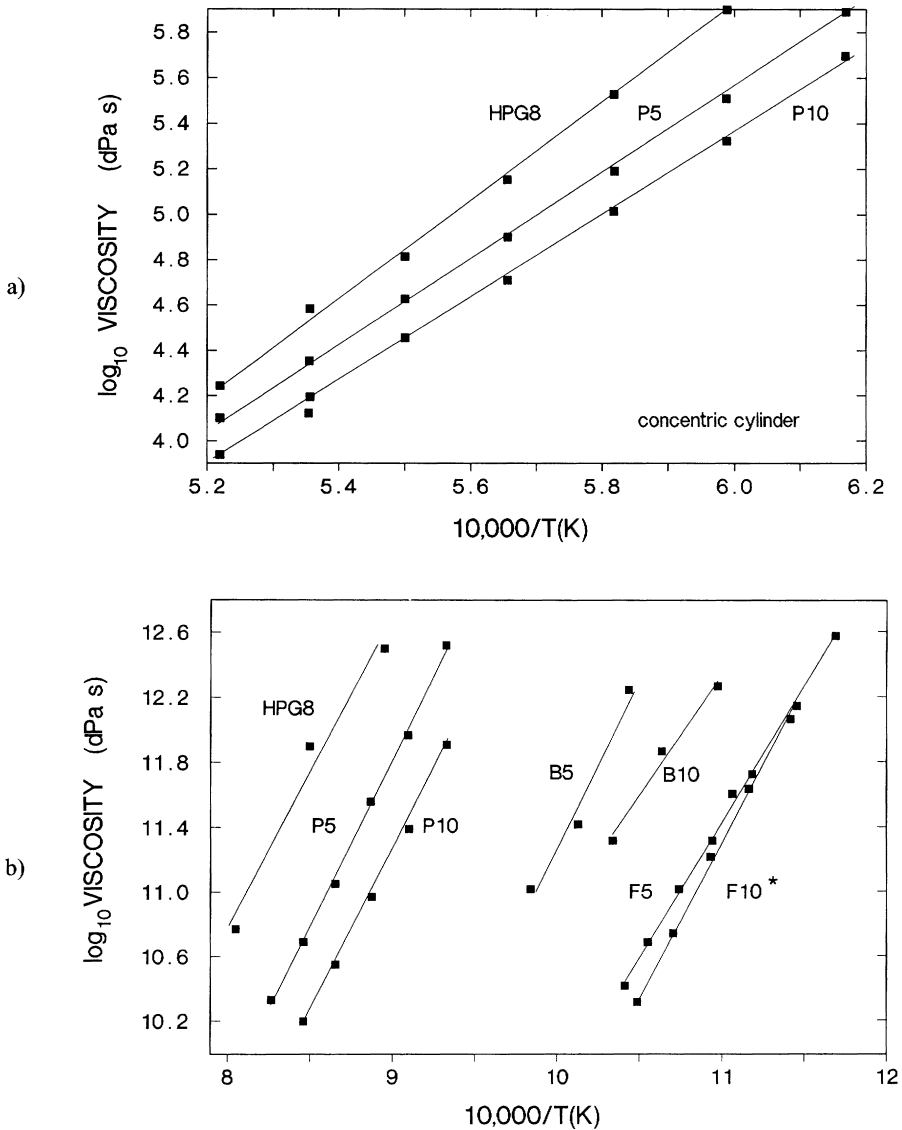
a)

b)

Fig. 1. The viscosity of haplogranite melts with added P_2O_5 determined using (a) concentric cylinder and (b) micropenetration methods. (Fig. 1b includes data for the addition of B_2O_3 and F to the same haplogranitic melt (data from Dingwell et al., 1992 and this study).

sizes, together with an indentation distance less than 100 μm and an indenter radius of 3 mm, no edge effects and no end effects were observed in this range of viscosities. No reaction between the alumina sphere and the melts was observed.

The concentric cylinder experiments were performed on the remainder of the batch melts that had been remelted into cylindrical viscometry crucibles and stirred to a bubble-free state. The shear viscosities of the liquids were determined using the concentric cylinder method at 1 atm in equilibrium with air.

The high temperature viscosities were measured with a Brookfield HBTD head (full-scale torque = 5.75 x 10^{-1} N m) and rotation speeds of 0.5 to 20 rpm. This study used the crucible and high-viscosity spindle design of Dingwell & Virgo (1988). The furnace, viscome-
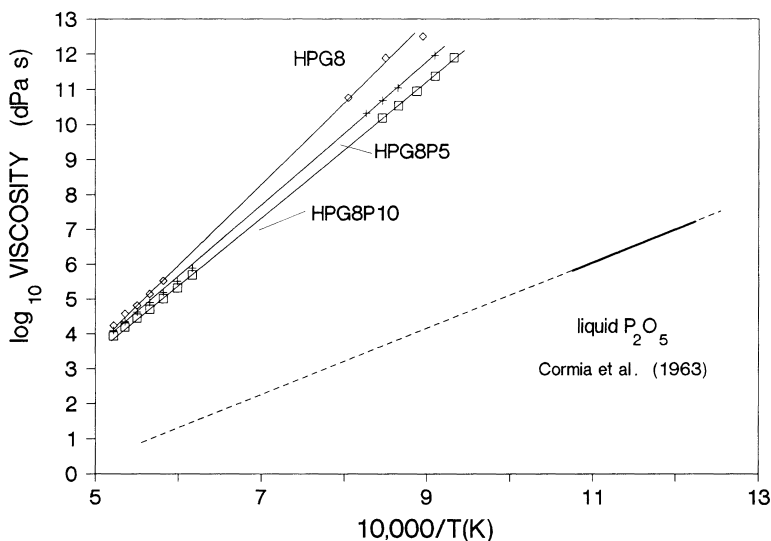
Fig. 2. Comparison of the viscosity-temperature relationship of haplogranite + P$_2$O$_5$ with that of P$_2$O$_5$ liquid. Note that all melts exhibit Arrhenian temperature-dependence of viscosity.

ter assembly and computer interface, as well as the operating method and calibration are described by Dingwell (1989a, b ; 1990). The viscosities measured are relative. The instrument has been calibrated most recently by standard soda-lime glass DGG-1 available from the Deutsche Glastechnische Gesellschaft. The viscosity data are accurate to ± 5% at 1σ. Newtonian rheology was observed over the limited dynamic range of these measurements (approx. 0.3 log$_{10}$ unit). This result is consistent with the fact that the calculated relaxation times for shear in these liquids using the Maxwell approximation (Dingwell & Webb, 1989, 1990) and the Newtonian viscosity data from this study are several log$_{10}$ units lower than the inverse of our experimental strain rates. We appear to be observing relaxed viscosities of a liquid.

After the viscometry was completed, each sample was removed from the furnace, cooled to room temperature and drilled out of the crucible with diamond coring bits. The crucible was cleaned in HF and used for the next sample.

3. Results and discussion

The viscosity data for HPG8, HPG8P5 and HPG8P10 are presented in Table 2a, b. The temperature-dependent viscosities were regressed using an equation of the form:

$$\log_{10}\eta \ (\text{dPa s}) = a + b/T \qquad (2)$$

and the a and b parameters are included in Table 3. The viscosity data from both micropenetration and concentric cylinder measurements can be described within error using equation (2) as illustrated in Fig. 1a, b. The temperature-dependence of viscosity yields an activation energy, E in the Arrhenius equation

$$\log_{10}\eta \ (\text{dPa s}) = \log_{10}\eta_0 + E/(2.303RT) \qquad (3)$$

The values of E derived from the regressions using equation (3) range from 437 kJ mol^{-1} for the haplogranite to 372 kJ mol^{-1} with the addition of 10 wt.% P$_2$O$_5$.

The viscosity - temperature data of the HPG8P series are compared with liquid P$_2$O$_5$ data of Cormia et al. (1963) in Fig. 2. The P$_2$O$_5$ liquid exhibits an Arrhenian temperature-dependence of viscosity with an activation energy of 174 kJ mol^{-1}.

The effect of P$_2$O$_5$ on the viscosity of haplogranite melt is represented as a series of isotherms in Fig. 3. The effect of P$_2$O$_5$ on viscosity increases with decreasing temperature. At 800°C the addition of 1 wt.% of P$_2$O$_5$ to haplogranite reduces viscosity by 0.2 order of magnitude. The reduction in viscosity accompanying the addition of P$_2$O$_5$ to haplogranite can be compared with the measured viscosity decreases re-
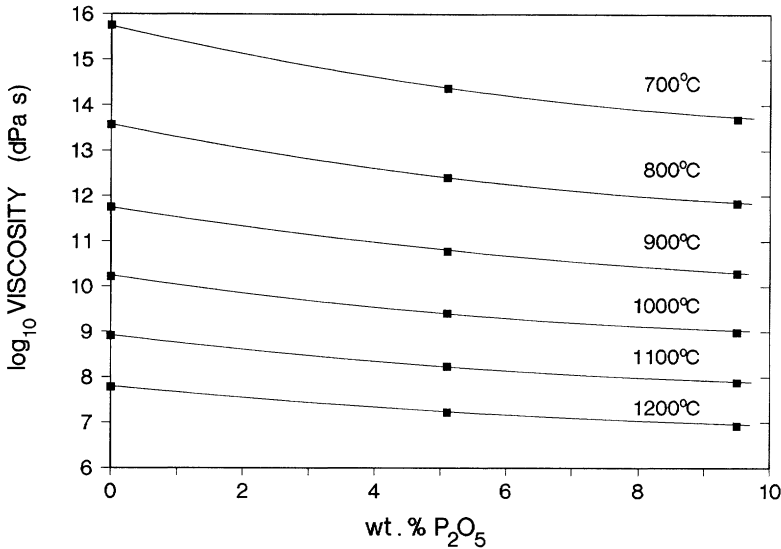
Fig. 3. The effect of P_2O_5 addition on the viscosity of haplogranite melts. Isotherms drawn at 100°C intervals. The effect of P_2O_5 increases with decreasing temperature.

sulting from the addition of F_2O_{-1} (included in Table 2) and B_2O_3 to the same haplogranite melt (Dingwell *et al.*, 1992 a). Fig. 4 compares, on a weight percent basis, the effects of B_2O_3, P_2O_5 and F on the viscosity of HPG8 composition at 1000°C. In contrast to the case for B_2O_3 and F_2O_{-1},

P_2O_5 has only a moderate effect on melt viscosity in haplogranites.

The solution of phosphorus into silicate melts is complex. The substitution of P_2O_5 into alkali aluminosilicate glasses has been recently investigated by Gan & Hess (1989) who report that
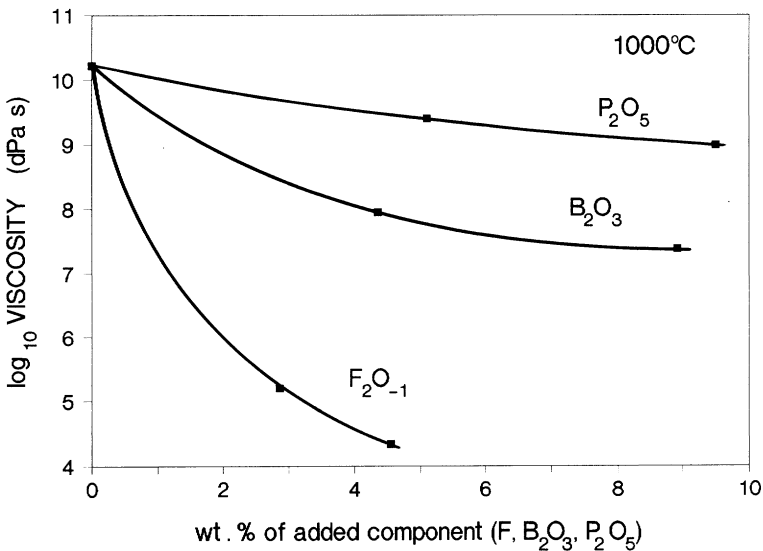

Fig. 4. The relative effects of phosphorus, boron and fluorine on the viscosity of haplogranite, compared on the basis of wt.% P_2O_5, B_2O_3 and F.

potassium phosphate complexes are stable in peralkaline compositions whereas aluminum phosphate (AlPO$_4$) complexes are formed in peraluminous compositions. The stabilization of octahedral silicon has been reported by Sekiya *et al.* (1988) in the SiO$_2$-P$_2$O$_5$ system. There is no volumetric evidence of octahedral silicon in the volume data for these compositions (Dingwell *et al.*, 1992 b) but amounts less than 0.1% would be difficult to detect using the volume relations. The stabilization of higher coordination of Si has been discussed in the context of the viscous flow process by several workers (Brawer, 1985 ; Stebbins & Farnan, 1989). It is reasonable to assume that if measurable quantities of higher coordinated Si are stabilized in P$_2$O$_5$-rich silicophosphate glasses then minor to trace levels of these higher coordination forms exist below the range of macroscopic or microscopic detection in the present samples. Despite the possibility of enhanced contents of high-coordinated Si in these melts, the viscosity decrease is relatively weak implying that a simple relation between viscosity and high coordination of Si is not valid.

We note that the addition of P$_2$O$_5$ to haplogranite results in Arrhenian behavior, and that even P$_2$O$_5$ has Arrhenian behavior (Cormia *et al.*, 1963 ; Martin & Angell, 1986). This contrasts with the case of B$_2$O$_3$ where the pure liquid is strongly non-Arrhenian and that of the F$_2$O$_{-1}$ component where again fluoride melts are strongly non-Arrhenian (Dingwell & Webb, 1992). This apparent contrast of P$_2$O$_5$ versus B$_2$O$_3$ and F$_2$O$_{-1}$ indicates that the temperature-dependence of the intermediate structure controlling viscous flow in the P$_2$O$_5$-bearing melts is slight compared with that of the B$_2$O$_3$ - and F-containing melts. The P$_2$O$_5$-bearing liquids remain "strong" in the sense of Angell (1984) whereas the others become increasingly "fragile". Richet and co-workers (Richet, 1984 ; Richet *et al.*, 1986 ; Neuville *et al.*, 1992) have argued that the entropy-based theory of Adam & Gibbs (1965) furnishes a powerful model for the composition- and temperature-dependence of silicate melt viscosity. In the context of that theory, the temperature-dependence of the configurational entropy would be expected to be small for the case of the present P$_2$O$_5$-bearing liquids. The temperature-dependent heat capacities of these liquids, accessible by high temperature drop calorimetry should be able to provide a test of this proposal.

4. Conclusions

The effect of P$_2$O$_5$ on the viscosity of haplogranitic melts has been measured over a wide range of temperature and viscosity. The addition of P$_2$O$_5$ to haplogranitic melt reduces viscosity but the reduction is small compared with other elements commonly enriched in pegmatitic melts (*e.g.* B, F). The viscosity-reducing effect of P$_2$O$_5$ will however be significant in granitic and pegmatitic melts containing 0.5 to 1.0 wt.% P$_2$O$_5$.

References

Adam, G. & Gibbs, J.H. (1965) : On the temperature-dependence of cooperative relaxation properties in glass-forming liquids. *J. Chemical Physics*, **43**, 139-146.

Angell, C.A. (1984) : Strong and fragile liquids. *In:* K.L. Ngai and G.B. Wright (eds.) Relaxations in Complex Systems. Office of Naval Research and Technical Information Service.

Bansal, N.P. & Doremus, R.H. (1986) : Handbook of Glass Properties. Academic Press, 680 p.

Brawer, S. (1985) : Relaxations in viscous liquids and glasses. American Ceramic Society, Columbus, Ohio, 220 p.

Černy, P. (1991): Rare-element pegmatites Part II: Regional to global environments and petrogenesis. *Geoscience Canada*, **18**, 68-81.

Černy, P., Meintzer, R.E. & Anderson, A.J. (1985) : Extreme fractionation in rare-element granitic pegmatites : selected examples of data and mechanisms. *Can. Mineral.*, **23**, 381-421.

Cormia, R.L., MacKenzie, J.D. & Turnbull, D. (1963) : Viscous flow and melt allotropy of phosphorus pentoxide. *J. Applied Physics*, **34**, 2245-2248.

Dingwell, D.B. (1989 a) : The effect of fluorine on the viscosity of diopside melt. *Am. Mineral.*, **74**, 333-338.

— (1989 b) : Shear viscosities of ferrosilicate liquids. *Am. Mineral.*, **74**, 1038-1044.

— (1990) : Shear viscosities of galliosilicate liquids. *Am. Mineral.*, **75**, 1231-1237.

Dingwell, D.B. & Virgo, D. (1988) : Melt viscosities in the Na$_2$O-FeO-Fe$_2$O$_3$-SiO$_2$ system and factors controlling the relative viscosities of fully polymerized silicate melts. *Geochim. Cosmochim. Acta*, **52**, 395-403.

Dingwell, D.B. & Webb, S.L. (1989) : Structural relaxation in silicate melts and of non-Newtonian melt rheology in geologic processes. *Phys. Chem. Minerals*, **16**, 508-516.

—, — (1990) : Relaxation in silicate melts. *Eur. J. Mineral.*, **2**, 427-449.

—, — (1992) : The fluxing effect of fluorine at magmatic temperatures (600-800°C) : a scanning calorimetric study. *Am. Mineral.*, **77**, 30-33.

Dingwell, D.B., Knoche, R., Webb, S.L. & Pichavant, M. (1992 a) : The effect of B₂O₃ on the viscosity of haplogranitic melts. *Am. Mineral.*, **77**, 457-461.

Dingwell, D.B., Knoche, R. & Webb, S.L. (1992 b) Partial molar volumes for P₂O₅, B₂O₃ and F₂O₋₁ in haplogranitic liquids at magmatic temperatures. *Terra Nova Abstract Supplement 1*, 14.

Gan, H. & Hess, P.C. (1989) : Phosphorus effects upon the structure of potassium aluminosilicate glasses : Inference from Raman and NMR. *EOS*, **43**, 1375.

Holtz, F., Behrens, H., Dingwell, D.B. & Taylor, R.P. (1992) : Water solubility in aluminosilicate melts of haplogranitic composition at 2 kbar. *Chemical Geol.*, Special Issue on Silicate Melts, Y. Bottinga, D. Dingwell & P Richet, (eds.). **96**, 289-302.

Kushiro, I. (1975) : On the nature of silicate melt and its significance in magma genesis: regularities in the shift of the liquidus boundaries involving olivine, pyroxene, and silica minerals. *Amer. Jour. Sci.*, **275**, 411-431.

London, D., Černy, P., Loomis, J.L. & Pan, J. (1990a) : Phosphorus in alkali feldspars of rare-element granitic pegmatites. *Can. Mineral.*, **28**, 771-786.

London, D., Loomis, J.L., Huang, W. & Morgan, G.B. VI (1990b) : Behavior and effects of phosphorus in the system Ab-Or-Qz-H₂O at 200 MPa (H₂O). GSA/MSA Abstracts with Programs, **22**, A302.

Martin, S.W. & Angell, C.A. (1986) : On the glass transition and viscosity of P₂O₅. *J. Phys. Chem.*, **90**, 6736-6740.

Montel, J.-M. (1986) : Experimental determination of the solubility of Ce-monazite in SiO₂-Al₂O₃-K₂O-Na₂O melts at 800°C, 2 kbar, under H₂O-saturated conditions. *Geology*, **14**, 659-662.

Moore, P.B. (1982) : Pegmatite minerals of P (V) & B (III). *in* Černy, P. (ed.) Short course in granitic pegmatites in science and industry. Mineralogical Association of Canada, 267-291.

Mysen, B.O. (1988) : Structure and Properties of Silicate Melts. Elsevier, 354 p.

Neuville, D., Courtial P., Dingwell, D.B. & Richet, P. (1992) : Thermodynamic properties of rhyolite and andesite melts. (in press - *Contrib. Mineral. Petrol.*)

Pichavant, M., Valencia Herrera, J., Boulmier, S., Briqueu, L., Joron, J-L., Juteau, M., Marin, L., Michard, A., Sheppard, S.M.F., Treuil, M. & Vernet, M. (1987) : The Macusani glasses, SE Peru : evidence of chemical fractionation in peraluminous magmas. Geochemical Society Special Publication 1, 359-373.

Pocklington, H.C. (1940) : Rough measurement of high viscosities. *Proc. Cambridge Phil. Society*, **36**, 507-508.

Rapp, R.P. & Watson, E.B. (1986) : Monazite solubility and dissolution kinetics: implications for the thorium and light rare earth chemistry of felsic magmas. *Contrib. Mineral. Petrol.*, **94**, 304-316.

Richet, P. (1984) : Viscosity and configurational entropy of silicate melts. *Geochim. Cosmochim. Acta*, **48**, 471-483.

Richet, P. Robie, R.A. & Hemingway, B.S. (1986) : Low-temperature heat capacity of diopside glass (CaMgSi₂O₆) : a calorimetric test of the configurational entropy theory applied to the viscosity of liquid silicates. *Geochim. Cosmochim. Acta*, **50**, 1521-1533.

Ryerson, F.J. & Hess, P.C. (1980) : The role of P₂O₅ in silicate melts. *Geochim. Cosmochim. Acta*, **44**, 611-624.

Scholze, H. (1988) : Glas : Natur, Struktur und Eigenschaften. Springer, NY, 407 pp.

Sekiya, T. Mochida, N., Ohtsuka, A. & Uchida, K. (1988) : 6-coordinated Si⁴⁺ in SiO₂-PO₅/₂ glasses. *J. Japan. Ceram. Soc.*, **96**, 571-573.

Stebbins, J.F. & Farnan, I. (1989) : NMR spectroscopy in the Earth Sciences. Structure and dynamics. *Science*, **245**, 257-263.

Tobolsky, A.V. & Taylor, R.B. (1963) : Viscoelastic properties of a simple organic glass. *J. Phys. Chemistry*, **67**, 2439-2442.

Watson, E.B. (1979) : Apatite saturation in basic to intermediate magmas. *Geophys. Res. Letters*, **6**, 937-940.

Watson, E.B. (1980) : Apatite and phosphorus in mantle source regions: an experimental study of apatite/melt equilibria at pressures to 25 kbar. *Earth Planet. Science Lett.*, **51**, 322-325.

Wyllie, P.J. & Tuttle, O.F. (1964) : Experimental investigation of silicate systems containing two volatile components. Part III. The effects of SO₃, P₂O₅, HCl and Li₂O in addition to H₂O on the melting temperature of albite and granite. *Amer. Jour. Sci.*, **262**, 930-939.