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The effect of phosphorus on the iron redox ratio, viscosity, and density of an evolved ferro-basalt

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Abstract Despite the abundant evidence for the enrichment of phosphorus during the petrogenesis of natural ferro-basalts, the effect of phosphorus on the physical properties of these melts is poorly understood. The effects of phosphorus on the viscosity, density and redox ratio of a ferro-basaltic melt have been determined experimentally. The viscosity measurements were obtained using the concentric cylinder method on a ferro-basaltic melt above its liquidus, at 1 atm, in equilibrium with air and with CO_2. The density measurements were performed using the double Pt-bob Archimedean method at superliquidus conditions under 1 atm of air. The redox ratio was obtained by wet chemical analysis of samples collected during physical property measurements. Phosphorus pentoxide reduces ferric iron in ferro-basaltic melt. The reduction due to P_2O_5 is much larger than that for most other oxide components in basaltic melts. A coefficient for the reduction of ferric iron has been generated for inclusion in calculation schemes. The effect of P_2O_5 on the viscosity is shown to be complex. The initial reduction of ferric iron with the addition of P_2O_5 results in a relatively small change in viscosity, while further addition of P_2O_5 results in a strong increase. The addition of phosphorus to a ferro-basaltic melt also reduces the density. A partial molar volume of 64.5 $\pm$ 0.7 cm^3/mol for P_2O_5 in this melt has been obtained at 1300° C, yielding a volume of 12.9 cm^3/mol per oxygen, consistent with a tetrahedral coordination for this high field strength cation. The effects of P_2O_5 on redox state, density and viscosity provide constraints on the structural role of phosphorus in these melts. The results suggest a complex interaction of phosphorus with the aluminosilicate network, and tetrahedral ferric iron. In light of the significant effects of phosphorus on the physical and chemical properties of ferro-basaltic liquids, and the extreme enrichments possible in these liquids in nature, the role of phosphorus in these melts should, in future, be considered more carefully.

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Introduction

Due to the incompatible behaviour of P_2O_5 during the early stages of crystallization, and the relatively large solubility of P in basic melts (Watson 1979; Harrison and Watson 1984), phosphorus enrichment in natural basaltic magmas may reach the weight percent level before the saturation of a phosphate phase (Anderson and Greenland 1969; Leeman et al. 1976; Beswick and Carmichael 1978; Philpotts 1982). Enrichment of P to these levels will, however, only occur after extensive fractionation, and magmas enriched in phosphorus will necessarily also be rich in iron.

Even at these concentrations phosphorus is known to lower the liquidus temperature dramatically, cause the deflection of liquidus boundaries to lower silica content, and increase the liquid-liquid immiscibility gap in many simple and complex silicate systems (Wyllie and Tuttle 1964; Kushiro 1975; Watson 1976; Ryerson and Hess 1978, 1980; Visser and Koster van Groos 1979; Ryerson 1985; London et al. 1990, 1993; Toplis et al. 1994). Both the above experimental work, and spectroscopic studies (Nelson and Tallant 1984;

Duprée et al. 1988; Mysen 1992; Gan and Hess 1992) suggest that the addition of P to silicate melts causes important, and complex changes in the silicate melt structure (see also Mysen 1988). These inferred structural changes may therefore also be expected to have important consequences for the physical properties of these silicate liquids. Furthermore, in iron-bearing systems recent studies suggest that P_2O_5 may also cause variations in the ratio of ferric and ferrous iron (Mysen 1992; Gwinn and Hess 1993). Variations in the ferric-ferrous ratio may result in significant changes in both the density and viscosity of iron-bearing silicate melts (Lange and Carmichael 1990; Dingwell 1991) and thus the addition of phosphorus to these melts may result in complex variations of the physical properties.

The effects of P_2O_5 on the physical and chemical properties of such iron-rich basaltic magmas are, however, poorly understood. Phosphorus does not appear in the commonly used calculation schemes of density (Lange and Carmichael 1990), or ferric-ferrous ratio (Sack et al. 1980; Kilinc et al. 1983), and it is simply summed with SiO_2 for the calculation of viscosity (Bottinga and Weill 1972). In order to clarify this situation we have determined the effect of the addition of P_2O_5 on the ferric-ferrous ratio, viscosity and density of a melt of ferro-basaltic composition. Viscosity has been measured at two different oxygen fugacities (air and CO_2) over a large superliquidus range of temperature, and density has been measured in air for the same melt composition containing up to 10 wt% P_2O_5. This study provides data for the calculation of the partial molar volume and viscosity coefficient of P_2O_5 in basic magmas. However, the effect of phosphorus on the iron redox ratio must be considered carefully and taken into account when interpreting the variation of density and viscosity as a function of P_2O_5. The results have implications for petrogenetic processes involving the mass transport of crystals and melts in magma chambers, and may also be used to constrain models for the interaction of phosphorus with iron in ferro-basaltic melts.

Experimental methods

A phosphorus-free ferro-basaltic composition (SC4, from Toplis et al. 1994) to which various quantities of P_2O_5 were added, was used in this study. The selected P-free starting composition is an evolved basalt [$Mg^{\#}$; $Mg/(Mg + Fe_{total}) = 0.37$]. This composition corresponds to a residual liquid obtained from crystallization experiments on a synthetic analogue of the basaltic dyke C of Brooks and Nielsen (1978), which was considered by those authors as a possible parental liquid for the exposed portion of the Skaergaard intrusion, and may be considered typical of many ferro-basaltic compositions. The starting materials for all experiments were synthetic glasses prepared from mixtures of reagent grade oxides and carbonates (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, $CaCO_3$, Na_2CO_3, K_2CO_3). Phosphorus was added as NH_4PO_3. Oxide mixtures were fused directly for several hours at 1600° C in a $MoSi_2$ box furnace in a 75 cm^3 thinwalled Pt crucible. The bubble- and crystal-free products were then poured onto a cold steel plate and allowed to cool to room temperature. A new batch of 100 g of SC4 (+ P_2O_5) was synthesized before each viscosity experiment.

The shear viscosities were measured at 1 atm and temperatures in the range of 1200 to 1600° C in air and in CO_2 using the concentric cylinder method. This apparatus, its mode of operation and modifications to the software and hardware have been discussed previously (Dingwell 1989). The viscometer head is a Brookfield DV-II$_+$ (with a full-scale torque of 7.20×10^{-2} N-m). The spindle and crucible are fabricated from $Pt_{80}Rh_{20}$, and the spindle geometry is identical to that described by Dingwell and Virgo (1987). The viscometry installation is capable of measurements in the range of 1 to 10^6 dPa s (poise) with an accuracy of 5% at 2σ. The rotation rates used for the measurements vary with the viscosity of the sample between 5 and 100 rpm with the consequence that higher viscosities are measured at lower strain rates. Nevertheless, it can be demonstrated that the measurements are Newtonian over the strain rate range investigated. This is fully consistent with estimates of the viscous relaxation timescales in silicate melts of these viscosities (Dingwell and Webb 1989). The first measurements were taken at approximately 1600° C and then carried out lowering the temperature, generally in steps of 25 or 50° C, until either phase separation (e.g. crystallization, liquid-liquid unmixing) or an instrumental limit is reached. At the end of the lowest temperature measurement, the highest temperature condition is reoccupied and the comparison of first and last high temperature measurements serves as a check against instrumental drift. The measurements of viscosity are not absolute; rather the crucible, spindle, and head combination is calibrated against a standard of known viscosity. In this case SRM 711 lead-silicate glass was obtained from the National Institute of Standards and Testing (NIST) and used for this purpose.

Density determinations of the ferro-basaltic liquids were performed using the double Pt bob Archimedean technique. The apparatus is illustrated in Dingwell et al. (1988) and consists of a balance suspended above a vertically mobile high temperature furnace. The methods of operation and data gathering include the software modifications used by Dingwell (1992). Signals of bob buoyancy are electronically gathered, stored and later averaged. The method has been checked against NaCl and $Na_2Si_2O_5$ melts. The determination of density using this device carries an imprecision of 0.2% at 1σ.

The melts were sampled by dipping an alumina rod into the melt which was then withdrawn and plunged into H_2O for quenching. For viscosity measurements in air, samples were taken each 50° C in the range 1600° C to 1400° C, and for experiments in CO_2 samples were taken each 100° C in the range 1600 to 1400° C. For density measurements samples were taken at the start of each set of measurements. Glass chips were mounted as polished sections for petrographic and electron microprobe analysis. Electron microprobe analyses were carried out using a CAMECA SX50 at the Bayerisches Geoinstitut using operating conditions of 20 or 30 s counting times, 12 nA beam current, 15 kV accelerating voltage, and a 10 μm beam size. The following standards were used: albite – Na; apatite – P; orthoclase – K, Si; Fe_2O_3 – Fe; wollastonite – Ca; enstatite – Mg; $MnTiO_3$ – Ti; spinel – Al. Results from the electron microprobe show no significant loss of alkalis, phosphorus or iron during the sampled high temperature part of viscosity measurements. Averages of run products are shown in Table 1 for viscosity determinations in air (Run no. MTV1-4), in CO_2 (Run no. MTV6-9) and density determinations (Run no. MTD2-6). The remaining product was used for a determination of the ferric-ferrous ratio using wet chemical techniques at the Centre de Recherches Petrographiques et Geochimiques, Nancy.

Results

The effect of phosphorus on the iron redox ratio

Variations in density and viscosity due to the addition of phosphorus cannot be interpreted without a

Table 1 Run compositions (*FeO** total iron expressed as ferrous)

Viscosity (Air) Run no.	MTV2		MTV4		MTV3		MTV1	
SiO_2	50.87(33)[a]	*51.96*[b]	50.66(30)	*52.27*	50.52(30)	*54.14*	47.42(11)	*51.99*
TiO_2	4.05(6)	*4.14*	3.95(3)	*4.08*	3.39(1)	*3.64*	3.78(5)	*4.14*
Al_2O_3	11.36(6)	*11.60*	11.35(7)	*11.72*	11.09(14)	*11.89*	10.46(5)	*11.47*
FeO*	14.20(31)	*14.51*	13.90(14)	*14.35*	12.61(25)	*13.52*	13.40(20)	*14.69*
MgO	4.23(3)	*4.32*	3.94(2)	*4.07*	3.86(5)	*4.14*	4.02(2)	*4.40*
CaO	9.62(12)	*9.83*	9.60(5)	*9.91*	8.48(10)	*9.08*	9.38(8)	*10.28*
Na_2O	3.06(3)	*3.12*	2.98(2)	*3.08*	2.85(15)	*3.05*	2.36(13)	*2.58*
K_2O	0.52(1)	*0.53*	0.51(1)	*0.53*	0.51(2)	*0.55*	0.41(1)	*0.45*
P_2O_5	0.09(1)	–	2.40(6)	–	5.62(18)	–	9.54(6)	–
Total	98.00	*100.0*	99.29	*100.0*	98.93	*100.0*	100.77	*100.0*
Viscosity (CO_2) Run no.	MTV6		MTV9		MTV7		MTV8	
SiO_2	50.84(41)	*51.01*	49.61(46)	*50.94*	49.04(37)	*51.16*	47.15(10)	*51.36*
TiO_2	4.26(4)	*4.27*	4.27(3)	*4.38*	4.18(2)	*4.36*	4.03(4)	*4.39*
Al_2O_3	11.38(2)	*11.41*	11.01(11)	*11.3*	10.92(7)	*11.39*	10.48(4)	*11.42*
FeO*	15.05(34)	*15.09*	14.73(48)	*15.12*	14.46(5)	*15.08*	13.90(22)	*15.14*
MgO	4.42(11)	*4.43*	4.46(9)	*4.58*	4.28(4)	*4.46*	4.11(3)	*4.47*
CaO	10.18(23)	*10.21*	10.04(17)	*10.31*	9.76(3)	*10.18*	9.49(3)	*10.34*
Na_2O	3.01(4)	*3.02*	2.81(3)	*2.88*	2.66(2)	*2.77*	2.24(1)	*2.44*
K_2O	0.55(2)	*0.55*	0.47(1)	*0.48*	0.57(1)	*0.59*	0.41(1)	*0.44*
P_2O_5	0.04(1)	–	2.51(4)	–	4.92(14)	–	9.45(7)	–
Total	99.73	*100.0*	99.91	*100.0*	100.79	*100.0*	101.26	*100.0*
Density (Air) Run no.	MTD4		MTD6		MTD5		MTD2	
SiO_2	50.86(16)	*51.19*	49.72(38)	*51.02*	50.64(19)	*53.11*	47.42(11)	*51.99*
TiO_2	4.26(6)	*4.29*	4.24(3)	*4.35*	3.53(6)	*3.70*	3.78(5)	*4.14*
Al_2O_3	11.32(7)	*11.39*	11.09(11)	*11.38*	11.05(7)	*11.59*	10.46(5)	*11.47*
FeO*	14.89(17)	*14.99*	14.72(25)	*15.11*	13.49(16)	*14.15*	13.40(20)	*14.69*
MgO	4.42(4)	*4.45*	4.43(5)	*4.55*	3.96(5)	*4.15*	4.02(2)	*4.40*
CaO	10.06(9)	*10.13*	9.98(19)	*10.24*	9.15(11)	*9.60*	9.38(8)	*10.28*
Na_2O	3.05(5)	*3.07*	2.80(3)	*2.87*	2.85(4)	*2.99*	2.36(13)	*2.58*
K_2O	0.49(2)	*0.49*	0.47(1)	*0.48*	0.68(3)	*0.71*	0.41(1)	*0.45*
P_2O_5	0.08(3)	–	2.50(5)	–	5.66(23)	–	9.54(6)	–
Total	99.43	100.0	99.95	*100.0*	101.01	*100.0*	100.77	*100.0*

[a] Analyses by electron microprobe in weight percent. Number in parentheses represents standard deviation in terms of least units cited
[b] Numbers in italics are the phosphorus free component of each composition, normalized to 100%

knowledge of the effect of phosphorus on the ferric-ferrous ratio. Samples were therefore collected during physical property measurements, and although they were not rapidly quenched, they nevertheless provide quantitative information regarding the effect of P on the ferric-ferrous ratio. Table 2 shows the experimental conditions and ferric-ferrous determination for each of the samples taken during the measurements of viscosity and density. The iron redox ratio, expressed as ln ($XFe_2O_3/XFeO$), as a function of the mole percent P_2O_5 added, in air and in CO_2, at various temperatures is shown in Fig. 1. The addition of P_2O_5 to this ferro-basaltic composition causes a reduction of ferric iron in both air and CO_2 for all measured temperatures. The samples collected in air contain more ferric iron at lower temperature, consistent with the fact that conditions become more oxidized with respect to the fayalite-magnetite-quartz (FMQ) buffer, along with ferric-ferrous ratios have been shown to remain approximately constant (Kress and Carmichael 1988). In a CO_2 atmosphere, the samples collected at 1400 and 1500° C have very similar oxidation states in agreement with the fact that the pure CO_2 buffer remains approximately parallel to FMQ over the studied temperature range. Experiments at 1600° C, in CO_2, however, have a higher ferric-ferrous ratio, suggesting that oxidation has occurred due to the rapid diffusion of oxygen at this high temperature, and the relatively slow nature of the quench method. These data have therefore been disregarded for the discussion of the effect of phosphorus on the iron redox equilibria. We cannot discount the possibility that oxidation has also occurred in the other samples, particularly at high temperature, but at fixed temperature and f_{O_2} this will not be expected to change the conclusions concerning the effect of P_2O_5 in these melts.

Table 2 Ferric-ferrous determinations

Sample no.	P_2O_5(wt%) (mol%)[a]	$T°C$	Gas	Conditions $\log_{10} f_{O_2}$	ΔFMQ	Iron redox Fe^{3+}/Fe^{2+}	$\ln Fe_2O_3/FeO$	$Fe^{2+}/\Sigma Fe$
MTV207	0.09	1594	Air	− 0.68	3.94	1.557	− 0.251	0.391
MTV201	*0.04*	1545	Air	− 0.68	4.34	1.575	− 0.239	0.388
MTV202		1496	Air	− 0.68	4.76	1.677	− 0.176	0.373
MTV203		1446	Air	− 0.68	5.20	1.745	− 0.136	0.364
MTV205		1348	Air	− 0.68	6.13	2.292	+ 0.136	0.304
MTV206		1299	Air	− 0.68	6.63	2.931	+ 0.382	0.254
MTV401	2.40	1594	Air	− 0.68	3.94	1.283	− 0.444	0.438
MTV402	*1.11*	1545	Air	− 0.68	4.34	1.352	− 0.392	0.425
MTV403		1496	Air	− 0.68	4.76	1.456	− 0.317	0.407
MTV404		1446	Air	− 0.68	5.20	1.593	− 0.227	0.386
MTV405		1397	Air	− 0.68	5.65	2.030	+ 0.015	0.330
MTV302	5.62	1496	Air	− 0.68	4.76	1.213	− 0.500	0.452
MTV303	*2.63*	1446	Air	− 0.68	5.20	1.464	− 0.312	0.406
MTV304		1397	Air	− 0.68	5.65	1.699	− 0.163	0.371
MTV305		1248	Air	− 0.68	7.18	1.798	− 0.107	0.357
MTV101	9.54	1570	Air	− 0.68	4.14	1.001	− 0.692	0.500
MTV102	*4.47*	1545	Air	− 0.68	4.34	1.206	− 0.506	0.453
MTV104		1446	Air	− 0.68	5.20	1.351	− 0.393	0.425
MTV105		1397	Air	− 0.68	5.65	1.604	− 0.221	0.384
MTV601	0.04	1600	CO_2	− 2.46	2.12	1.586	− 0.232	0.387
MTV602	*0.02*	1500	CO_2	− 2.74	2.66	0.851	− 0.854	0.540
MTV603		1400	CO_2	− 3.07	3.24	0.918	− 0.779	0.521
MTV904	2.51	1600	CO_2	− 2.46	2.12	1.078	− 0.618	0.481
MTV902	*1.14*	1500	CO_2	− 2.74	2.66	0.836	− 0.872	0.545
MTV903		1400	CO_2	− 3.07	3.24	0.965	− 0.729	0.509
MTV701	4.92	1600	CO_2	− 2.46	2.12	0.951	− 0.743	0.513
MTV702	*2.32*	1500	CO_2	− 2.74	2.66	0.738	− 0.997	0.575
MTV703		1400	CO_2	− 3.07	3.24	0.766	− 0.960	0.566
MTV801	9.45	1600	CO_2	− 2.46	2.12	0.688	− 1.067	0.592
MTV802	*4.41*	1500	CO_2	− 2.74	2.66	0.589	− 1.222	0.629
MTV803		1400	CO_2	− 3.07	3.24	0.595	− 1.213	0.627
MTD4	0.08	1292	Air	− 0.68	6.71	3.125	+ 0.446	0.242
MTD6	2.50	1292	Air	− 0.68	6.71	3.068	+ 0.428	0.246
MTD5	5.66	1292	Air	− 0.68	6.71	2.323	+ 0.150	0.301
MTD2	9.54	1292	Air	− 0.68	6.71	2.153	+ 0.074	0.317

[a] P_2O_5 contents shown as average values for each experiment in both wt% and mol%. The standard deviations of these values are shown in Table 1

The ln ($XFe_2O_3/XFeO$) along each isotherm decreases linearly with respect to molar P_2O_5 content within the uncertainties of the measurements (Fig. 1). In air, the gradient ($\Delta\ln(XFe_2O_3/XFeO)/\Delta XP_2O_5$) varies from 5.4 to 6.9. A similar reduction of ferric iron by phosphorus has been observed for a calcium silicate melt containing 5 wt% Fe_2O_3, in air (Mysen 1992). In CO_2, the gradient ranges from 8.8 to 10.9, suggesting that the reducing effect of phosphorus may become more important at lower oxygen fugacity, although more experiments are needed to verify this.

The effect of phosphorus on viscosity

The viscosity data for all experiments are presented in Table 3. Figs. 2a, b show the temperature dependence of the viscosity of the studied compositions in air and CO_2 respectively. The temperature dependence of the viscosity of silicate melts may be described by the Arrhenius Equation;

$$\log_{10}\eta\,(\text{dPa}\,s) = \log_{10}\eta_0\,(\text{dPa}\,s) + 2.303E/RT \quad (1)$$

where η is the viscosity, E is the activation energy, R is the gas constant and T is the absolute temperature. The curves shown in Fig. 2 are not linear and show an increasing departure from Arrhenian behaviour with falling temperature. This is consistent with the observation that systems poor in silica are in general non Arrhenian (e.g. Richet 1984). However, despite the departure from Arrhenian behaviour towards lower temperature, Eq. (1) satisfactorily describes the viscosity

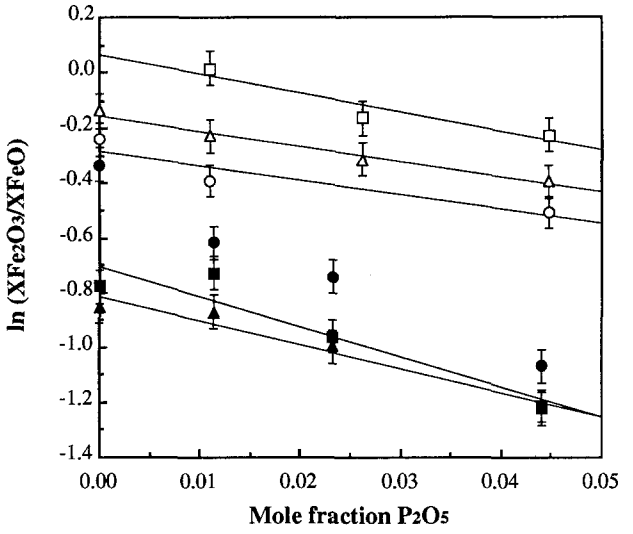

Fig. 1. The iron redox ratio [expressed as ln ($XFe_2O_3/XFeO$)] as a function of the mole fraction of P_2O_5 added. *Filled symbols* represent experiments carried out in a CO_2 atmosphere (*squares* 1400°C, *triangles* 1500°C, *circles* 1600°C), and the *open symbols* represent experiments carried out in air (*squares* 1397°C, *triangles* 1446°C, *circles* 1545°C). A linear regression of each data set is also shown (the fit to the data r^2 varies between 0.87 and 0.98). The gradient varies from 5.4 to 6.9 in air, and from 8.8 to 10.9 in CO_2. Experiments in CO_2 at 1600°C are not considered due to potential oxidation (as discussed in the text)

of these compositions over the studied temperature range. This contrasts with the viscosity of pure molten P_2O_5, which shows Arrhenian behaviour over a large temperature range (Cormia et al. 1963). For each composition the data have been regressed using an equation of the form:

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

The a and b parameters and calculated values of the activation energy E using Eq. (1) are shown in Table 4.

The effect of the addition of P_2O_5 on viscosity is shown in Figs. 3a–c along three isotherms covering the studied range of temperature. At low P contents in air there is an initial decrease in viscosity at all the studied temperatures. In a CO_2 atmosphere at 1600° C a decrease in viscosity at low P content is also observed, while at 1400 and 1250° C the viscosity shows a small initial increase. Further addition of phosphorus leads to a large increase in the viscosity of the melt in both air and CO_2. The viscosity of a fixed composition measured in CO_2 is always lower than that measured in air. The magnitude of this decrease is greatest in phosphorus-free melts (typically 10% relative) and decreases to almost zero for the composition containing 9.5 wt% P_2O_5 (Figs. 3a–c). This range of variation in viscosity due to changing oxidation state is consistent with that observed for various ferro-silicate compositions (Dingwell and Virgo 1987; Dingwell 1991).

When considering the variation of viscosity due to the addition of phosphorus, the reduction of ferric to ferrous iron must also be taken into account. The viscosity of the Fe-bearing silicate melts studied by Dingwell (1991) all showed the same general dependence on oxidation state. At oxidizing conditions ($Fe^{2+}/\Sigma Fe < 0.3$) the reduction of ferric to ferrous iron causes a large decrease in viscosity. However, with further reduction, the viscosity decrease (i.e $\Delta\eta/\Delta Fe^{2+}/\Sigma Fe$) diminishes to zero, and the viscosity reaches a steady value, independent of the ferric-ferrous ratio. At fixed temperature and f_{O_2}, the variation of viscosity on addition of P_2O_5 is therefore considered to be controlled by: (1) a reduction of ferric iron which favours a decrease in viscosity; (2) a change in melt structure which favours an increase in viscosity. With decreasing ferric iron content, process (2) becomes progressively dominant, and the increase in viscosity, with addition of phosphorus, will approach linearity. Under these conditions, the viscosity may be approximated by an equation of the form:

$$\log_{10}\eta\,(\text{dPa}\,s) = \Sigma X_i D_i \tag{3}$$

where η is the viscosity, X_i is the mole fraction of the oxide component i and D_i is an empirical constant associated with component i for a given temperature. The gradient of the linear portion of Figs. 3a–c thus allows us to estimate values for $D_{P_2O_5}$ (the viscosity coefficient of phosphorus, in the sense of Bottinga and Weill 1972) in this melt at various temperatures. Values for the viscosity coefficient at 50° C intervals between 1600 and 1250° C are shown in Table 5.

The effect of P_2O_5 on density

The densities of the studied compositions are shown graphically in Fig. 4a as a function of the weight percent P_2O_5 added. The measured values of density, the calculated molar mass (using the measured values of ferric and ferrous iron), and the calculated molar volumes (= molar mass/density) of these compositions are shown in Table 6. Figure 4b shows the calculated molar volume as a function of the mole percent P_2O_5 in the liquid. The data show that addition of phosphorus causes a significant decrease in the density of the ferro-basaltic starting composition (Fig. 4a). The rate of decrease of density and increase of the molar volume are linear within the error of the experimental measurements. If the partial molar volume (V_m) of the SC4 component (i.e. the P_2O_5-free fraction of the melt) remains constant then the molar volume of the system is described by:

$$V_m = (1-x)V_m^{SC4} + xV_m^{P_2O_5} \tag{4}$$

where x is the mole fraction of P_2O_5. Rearranging Eq. (4) gives V_m as a function of x and the y-intercept is

Table 3 Viscosity measurements

Air Run no.	P_2O_5 (wt%) (mol%)	$T°$ C	Log_{10} viscosity (dPa s)	CO_2 Run no.	P_2O_5 (wt%) (mol%)	$T°$ C	Log_{10} viscosity (dPa s)
MTV2	0.09	1594	0.978	MTV6	0.04	1600	0.955
	0.04	1545	1.112		0.02	1550	1.075
		1496	1.261			1500	1.217
		1446	1.423			1450	1.367
		1397	1.587			1400	1.530
		1348	1.767			1350	1.716
		1299	1.976			1300	1.919
		1249	2.216			1250	2.155
MTV4	2.40	1594	0.946	MTV9	2.51	1600	0.936
	1.11	1545	1.088		1.14	1550	1.075
		1496	1.238			1500	1.225
		1446	1.399			1450	1.388
		1397	1.565			1400	1.551
						1350	1.733
						1300	1.938
						1250	2.173
MTV3	5.62	1594	1.051	MTV7	4.92	1600	0.995
	2.63	1545	1.185		2.32	1550	1.128
		1496	1.337			1500	1.283
		1446	1.498			1450	1.446
		1397	1.672			1400	1.623
		1348	1.851			1350	1.809
		1299	2.072			1300	2.027
		1249	2.316			1250	2.275
MTV1	9.54	1594	1.135	MTV8	9.45	1600	1.101
	4.47	1570	1.194		4.41	1550	1.248
		1545	1.267			1500	1.412
		1496	1.427			1450	1.571
		1446	1.589			1400	1.749
		1397	1.761			1350	1.956
		1348	1.966			1300	2.188
		1299	2.199			1250	2.457
		1249	2.446				
		1200	2.760				

V_m^{SC4}. This gives a calculated $V_m^{P_2O_5}$ of 59.7 cm^3/mol for P_2O_5 at 1292° C in this melt. However, because there is a change of ferric-ferrous ratio associated with the addition of phosphorus, the molar volume of the SC4 component does not remain constant. The magnitude of this effect has been evaluated by calculating the V_m^{SC4} for the normalized P-free portion of each melt, using the major element data from Table 1, the ferric-ferrous determinations from Table 2, and the calculation procedure of Lange and Carmichael (1990). These values are shown in Table 6 and plotted in Fig 4b. This effect leads to a decrease of V_m^{SC4} which is small compared to the increase due to the addition of P_2O_5 but must be corrected for in the calculation of $V_m^{P_2O_5}$. This gives a revised value for the partial molar volume of P_2O_5 in this melt at 1292° C of 64.5 $\pm$ 0.7 cm^3/mol. This partial molar volume is 12.9 cm^3/mol per oxygen, consistent with a tetrahedral coordination for this high field strength cation (Lange and Carmichael 1990).

Discussion

Estimation of the physical properties of P_2O_5-bearing melts using existing calculation schemes

A knowledge of the physical properties of magmas is essential for a complete understanding of magmatic processes and interpretation of field observations, thus calculation schemes for estimating their values have become invaluable aids to petrologists. Despite the minor element concentrations of P_2O_5 in most natural compositions, it does not appear in the commonly used schemes for the calculation of ferric-ferrous ratio (Kilinc et al. 1983) or density (Lange and Carmichael 1990) and is simply added to silicon in the scheme of Bottinga and Weill (1972) for viscosity. Below we assess the success of the above models to predict these parameters in phosphorus-bearing systems.

Although the ferric-ferrous ratio of a magma is

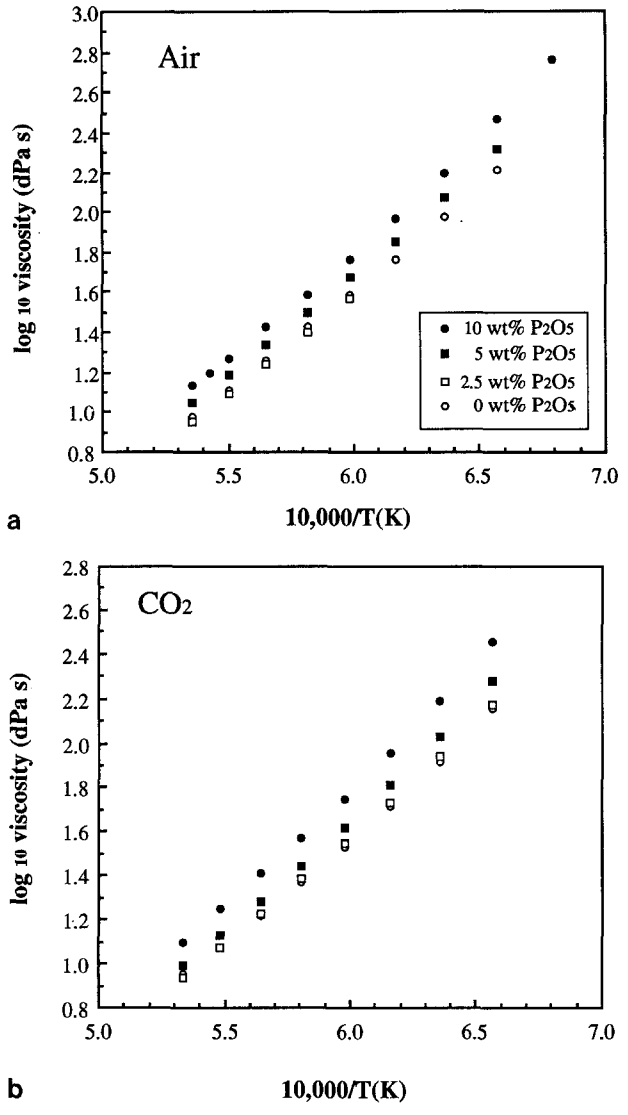

Fig. 2a, b The viscosity-temperature relationship of ferro-basaltic melts with added P_2O_5 in (**a**) air; (**b**) CO_2. (*Open circles* P-free composition, SC4, *open squares* SC4 + 2.5 wt% P_2O_5, *filled squares* SC4 + 5 wt% P_2O_5, *filled circles* SC4 + 10 wt% P_2O_5). See Table 1 for the exact compositions

primarily controlled by temperature and oxygen fugacity, there is also an important compositional dependence (Fudali 1965; Thornber et al. 1980; Sack et al. 1980; Kilinc et al. 1983). The most successful method to date for the estimation of ferric-ferrous ratios, first used by Sack et al. (1980), uses an empirical equation of the form below:

$$\ln(X\mathrm{Fe_2O_3}/X\mathrm{FeO}) = a\ln f_{\mathrm{O_2}} + b/T + c + \Sigma d_i X_i \quad (5)$$

where T is the absolute temperature, X_i is the mole fraction of the species i, and a, b, c, d_i are constants calculated from a linear regression of experimentally determined ferric-ferrous ratios over a wide range of composition, temperature and f_{O_2}. The commonly used regression of Kilinc et al. (1983) contains compositional

Table 4 Fit parameters and calculated activation energies for the studied melts assuming Arrhenian behaviour

Run no.	a	b ($\times 10^4$)	E(kJ mol^{-1})	n
MTV2	− 4.46[b]	1.012[a]	193.8	8
MTV4[a]	− 4.30	0.980	187.7	5
MTV3	− 4.51	1.036	198.4	8
MTV1	− 4.91	1.121	214.6	10
MTV6	− 4.28	0.975	186.7	8
MTV9	− 4.41	1.000	191.4	8
MTV7	− 4.57	1.038	198.7	8
MTV8	− 4.75	1.093	209.2	8

[a] NB only five data points
[b] The fit r^2 is > 0.995 in all cases (n number of data points used in the regression)

terms only for K_2O (d_{K_2O}, + 9.6); Na_2O (d_{Na_2O}, + 8.4); CaO (d_{CaO}, + 3.0); total iron as FeO (FeO*) (d_{FeO^*}, + 1.6); Al_2O_3 ($d_{Al_2O_3}$, − 2.2). The gradient of Fig. 1 suggests that $d_{P_2O_5}$ has a value of *at least*-6, implying that P_2O_5 has a greater reducing effect than any of the quoted oxide components. Furthermore, Fig. 1 suggests even greater absolute values of $d_{P_2O_5}$ at lower f_{O_2}. The success of the formulation of Kilinc et al. (1983) in estimating the ferric-ferrous ratio of these melts is shown in Fig. 5. The data lie within an acceptable range given the relatively large uncertainties ($\pm$ 0.2 ln units) associated with the model. In general, low phosphorus glasses (open symbols) lie below the 1 : 1 correlation, while high phosphorus glasses (filled symbols) lie above it, in agreement with the observed reducing effect of phosphorus. In the light of the potential problems of oxidation during the quench discussed earlier, the measured values will tend to overestimate the ferric-ferrous ratio, particularly at high temperature. If the values measured at high temperature are qualitatively shifted to lower ferric-ferrous ratios, the phosphorus-rich compositions will then lie well above the 1 : 1 correlation, i.e. the model of Kilinc et al. (1983) will underestimate the ferric-ferrous ratio. For a large range of basaltic melts the formulations of Kilinc et al. (1983) remains the best possible means of calculating ferric-ferrous ratios. However, in the light of these results, we suggest that for phosphorus-bearing basaltic melts, a compositional term for P_2O_5 of at least-6 should be used.

In order to estimate the viscosity of natural melts, Bottinga and Weill (1972) used a large set of viscosity measurements to evaluate viscosity coefficients for many melt components (using the form of Eq. 3), at 50° C and restricted SiO_2 mole fraction intervals. There is no phosphorus-bearing component in this model, although the authors suggest that phosphorus should be added to silicon. Our experimental results and the calculated viscosities using the model of Bottinga and Weill (Fig. 6) are in good agreement, and well within the errors stated for the model ($\pm$ 0.2 $\log_{10}$ units). The

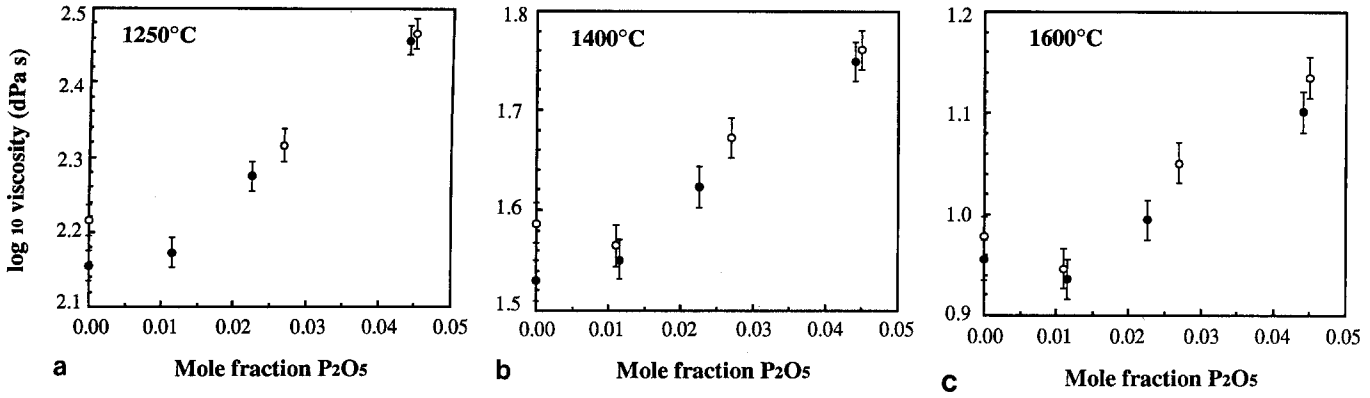

Fig. 3a–c The viscosity as a function of mole fraction P_2O_5 added at (**a**) 1250°C; (b) 1400°C; (**c**) 1600°C. The exact temperatures are marked in Table 3. (*Filled symbols* experiments carried out in CO_2, *open symbols* experiments carried out in air

Table 5 Viscosity coefficients for P_2O_5

$T°C$	$D_{P_2O_5}$ $\log_{10}$ dpa mol^{-1}	$D_{PO_{2.5}}$ ln dpa mol^{-1}	D_{SiO_2}(B + W 72)[a] ln dpa mol^{-1}
1600	5.06	5.83	4.87[b]– 6.80[c]
1550	5.36	6.17	5.39 – 7.35
1500	5.79	6.67	6.00 – 7.97
1450	5.66	6.52	6.60 – 8.58
1400	6.06	6.98	7.26 – 9.25
1350	6.86	7.90	7.97 – 9.97
1300	7.66	8.82	8.70 –10.72
1250	8.70	10.02	9.50 –11.52

[a] Values quoted by Bottinga and Weill (1972)
[b] For $XSiO_2 = 0.45$–0.55
[c] For $XSiO_2 = 0.55$–0.65

addition of phosphorus to silicon thus seems to be appropriate. This may be understood in terms of the similarity of the calculated viscosity coefficients for $PO_{2.5}$ and SiO_2 at the same temperature (Table 5). Thus the addition of phosphorus to ferro-basaltic melts increases the viscosity in an almost identical manner to that of SiO_2.

The partial molar volume data presented by Lange and Carmichael (1990) represent the most recent method of estimating the densities of natural magmas. The quoted values for partial molar volume are assumed to be compositionally independent although there are data indicating that the partial molar volumes of Fe_2O_3 and TiO_2 exhibit compositional dependence (for Fe_2O_3 see Dingwell and Brearley 1988; Hara et al. 1988; Dingwell 1990; for TiO_2 see Johnson and Car michael 1987; Dingwell 1992 also see review by Lange and Carmichael 1990) and the case of Al_2O_3 remains unclear (Ghiorso and Carmichael 1984; Bottinga et al. 1982, 1984). The values of density obtained here, even in the phosphorus-free system, show considerable discrepancy with the values calculated using the scheme of Lange and Carmichael (1990). This may result from the

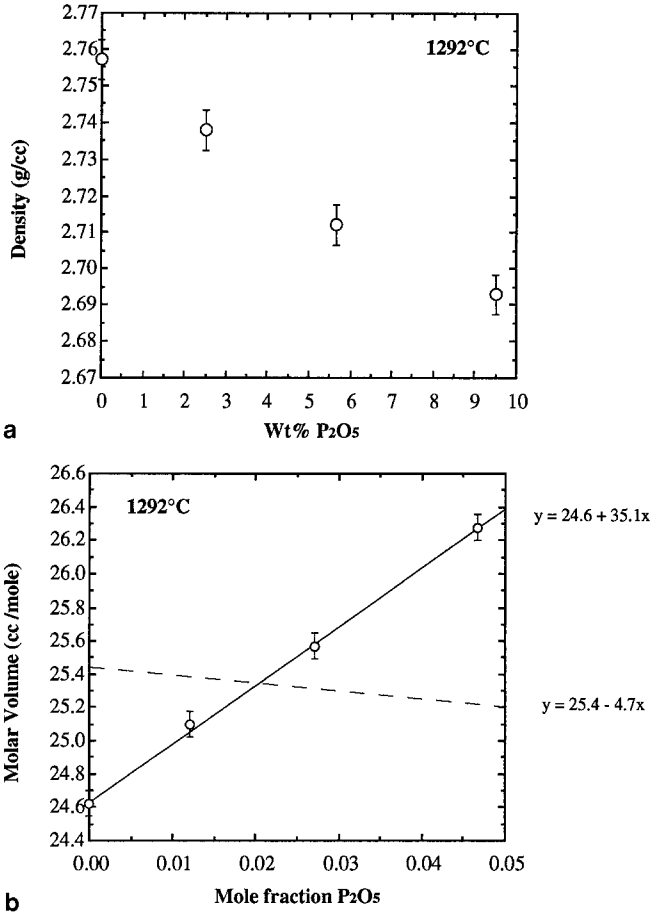

Fig. 4a The measured density of the studied melts as a function of the weight percent P_2O_5 in the liquid. The error *bars* represent the error of measurement, 0.2%. **b** The molar volumes of the studied melts (estimated from the measured densities) as a function of the mole fraction of P_2O_5 added. The change in the molar volume of the P-free fraction, due to changing ferric-ferrous ratio, estimated from the data of Lange and Carmichael (1990), is also shown (*dashed line*)

ferric iron- and titanium-rich nature of the studied composition. Figure 4b shows the important increase in partial molar volume associated with the addition of phosphorus to this composition. Therefore, the calculated partial molar volume of 64.5 cm^3/mol at 1300° C for P_2O_5 should be included in the calculation of basaltic liquid densities.

Table 6 Density determinations

Run no.	Wt%P_2O_5	Mol%P_2O_5	Measured ($SC4 + P_2O_5$) Density (g/cc)	Molar mass	Molar volume	SC4 Component Molar mass	Molar volume L + C90[a]	Density (g/cc) L + C90
MTD4	0.08	0.04	2.757	67.87	24.62	67.84	25.44	2.667
MTD6	2.51	1.20	2.738	68.73	25.10	67.84	25.38	2.673
MTD5	5.66	2.71	2.712	69.33	25.57	67.31	25.47	2.642
MTD2	9.50	4.67	2.693	70.76	26.27	67.27	25.22	2.667

[a] Calculated from the normalized P-free compositions (Table 1), the measured ferric and ferrous iron contents (Table 2), and the oxide partial molar volumes of Lange and Carmichael (1990)

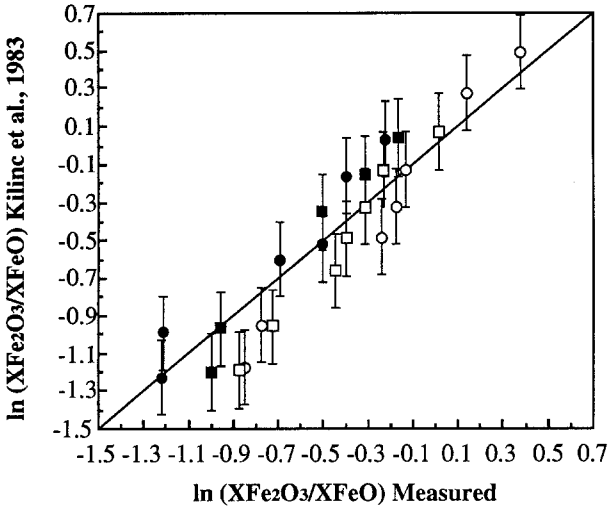

Fig. 5 Measured values of the iron redox ratio [expressed as ln ($XFe_2O_3/XFeO$)] compared with values calculated using the scheme of Kilinc et al. (1983). Symbols are the same as Fig. 2. Samples taken above 1570°C are not shown due to potential oxidation (as discussed in the text)

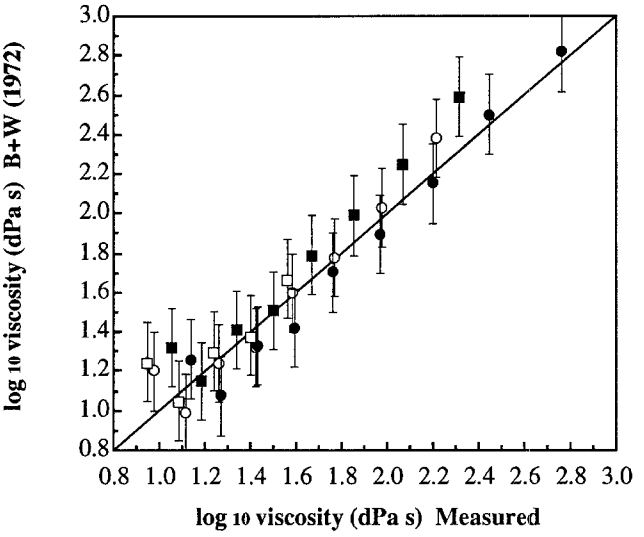

Fig. 6 Comparison of measured values of the melt viscosity for experiments carried out in air, with values calculated using the scheme of Bottinga and Weill (19782). Symbols as in Fig. 2

Implications for the structural role of P in ferro-basaltic melts

The solution behaviour of phosphorus in silicate melts is complex. The addition of P_2O_5 to pure SiO_2 lowers the liquidus temperatures of silica polymorphs, indicating a decrease of the silica activity (a_{SiO_2}), caused by depolymerization via the formation of P–O–Si bonds in the silicate network (Ryerson and Hess 1980). In contrast, spectroscopic (Nelson and Tallant 1984; Duprée et al. 1988; Mysen 1992; Gan and Hess 1992) and phase equilibria (Kushiro 1975; Ryerson and Hess 1980; Ryerson 1985) evidence from melts rich in network modifying metal cations suggests that addition of phosphorus removes these metal cations to form discrete phosphate (PO_4^{3-}) complexes outside of the aluminosilicate network where P is tetrahedrally coordinated (consistent with the calculated partial molar volume per oxygen of phosphorus in this melt). This results in the formation of more Si–O–Si bonds, by a reaction of the type:

$$2Si\text{–}O\text{–}M + P\text{–}O\text{–}P \Leftrightarrow Si\text{–}O\text{–}Si + 2P\text{–}O\text{–}M \quad (6)$$

where M is a metal cation. The increase in polymerization of the aluminosilicate network associated with reaction (6) may be expected to cause an increase in viscosity, because silicate melts rich in network forming cations are generally more viscous than those rich in network modifying cations. The overall increase in viscosity with the addition of P_2O_5 observed for this melt (Fig. 3) is a rare exception to the rule that the dilution of SiO_2 and Al_2O_3 in basic melts reduces the viscosity, and supports the evidence that reaction (6) is a plausible mechanism to describe the solution behaviour of phosphorus in these melts. However, if reaction (6) alone was controlling the variation of viscosity as P_2O_5 is added, one would expect the η versus XP_2O_5 curves (Fig. 3) to be linear, which at low P_2O_5 contents they are not. As stated previously, we attribute the

variation in viscosity at low P_2O_5 content to the observed reduction of ferric to ferrous iron. Under oxidizing conditions, ferric iron is known to be, at least in part, tetrahedrally coordinated in silicate melts (Mysen et al. 1980, 1985; Dingwell and Virgo 1987). The destabilization of tetrahedral (network forming) ferric iron will result in the formation of ferrous iron and the release of the charge balancing cations associated with the $Fe^{3} \leftrightarrow Si^{4+}$ substitution. These cations are most likely to occupy network modifying roles, thus decreasing the bulk polymerization and favouring a decrease of viscosity. With the addition of phosphorus, the overall viscosity change will therefore be a function of the increasing polymerization associated with reaction (6) and the decreasing polymerization due to the destabilization of tetrahedral ferric iron. The observed form of the η versus XP_2O_5 curves suggests that at low P content, the reduction of ferric iron has an influence on the viscosity which is of the same order of magnitude as that caused by the polymerizing effect of P_2O_5. In air, where ferric iron contents are greatest, this effect may cause a decrease in viscosity, while in a CO_2 atmosphere, where ferric iron contents are lower, reaction (6) just dominates. The subsequent strong increase of viscosity with further addition of P_2O_5 implies that reaction (6) has an increasing influence on the overall viscosity change, despite the fact that ferric iron is still being reduced. This is consistent with the viscosity data of Dingwell (1991), where the viscosity decrease due to the reduction of ferric iron is strong at oxidizing conditions, but diminishes to zero with increasing reduction. This may be explained by ferric iron becoming increasingly in octahedral rather than tetrahedral coordination as the oxidation state falls, as has been suggestedfrom Mössbauer spectra of various iron-bearing melts (Mysen et al. 1985).

Indications of the structural role of phosphorus in this basaltic melt may also be inferred from the rate of increase of viscosity at high P content (i.e $D_{P_2O_5}$). The fact that $D_{PO2.5}$ and D_{SiO_2} have similar values (Table 5), implies that the equimolar addition of $PO_{2.5}$ and SiO_2 results in a comparable increase in viscosity. This is entirely consistent with Eq. (6), where the addition of phosphorus (P–O–P) results in the formation of Si–O–Si bonds. The increase in viscosity associated with the addition of phosphorus may be viewed thermodynamically as a combination of an increase in mean cation oxygen bond strength due to the increased number of Si–O–Si bonds (enthalpic effect), as well as a contribution from increased ordering in the liquid structure due to the non-participation of P in the silicate network (entropic effect).

The studied ferro-basaltic composition is rich in network modifying cations, and reaction (6) may proceed to the right for the entire range of studied P_2O_5 content. A comparison of our results with those obtained in a granitic system, where insufficient cations are available to allow reaction (6) take place, (Dingwell et al. 1992, 1993; Gwinn and Hess 1993) are summarized in Table 7. The observed variations and effects of phosphorus on the viscosity, density and ferric-ferrous ratio of this ferro-basalt all contrast with the results obtained in the granitic system. This provides further evidence that the speciation of phosphorus is very different in silica-rich and silica-poor melts (e.g. Mysen 1988). Such a large dependence of the effects of phosphorus on bulk composition highlights the danger of extrapolation of results outside of the compositional range where they were collected.

Implications for natural systems

A number of natural ferro-basaltic systems, with compositions similar to those studied here have been reported to have important enrichments in P_2O_5. The Skaergaard Intrusion is an example where the coexisting liquid has been estimated to have contained a maximum of 1.3–1.75 wt% P_2O_5 (Wager and Brown 1967; McBirney and Naslund 1990). This range of values may be typical of layered basic intrusions where phosphorus enriches in the melt until the crystallization of a phosphate phase. Monzonoritic compositions found in association with many massive anorthosites commonly contain in excess of 2wt% P_2O_5 (Morse 1982; Duschene 1984), and enrichments of up to 8wt% P_2O_5 have been documented for some iron-rich immiscible liquid globules (Philpotts 1982).

Table 7 Summary and comparison with granitic system

Property	Composition Ferrobasalt	Granite
Effect on ferric-ferrous ratio	Large decrease	Small increase[a]
Effect on viscosity	Large increase	Small decrease[b]
Arrhenian behaviour	No	Yes[b]
Activation energy (kJ/mol)	187–215	372–436[b]
Partial molar volume (cc/mol	64.5 at 1292° C	67.1 at 750° C[c]

[a] From Gwinn and Hess (1993)
[b] From Dingwell et al. (1993)
[c] From Dingwell et al. (1992)

The observed reduction of ferric to ferrous iron in these liquids may affect the stability of Fe–Ti oxides at lower temperature. Indeed, Toplis et al. (1994) observed that the addition of phosphorus to this same composition (SC4), resulted in a large destabilization of magnetite. Although this destabilization was attributed to formation of $P–Fe^{3+}$ complexes in the melt, the results of this study indicate that the reduction of ferric iron will also play a role. More experiments are needed to clarify the relative roles of these two processes at conditions around the FMQ buffer, relevant to the crystallization of natural basaltic systems (Carmichael 1991).

The viscosity of a magma controls many of the physical processes occurring in crustal magma chambers. This study shows that for melts rich in ferric iron, enrichment in phosphorus of a few weight percent may not greatly affect the viscosity. However, natural basalts have low ferric iron contents, due to the low f_{O_2} prevailing during crystallization. Therefore, the effect of phosphorus will, above all, be to increase the viscosity. This increase is of the order of 15% relative per wt% P_2O_5 (Fig. 3a) at temperatures relevant to the crystallization of natural basalts (1100–1200° C). Thus this effect of phosphorus on the viscosity must be taken into account when estimating physical processes, such as flow mechanisms and mass transfer of natural basaltic magmas.

The trend of iron enrichment during tholeiitic differentiation generally leads to an increase in melt density, until the appearance on the liquidus of an Fe–Ti oxide (e.g. Snyder et al. 1992). Due to the incompatible nature of phosphorus during the early stages of crystallization, the melt phase will become enriched in both iron and phosphorus. This study shows that the phosphorus enrichment will tend to counteract the increase in density due to the iron enrichment. This implies that as differentiation proceeds, the density of the residual liquids may be considerably lower than that predicted by the calculation scheme of Lange and Carmichael (1990). This in turn may affect conclusions reached concerning the relative buoyancy of liquids and crystals, or interstitial and overlying liquids in a cumulate pile. This underlines the fact that phosphorus *must* be taken into account in calculations of density in ferro-basaltic systems.

Conclusions

The effects of P_2O_5 on the redox ratio, viscosity and density of a ferro-basaltic melt under oxidizing conditions have been determined experimentally. The addition of P_2O_5 causes: (1) a reduction of ferric iron; (2) an initial decrease and subsequent strong increase in viscosity; (3) a decrease of density. The variation of all these parameters is shown to be significant. The magnitude of the reduction of ferric iron is greater than that of all the quoted oxide components in the calculation scheme of Kilinc et al. (1983). The overall increase in viscosity at 1200° C is estimated to be of the order of 15% relative per wt% P_2O_5, which is of the same order of magnitude as SiO_2. A partial molar volume for P_2O_5 of 64.5 cm^3/mol has been determined for this ferro-basalt at 1300° C, consistent with a high field strength cation in tetrahedral coordination.

The non linear variation of viscosity may be explained in terms of the competing effects of: (1) the depolymerizing effect caused by the destabilization of tetrahedral ferric iron; (2) the removal of network modifying cations and the formation of more Si–O–Si bonds caused by the addition of P. Thus the addition of phosphorus to ferro-basaltic melts causes variations in both the mean cation-oxygen bond strength and the degree of ordering in the melt structure, that is enthalpic as well as entropic effects.

This study suggests that enrichment in phosphorus during basaltic differentiation may: (1) contribute to the destabilization of magnetic by reduction of ferric iron; (2) influence flow mechanisms and mass transfer processes by the increase in viscosity; (3) affect the relative buoyancy of liquids and crystals as crystallization proceeds; (4) counteract the density increase associated with iron enrichment. However, comparison of the data in ferro-basaltic and granitic systems illustrates the strong compositional dependence of the effect of phosphorus on physical and chemical properties. Extrapolation of these properties outside of the compositional range where they were collected is therefore not advised.

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