Dependence of Fe³⁺/Fe²⁺ ratio on oxygen fugacity and temperature in melts of granitoid composition on experimental data

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The experiments with melts of granitic and pantelleritic compositions conducted within temperature range 1220÷1420°C and fO_2 10^{-0.7}÷10⁻¹¹ bar (P_{tot} = 1 atm) showed that the dependence of Fe³⁺/Fe²⁺ in melt on oxygen fugacity (fO_2) in isothermal conditions is described by equation $\log(Fe^{3+}/Fe^{2+}) = k*\log(fO_2) + q$, where k and q are constants depending on melt composition and temperature. Under given fO_2-T conditions the degree of iron oxidation in more alkaline and iron enriched pantelleritic melt is higher than that in granitic melt. The Fe³⁺/Fe²⁺ ratio decreases in both types of melts with temperature increase at $fO_2 = \text{const}$. The data obtained are compared with results of other experimental investigations of granitoid melts, as well as calculations made using a previously proposed empirical equations (Fe³⁺/Fe²⁺)_{melt} = f(T, fO_2 , melt composition). It is shown that the available empirical equations, that adequately describe the experimental data for two types of silicic aluminosilicate melts, namely, granite and comendite-pantellerite compositions respectively, within temperature range ~ 1200(1100)– 1450°C.

Key words: redox state of iron, silicic aluminosilicate melts, oxygen fugacity, granite, pantellerite

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Introduction

The redox state of iron in melts, which controls to a large extent their physical properties and direction of evolution during crystallization differentiation depends on number of external and internal parameters: temperature, pressure, oxygen fugacity and melt chemistry. The knowledge of the influence of these parameters on ferric-ferrous ratio of natural aluminosilicate melts provides means for the reconstruction of redox conditions of their formation. Up to date, several empirical equations have been derived on the basis of extensive experimental data to connect redox state of iron, temperature, oxygen fugacity and melt composition [*Sack et al., 1980; Kilinc et al., 1983; Mysen, 1991; Борисов, Шалкин, 1989; Kress, Carmichael, 1991; Николаев и др., 1996; Jayasuriya et al., 2004*]. They describe fairly well the dependence of these parameters at magmatic T-fO₂ conditions for a wide range of natural silicate melts, mainly of basic composition. However, their validity for granitoid melt remains questionable. Although a number of earlier experimental investigations have been reported [*Sack et al., 1980; Kilinc, et al., 1983; Bychkov, Borisov, 1992; Moore et al., 1995*], the influence of *f*O₂ and *T* on Fe³⁺/Fe²⁺ ratio in silicic aluminosilicate melts is still poorly understood. New experimental data obtained by us for silicic melts of granite and pantellerite composition [*Volovetsky et al, 2012*] allow to consider this problem in more detail.

Experimental data

Experiments with melts of granite (I2) and pantellerite (P9) compositions (Table 1) were conducted within temperature range $1220 \div 1420^{\circ}$ C and $fO_2 \ 10^{-0.7} \div 10^{-11}$ bar at a total pressure of 1 atm [*Volovetskii et al., 2012*] using high-temperature furnace, which provides given partial pressure of oxygen during the experiments [*Kargal'tsev et al., 2010*]. The valence state of iron in quenched glasses obtained after the runs was determined by Mössbauer spectroscopy.

Table 1. Chemical composition of initial samples

Sample SiO ₂ TiO ₂ Al ₂ O ₃ Fe	* MnO MgO Ca	O Na ₂ O K ₂ O Cl	ZrO_2 Σ
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Granite I2	70.46	0.06	15.28	3.41	0.05	0.14	2.06	4.07	3.95	-	-	99.53
Pantel. P9	69.28	0.36	7.69	7.82	0.31	0.07	0.34	6.61	4.37	0.51	0.33	97.36

Influence of fO_2 **.** The results of experiments that demonstrate the dependence of redox state of iron in melts (quenched glasses) from oxygen fugacity at temperatures of 1220, 1340(1320) and 1420°C are shown in Fig. 1. The fO_2 increase under isothermal conditions is accompanied by the increase of ferric iron fraction in both types of silicic melts. The diagrams show linear approximation of the dependence of $\log(Fe^{3+}/Fe^{2+})$ from $\log(fO_2)$ at constant temperature describing experimental data in the form of equations:

 $\log(Fe^{3+}/Fe^{2+}) = k \log(fO_2) + q$,

(1)

where k and q - constants. Under given fO_2 -T conditions the degree of iron oxidation in more alkaline and iron enriched pantelleritic melt is higher than that in granitic melt. This is most clearly expressed under oxidizing conditions at relatively high fO_2 . The coefficient k, which determines the slope of the isothermal line on the plot of $log(Fe^{3+}/Fe^{2+}) - log(fO_2)$ slightly differs for two melt compositions investigated: for I2 series 0.17 ± 1 at $1340^{\circ}C$ and 0.21 ± 3 at $1420^{\circ}C$; for P9 series at the same temperatures 0.22 ± 2 and 0.24 ± 1 , respectively. The value of coefficient k for each composition slightly increases with temperature increase. It should be noted that initial I2 and P9 melts undergo some changes during the experiments, especially at high temperatures 1320(1340) and $1420^{\circ}C$, mainly related to partial Na₂O loss and increasing content of Al₂O₃, due to the interaction of melt with the container material [*Volovetsky et al., 2012*]. Therefore, isothermal straight lines corresponding to different temperatures in each of the plots for I2 and P9, present the experimental data for melts of slightly different composition.



Fig. 1. Dependence of the Fe^{3+}/Fe^{2+} from the oxygen fugacity at different temperatures for granite (a) and pantellerite-comendite (b) melts.

1–4 – experimental data at different *T* (°C) (filled symbols – for I2 and P9 compositions [*Volovetskii et al., 2012*], empty symbols – for granitoid compositions according to literature data [*Sack et al., 1980; Kilinc et al., 1983; Bychkov, Borisov, 1992; Moore et al., 1995*]): 1 – 1200–1250 (1240 for I2 and 1220 for P9), 2 – 1300–1352 (1340 for I2 and 1320 ± 10 for P9), 3 – 1401–1454 (1420 for I2 and P9), 4 – 1557 and 1501 for the granite and comendite-pantellerite compositions, respectively. For I2 at 1240°C and log(fO_2) = -7 equilibrium of melt with furnace atmosphere, obviously, has not been reached.

The plots in Fig. 1 also shows the experimental data of other investigators obtained at 1 atm and different T-fO₂ conditions for natural granitoid melts of different composition. All experimentally studied melts, including I2 and P9, were divided into two groups (in wt.%): granite SiO₂>70 (73–76), FeO <3.5 (3.1–3.4), Al₂O₃ ≥12 (12.0–13.3), Na₂O+K₂O= 5.7–7.0 (Fig. 1a) and comendite-pantellerite (granites with high alkalinity and iron content) SiO₂>69 (69.3–75), FeO >5 (5.2–8.6), Al₂O₃ < 12 (8.1–11.2), Na₂O+K₂O=7.0–11 (Fig. 1b). The molar ratio (Na₂O+K₂O)/Al₂O₃ for the first group of melts is 0.6–0.8 (mean 0.75), for the second group 1.1–1.8 (mean 1.3). Dependences of log(Fe³⁺/Fe²⁺) on

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 $log(fO_2)$ for each of these groups of compositions under conditions close to isothermal (at 1225±25, 1326 ± 25 и $1427\pm 27^{\circ}$ C) can also be described by linear equations of the form (1) (dashed lines in Fig. 1a and b), that are generally in good agreement with data for I2 and P9 (Table 2).

Isothermal coefficients k for comendite-pantellerite melts have higher values as compared to granite melts. Their value for both types of melts increases with temperature increase (Table 2). Thus, the involvement of experimental data of other investigators confirmed the possibility of k value increase with temperature. However, this conclusion obviously requires further examination, due to the uncertainties of the experimental data used in the derivation of equations, that are connected with their scatter in temperature and chemical composition of the melt.

of	fO_2 on the H	Fe^{3+}/Fe^{2+} ratio in granite and comendi	te-pantelleri	te melts under isothermal conditions
	T,⁰C	I2, Granite group	T,°C	P9, Comendite-Pantellerite group
	1240	-	1220	$Y = 0.195*X + 1.21; R^2 = 0.999$
	-	-	1225 ± 25	$(Y = 0.181*X + 1.06 \cdot R^2 = 0.986)$

1320±10

1326±25

1420

 $Y = 0.224*X + 1.17; R^2 = 0.980$

 $(Y = 0.204*X + 0.96; R^2 = 0.939)$

 $Y = 0.244*X + 0.93; R^2 = 0.995$

 $Y = 0.167*X + 0.57; R^2 = 0.995$

 $(Y = 0.150*X + 0.45; R^2 = 0.942)$

 $Y = 0.211*X + 0.53; R^2 = 0.958$

1340

1420

 1322 ± 22

Table 2. Empirical equation $Y = k^*X + q$, where $X = log(fO_2)$, $Y = log(Fe^{3+}/Fe^{2+})$ describing the effect

1430±12	$(Y = 0.201*X + 0.46; R^2 =$	=0.957)	1427±27	(Y = 0.227)	$*X + 0.78; R^2$	=0.979)	
Note: in pare	entheses - equations for the	two grou	ups of melts	s obtained b	y processing	all availab	ole
experimental	data, including data for I2 ar	nd P9.					

Effect of temperature. Temperature increase at constant fO_2 leads to reduction of Fe^{3+} to Fe^{2+} in both types of melts. In a closed system, when the Fe^{3+}/Fe^{2+} in the melt is constant, a rise in temperature is accompanied by increase of fO_2 and vice versa – lowering T causes the decrease of fO_2 . Fig. 2 shows the changes in fO_2 with temperature for melts I2 and P9 with a constant ratio of Fe³⁺/ Σ Fe based on the calculated data from empirical equations (Table 2). The relatively narrow temperature range in which there are reliable experimental data (especially for I2), as well as the uncertainty arising in the derivation of empirical equations, are the cause a very approximate extrapolation of the lines with $Fe^{3+}/\Sigma Fe = const$ outside the studied range of temperatures. However, the plots in Fig. 2 reflect some important features of the temperature influence on the regime of fO₂ in granite and pantellerite melts in a closed system.



Fig. 2. Effect of temperature influence on fO_2 in granite I2 (a) and pantellerite P9 (b) melts with $Fe^{3+}/\Sigma Fe = const.$ The points are connected by thick lines – empirical data for the investigated temperature range. This line – extrapolation of these data in a wide temperature range. 1-3 – buffer equilibrium: 1 - magnetite-hematite (MH), 2 - Ni-NiO (NNO), 3 - wustite-magnetite (WM). 4 change of intrinsic fO_2 of tektite glasses with temperature by electrochemical data [Kadik et al, 2003]: the solid line in the range of measurements, dashed – the extrapolation to higher temperatures.

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As can be seen from the plots the slope of the lines with a constant ratio of $Fe^{3+}/\Sigma Fe$ depends on the degree of oxidation of iron in the melt. For oxidized melts ($Fe^{3+}/\Sigma Fe > 60-70\%$) the slope is close to the slope of the line buffer equilibrium magnetite-hematite. The slope of the lines decreases with decrease in the proportion of Fe^{3+} in the melt. This appears especially noticeable for granitic composition. The slope for a much more reduced melts ($Fe^{3+}/\Sigma Fe < 30-40\%$) becomes less than the slope of wustite-magnetite buffer. It should be noted that tektite glasses with $Fe^{3+}/\Sigma Fe \le 10\%$ have similar slope, according to measurement of intrinsic oxygen fugacity [*Kadik et al, 2003*]. Thus, in closed system, the lowering of temperature will be accompanied by much more significant decrease in fO_2 in reduced melts in comparison with that in oxidized melts.

Empirical equations $(Fe^{3+}/Fe^{2+})_{melt} = f(T, fO_2, melt composition)$

In Fig. 3 the experimental results for I2 and P9 expressed in the form of equations (1) (Table 2) are compared with calculations for the same melt, made with previously proposed empirical equations describing the dependence of iron redox state from the oxygen fugacity, temperature and melt composition:

$$lg(Fe^{3+}/Fe^{2+}) = h/TK + k lg(fO_2) + \Sigma d_i X_i + c , \qquad (2)$$

where *c*- constant; *h*, *k*, and d_i - regression coefficients, which are derived by processing of large sets of experimental data for the whole spectrum of magmatic silicate melts (from ultrabasite-basite to silicic) in wide range of *T* and *f*O₂; X_i – mole fractions of oxides of major elements.



Fig. 2. Comparison of experimental data for I2 (a) and P9 (b) melts at temperatures of 1340(1320) and 1420°C (solid lines) with the calculation results from empirical equations *Borisov and Shapkin* [1989] (dashed lines BSh) and *Kilinc et al.* [1983] (dashed line K)

The values of k coefficient calculated from these equations are close to values found experimentally for the I2 and P9. However, the results of calculations in general are in poor agreement with experimental data. Borisov and Shapkina equation [*Borisov, Shapkin, 1989*], which takes into account the dependence of h and k on the composition of the melt, much better describes the results of experiments with granite and pantellerite melts in the investigated fO_2-T area in comparison with similar equations with constant values of h and k [*Kilinc et al., 1983, and others*]. The last equations significantly underestimate the degree of oxidation of iron in the investigated granitic melts at given fO_2-T conditions.

We obtained new empirical equation of the form (2) for the two types of silicic aluminosilicate melts of granitic and comendite–pantellerite compositions by least squares method using all available experimental data. Granite group includes the results of 17 runs, mostly in the range 1300–1450 °C (+ one run at 1557°C), comendite-pantellerite group consists of 33 runs, mainly in the range 1196 - 1454°C (+ one run at 1005, 1103 and 1501°C). Regression coefficients values for each of these equations are presented in Table 3. The *h* and *k* coefficients are constant values and do not depend on melt composition and temperature.

Type of melt	k	h	С	d _{SiO2}	d_{TiO2}	d_{Al2O3}	d _{FeO} ∗	d_{MgO}	d _{CaO}	d_{Na2O}	d_{K2O}
Granite	0.181	619	-45.2	41.4	485.9	64.5	-6.8	1.2	35.6	62.1	134.1
Comed panteller.	0.196	3226	35.8	-38.6	-2.3	-35.4	-32.1	-93.0	-17.6	-32.7	-29.7

Table 3. Regression coefficients of equation (2) for two types of silicic melts–granite and comendite– pantellerite compositions

The agreement between experimental and calculated data for these equations is shown in Fig. 4 and 5. In almost all cases $Fe^{3+}/\Sigma Fe$ calculated values for granite melts differ from those measured in experimental samples by no more than 3%. Determination of log(fO_2) from the known Fe^{3+}/Fe^{2+} ratio in melt makes the difference for most of the experiments ± 0.2 log. units, but this discrepancy for significantly reduced or oxidized melts may reach up to 0.5–0.8 log. units. Testing for comendite-pantellerite melts demonstrates a more considerable variation between the calculated and experimental data: $Fe^{3+}/\Sigma Fe$ within 4-5%, in some cases up to 8–9%, and log(fO_2) for the main part of the experiments ± 0.4 log. units (maximum of ± 1.1 log. un.) (Fig. 5). It is quite expected, due to significantly greater heterogeneity of the samples in this group, both in composition and temperature.



Fig. 4. Comparison of experimental and calculated data for granite melts for temperature range 1300–1557°C. (N – number of experimental points).



Fig. 5. Comparison of experimental and calculated data for comendite–pantellerite melts for temperature range 1005–1557°C. (N – number of experimental points)

A similar regression equation obtained for the combined population of granitoid melts reveals a much larger discrepancy with the experimental data in comparison with the equations for each of the two groups. Deviations of more than half of the experiments on $Fe^{3+}/\Sigma Fe \ge 5\%$ ($\log(fO_2) \ge 0.5 \log$. units) and almost a quarter of the experiments $\ge 10\%$ (respectively, $\log(fO_2) \ge 1.2 \log$. units). Thus, only the equations proposed for each of the abovementioned granitoid groups may in first approximation satisfactorily describe the dependence of (Fe^{3+}/Fe^{2+})_{melt} = $f(T, fO_2, \text{ composition})$ obviously still in a relatively limited range of temperatures $\sim 1200(1100)-1450^{\circ}C$. The improvement of empirical equations of this kind (increasing their accuracy and extending the range of compositions and temperatures) appears to require additional experimental data that will enable to take into account the influence of composition and temperature on *k* and *h* coefficients in the equations.

Conclusions

1. The influence of oxygen fugacity on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ in granite and pantellerite melts under isothermal conditions (in the range 1220–1420 °C) is described by the equation $\log(\text{Fe}^{3+}/\text{Fe}^{2+}) = k*\log(fO2) + q$, where k and q – constants that depend not only on the composition of the melt, but also on the temperature (Table 2). Under given fO_2-T conditions the degree of iron oxidation in alkaline and iron enriched pantelleritic melt is higher than that in granitic melt.

2. Temperature increase at constant fO_2 causes reduction of Fe^{3+} to Fe^{2+} in both types of melts. In closed system, when the Fe^{3+}/Fe^{2+} in melt is constant, the increase of temperature is accompanied by increase in fO_2 and vice versa – lowering the temperature leads to a decrease in fO_2 . Decrease in Tcauses significant decrease in fO_2 in relatively more reduced melts in comparison with oxidized melts.

3. New empirical equations (Table 3), obtained by processing our own and the available experimental data allow satisfactorily in first approximation to describe the dependence of $(Fe^{3+}/Fe^{2+})_{melt.} = f(T, fO_2, melt composition)$ for two types of acidic silica-alumina melts granite and comendite-pantellerite compositions in relatively limited range of temperatures ~ 1200(1100)–1450°C.

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