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Ferric–Ferrous Ratio in Liquid Iron Oxides: Analysis and Applications to Natural Basaltic Melts

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Abstract—Experimental data on the proportions of ferrous and ferric iron in pure liquid oxides (Darken and Gurry, 1946) were used to test different redox models. The obtained inferences were used to evaluate possible problems in describing the dependence of Fe^{3+}/Fe^{2+} on oxygen fugacity in natural basaltic melts.

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INTRODUCTION

Elements of variable valence occurring in melts in two or more oxidation states (e.g., As^{5+}/As^{3+}, Ti^{4+}/Ti^{3+}, Fe^{3+}/Fe^{2+}, $Cr^{6+}/Cr^{3+}/Cr^{2+}$, $V^{5+}/V^{4+}/V^{3+}$) are of special interest for petrologists, metallurgists, and materials scientists, which has led to a wealth of experimental and theoretical studies on this problem.

Iron is the most important variable-valence element in magmatic processes. The relationships of iron oxide species in melts control to a large extent the oxygen fugacity of the system, as well as the sequence and fields of crystallization of most minerals, especially spinel, magnetite, and hematite.

This paper is aimed at drawing the attention of petrologists to the classic studied of redox states in iron-rich slags, primarily, the study of Darken and Gurry (1946). Their splendid experiments with pure liquid iron oxides have been undeservedly poorly discussed by both the authors and subsequent investigators. We will show that many theoretical problems of the behavior of di- and trivalent iron in multicomponent silicate melts can be approached on the basis of the analysis of the "pure" Fe–O system.

THERMODYNAMICS OF Fe^{3+}/Fe^{2+} EQUILIBRIUM IN MELTS AND PROBLEM FORMULATION

There are two ways of writing the reaction between iron oxides in melt:

$$2FeO + 1/2\,O_2 = Fe_2O_3, \quad (1)$$

$$FeO + 1/4\,O_2 = FeO_{1.5} \quad (2)$$

with the constants

$$K_1 = a_{Fe_2O_3}/(a_{FeO}^2 f_{O_2}^{1/2}) = (X_{Fe_2O_3}/X_{FeO}^2) \times (\gamma_{Fe_2O_3}/\gamma_{FeO}^2)/f_{O_2}^{1/2}, \quad (3)$$

$$K_2 = a_{FeO_{1.5}}/(a_{FeO} f_{O_2}^{1/4}) = (X_{FeO_{1.5}}/X_{FeO}) \times (\gamma_{FeO_{1.5}}/\gamma_{FeO})/f_{O_2}^{1/4}, \quad (4)$$

where a_i, γ_i, and X_i are the activity, activity coefficient, and mole fraction of the oxide in the melt, and f_{O_2} is the oxygen fugacity. Despite the apparent similarity, reactions (1) and (2) are fundamentally different. Assuming ideal behavior for oxides in the melt, $\log(X_{Fe_2O_3}/X_{FeO}^2)$, in the former case and $\log(X_{FeO_{1.5}}/X_{FeO})$ in the latter case are linear functions of $\log f_{O_2}$ and reciprocal absolute temperature.

The Fe^{3+}/Fe^{2+} equilibrium was usually expressed in the form of reaction (1) in early studies, both in metallurgy (White, 1938; Darken and Gurry, 1946) and in Earth sciences (Kennedy, 1948). Fudali (1965) analyzed the data of Kennedy (1948) and his own experiments and supposed that reaction (2) is more adequate. Materials scientists drew the same conclusion slightly earlier (Johnston, 1964), although they presented reaction (2) somewhat differently:

$$Fe^{2+} + 1/4\,O_2 = Fe^{3+} + 1/2\,O^{2-}, \quad (5)$$

where O^{2-} is the activity of oxygen ion in the melt as a generalized characteristic of melt basicity. Sack et al. (1980) approximated all the available experimental data using a linear function of $\ln(X_{Fe_2O_3}/X_{FeO})$ on $\ln f_{O_2}$ and $1/T$ (for a fixed melt composition). This is equivalent to the linear dependence of $\log(X_{\mathrm{FeO}_{1.5}}/X_{\mathrm{FeO}})$ on $\log f_{\mathrm{O}_2}$ and $1/T$, i.e., it was implicitly accepted that the redox equilibrium can be written as reaction (2).

Assuming the validity of either reaction (1) or reaction (2), and approximating $\log K_i$ by a linear function of reciprocal temperature, Eqs. (3) and (4) can be reduced for a given melt composition to

$$\log(X_{\mathrm{Fe_2O_3}}/X^2_{\mathrm{FeO}}) = k\log f_{\mathrm{O}_2} + h/T(\mathrm{K}) + s, \quad (6)$$

$$\log(X_{\mathrm{FeO}_{1.5}}/X_{\mathrm{FeO}}) = k\log f_{\mathrm{O}_2} + h/T(\mathrm{K}) + s, \quad (7)$$

where the theoretical slope against $\log f_{\mathrm{O}_2}$ (k) is 1/2 for reaction (6) and 1/4 for Eq. (7), $h \gg 0$, and s is a function of melt composition.

As was noted above, during the past four decades, an opinion has developed that Eq. (7) must be most adequate for the description of ferric–ferrous relationships in natural melts. However, the deviation of k from the ideal value (1/4) and the dependence of h and s on melt composition are still topics of debate. For instance, the group of I.S.E. Carmichael (Sack et al., 1980; Kilinc et al., 1983) proposed the following expression for the parameter s:

$$s = \Sigma d_i X_i + \mathrm{const}, \quad (8)$$

where X_i is the mole fraction of major component i, and d_i is the corresponding empirical coefficient. This expression implies that the influence of any oxide involved in the regression on $\log(X_{\mathrm{FeO}_{1.5}}/X_{\mathrm{FeO}})$ is constant and independent of melt composition, which is an oversimplification (e.g., Borisov and McCammon, 2010). In attempting to more accurately describe the influence of melt composition on the ferrous–ferric ratio, more sophisticated expressions were proposed (Kress and Carmichael, 1988, 1991; Borisov and Shapkin, 1989; Jayasuriya et al., 2004), but this study is focused mainly on the coefficient k.

Already Fudali (1965) revealed that k is not equal to a theoretical value of 0.25 but varies for different compositions from 0.16 to 0.26. Sack et al. (1980) and Kilinc et al. (1983) showed that, for natural basalts, k in Eq. (6) is close to 0.22. Kress and Carmichael (1988) also reported a similar value of $k = 0.207 \pm 0.007$ (2σ). Borisov (1988) demonstrated that, if the temperature slope (h) is assumed to depend on melt composition, k should also be dependent on melt composition.

On the other hand, Jayasuriya et al. (2004) performed experiments with a synthetic haplobasalt melt containing approximately 1% of total $\mathrm{Fe_2O_3}$ at a constant temperature of 1409°C and f_{O_2} from pure oxygen to 10^{-11} atm and obtained an almost ideal k value of 0.245 ± 0.004. Many investigators of this problem attributed the nonideality of k to interaction between ferrous and ferric oxides in natural relatively iron-rich melts (e.g., Kress and Carmichael, 1988; Jayasuriya et al., 2004). This interaction can be described by either applying the formalism of solid solutions (Jayasuriya et al., 2004) or assuming the existence of ferrous–ferric associates in melts (Kress and Carmichael, 1988, 1991). Note that already White (1938) used the end-members FeO, $\mathrm{Fe_2O_3}$, and $\mathrm{Fe_3O_4}$ to describe the behavior of $\mathrm{Fe^{3+}/Fe^{2+}}$ in the slags of the Fe–O system. Subsequently, Darken and Gurry tested, in addition to $\mathrm{Fe_3O_4}$, a number of other end-members for the same system, including Fe, $\mathrm{Fe_2O_4}$, and $\mathrm{Fe_4O_5}$, but with little success (Darken and Gurry, 1946, p. 814).

The difference of k from the ideal value of 0.25 would have been of less concern had it not been for the danger that the dependence of $\log(X_{\mathrm{FeO}_{1.5}}/X_{\mathrm{FeO}})$ on $\log f_{\mathrm{O}_2}$ may deviate in the reduced region from the line obtained experimentally under more oxidized conditions or even display a kink. Note that all the empirical equations for the $\mathrm{Fe^{3+}/Fe^{2+}}$ ratio in natural melts are based mainly on experiments under the T-f_{O_2} conditions from air to the quartz–fayalite–magnetite (QFM) buffer. The reason is that the analysis of more reduced glasses by the redox titration of FeO, microprobe determination of total iron ($\mathrm{FeO_t}$), and calculation of $\mathrm{Fe_2O_3}$ from the difference (e.g., Kilinc et al., 1983, p. 137) involves much higher errors. In the case of an inflection, the extrapolation of dependences similar to Eq. (6) into the reduced region will result in additional errors, even when the influence of composition is correctly described. As was noted above, there is no distinct kink or inflection in iron-poor synthetic melts (Jayasuriya et al., 2004), which does not eliminate similar problems for natural melts and, especially, iron-rich slags.

It was experimentally shown that the addition of a particular component to some initial basalt under given T-f_{O_2} parameters modifies the $\mathrm{Fe^{3+}/Fe^{2+}}$ ratio (Thornber et al., 1980). The same follows from Eq. (8). Thus, changing from natural silicate melts to the pure Fe–O system allows us to estimate more reliably the nonideality and nature of interaction of liquid iron oxides unaffected by the influence of other melt components.

FROM LIQUID IRON OXIDES TO SILICATE MELTS

Input Data

Darken and Gurry (1946) reported experiments under controlled oxygen fugacity, with f_{O_2} imposed by various buffer mixtures. Since Darken and Gurry (1946) did not report f_{O_2} values, they were calculated by us from the reported proportions of buffer gases using thermodynamic data for the C–O–H gas system

(Deines et al., 1974). Darken and Gurry (1946) reported 52 melting experiments, including 23 experiments in which two crucibles with different starting oxides (wüstite and Fe_2O_3) were simultaneously equilibrated with the furnace atmosphere. One of their experimental samples was analyzed two times (Darken and Gurry, 1946, Table 1). The whole dataset includes 76 experimental points and embraces a wide range of T-f_{O_2} conditions, from pure oxygen to the iron–wüstite buffer equilibrium (Fig. 1).

The ferrous/ferric ratio of slags was determined by redox titration, i.e., total iron (as FeO_t) and FeO content in samples were determined by the permanganate titration of appropriate solutions (see Darken and Gurry, 1946 for detail). Therefore, the (Fe^{2+} + Fe^{3+})/Fe^{2+} values given in Table 1 are in fact the ratios of the corrected amounts of permanganate consumed during FeO_t and FeO titration (Darken and Gurry, 1945, p. 1403) and are raw data. Depending on the model tested, they can be recalculated to either $X_{FeO_{1.5}}/X_{FeO}$, $X_{Fe_2O_3}/X^2_{FeO}$, or ratios of more complex end-members.

The experimental conditions are also given in Table 1. For convenience, the results are sorted from oxidized to reduced by the ΔQFM value, i.e., the difference between the experimental $\log f_{O_2}$ value and that of the QFM buffer at the experimental temperature calculated using the expression of O'Neill (1987).

Simplest Correlations

Let us estimate the correspondence of the experimental data to simplest Eqs. (6) and (7), i.e., approximate $\log(X_{Fe_2O_3}/X^2_{FeO})$ or $\log(X_{FeO_{1.5}}/X_{FeO})$ by linear functions of $\log f_{O_2}$ and reciprocal temperature. For the ideal k value, R^2 values of 0.680 and 0.771 were obtained for all experimental points (Table 2, models 1 and 2, respectively). The correlation is rather poor, taking into account that all the data were obtained by a single research team (i.e., systematic errors are insignificant, if any) and the melts show minor compositional variations (within the binary system FeO–Fe_2O_3).

Letting k vary significantly improves the fit increasing R^2 to 0.996 and 0.986 (Table 2, models 3 and 4, respectively). In both cases, the R^2 values are rather high and do not allow us to select one of the two reactions (1 or 2) on the basis of this parameter only as better describing the ferrous/ferric ratio in the slags. In both cases, the obtained k values are lower than the theoretical slopes. The k value is 0.238 ± 0.002 (1σ) for $\log(X_{Fe_2O_3}/X^2_{FeO})$, which is 54% lower than the predicted value of 0.5, and 0.183 ± 0.003 for $\log(X_{FeO_{1.5}}/X_{FeO})$, which is 27% lower than the predicted value of 0.25. In this respect, reaction (2) seems to be more adequate than reaction (1).

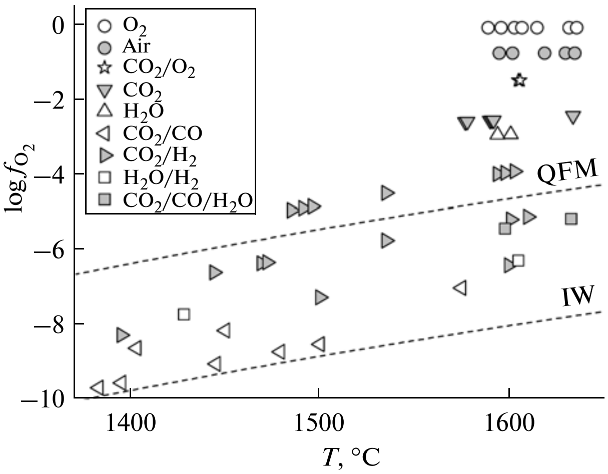

Fig. 1. Conditions of the Darken and Gurry (1946) experiments.

QFM is the quartz-fayalite-magnetite buffer according to O'Neill (1987), and IW is the iron-wüstite buffer according to O'Neill and Pownceby (1993).

Separate Approximations for Oxidized and Reduced Slags

At a first glance, simple linear equations (6) and (7) provide an excellent fit to all of the experimental results, from the most oxidized to the most reduced.

Consider now Figs. 2a and 2b showing the difference between the experimental and calculated $\log(X_{Fe_2O_3}/X^2_{FeO})$ and $\log(X_{FeO_{1.5}}/X_{FeO})$ values as a function of ΔQFM. It is evident that all of the slags can be separated at $f_{O_2} \approx$ QFM-1.2 into two groups, showing contrasting deviations from the average equation. These groups will be further conventionally referred to as oxidized and reduced slags (oxidizing and reducing experiments). We first note that almost all experiments with natural melts were conducted under oxidizing (in the above sense) conditions. This problem will be discussed in more detail below.

The separate approximation of oxidized (ΔQFM > −0.8, nos. 1–57 in Table 1) and reduced (ΔQFM < −1.6, nos. 58–76 in Table 1) glasses by Eqs. (6) and (7) yields correlation coefficients close to one (models 3a, 3b, 4a, and 4b in Table 2). Similar to the above case, the R^2 value alone does not allow us to prefer either $\log(X_{Fe_2O_3}/X^2_{FeO})$ or $\log(X_{FeO_{1.5}}/X_{FeO})$. Only the significantly smaller deviation of k from the theoretical value in model 4 compared with model 3 suggests that equilibrium (2) is more adequate than equilibrium (1). This model will be considered in more detail.

Table 1. Experimental conditions and the (Fe^{3+} + Fe^{2+})/Fe^{2+} values of liquid oxides in the Fe–O system according to the data of Darken and Gurry (1946)

No.	Starting oxide	Duration, h	T, °C	$\log f_{O_2}$[1]	ΔQFM[2]	Buffer, gas/mixture	$\frac{Fe^{3+} + Fe^{2+}}{Fe^{2+}}$
1	Fe_2O_3	6	1589	0.00	4.66	O_2	4.237
2	Fe_3O_4	6	1589	0.00	4.66	O_2	4.216
3	Fe_2O_3	1	1596	0.00	4.61	O_2	4.067
4	Fe_2O_3	1	1603	0.00	4.55	O_2	4.053
5	Fe_2O_3	4	1607	0.00	4.52	O_2	4.023
6	*Wu*	4	1607	0.00	4.52	O_2	4.007
7	Fe_2O_3	1	1615	0.00	4.46	O_2	3.881
8	Fe_2O_3	5	1632	0.00	4.33	O_2	4.033
9	*Wu*	5	1632	0.00	4.33	O_2	3.958
10	Fe_2O_3	1	1636	0.00	4.30	O_2	3.998
11	Fe_2O_3	2	1595	–0.68	3.94	air	3.529
12	Fe_2O_3	2	1602	–0.68	3.88	air	3.492
13	Fe_2O_3	3	1619	–0.68	3.75	air	3.439
14	Fe_2O_3	1	1630	–0.68	3.66	air	3.348
15	Fe_2O_3	6	1630	–0.68	3.66	air	3.308
16	Fe_2O_3	4	1635	–0.68	3.63	air	3.301
17	*Wu*	4	1635	–0.68	3.63	air	3.281
18	Fe_2O_3	7	1605	–1.41	3.13	CO_2/O_2	2.824
19	Fe_2O_3	7	1605	–1.41	3.13	CO_2/O_2	2.850
20	Fe_2O_3	3	1606	–1.41	3.12	CO_2/O_2	2.838
21	Fe_2O_3	5	1577	–2.52	2.24	CO_2	2.304
22	Fe_2O_3	2	1578	–2.52	2.24	CO_2	2.309
23	Fe_2O_3	3	1590	–2.48	2.17	CO_2	2.302
24	*Wu*	5	1591	–2.48	2.17	CO_2	2.291
25	Fe_2O_3	5	1592	–2.48	2.16	CO_2	2.286
26	Fe_2O_3	4	1634	–2.36	1.95	CO_2	2.256
27	Fe_2O_3	12	1594	–2.87	1.75	H_2O	2.074
28	*Wu*	12	1594	–2.87	1.75	H_2O	2.080
29	Fe_2O_3	18	1601	–2.86	1.71	H_2O	2.045
30	*Wu*	18	1601	–2.86	1.71	H_2O	2.055
31	*Wu*	2	1603	–3.86	0.70	CO_2/H_2	1.777
32	Fe_2O_3	2	1603	–3.86	0.70	CO_2/H_2	1.766
33	*Wu*	5	1598	–3.90	0.70	CO_2/H_2	1.758
34	Fe_2O_3	5	1598	–3.90	0.70	CO_2/H_2	1.752
35	*Wu*	2	1594	–3.93	0.70	CO_2/H_2	1.707
36	Fe_2O_3	2	1594	–3.93	0.70	CO_2/H_2	1.732
37	*Wu*	18	1535	–4.43	0.67	CO_2/H_2	1.710
38	Fe_2O_3	18	1535	–4.43	0.67	CO_2/H_2	1.720

Table 1. (Contd.)

No.	Starting oxide	Duration, h	*T*, °C	$\log f_{O_2}$[1]	ΔQFM[2]	Buffer gas/mixture	$\frac{Fe^{3+}+Fe^{2+}}{Fe^{2+}}$
39	*Wu*	6	1496	−4.79	0.65	CO_2/H_2	1.719
40	Fe_2O_3	6	1496	−4.79	0.65	CO_2/H_2	1.708
41	*Wu*	3	1491	−4.83	0.65	CO_2/H_2	1.710
42	*Wu*	4	1485	−4.89	0.64	CO_2/H_2	1.698
43	Fe_2O_3	2	1610	−5.06	−0.56	CO_2/H_2	1.431
44	*Wu*	2	1610	−5.06	−0.56	CO_2/H_2	1.427
45	*Wu*	4.5	1601	−5.13	−0.56	CO_2/H_2	1.427
46	Fe_2O_3	4.5	1601	−5.13	−0.56	CO_2/H_2	1.429
47	Fe_2O_3	3	1535	−5.70	−0.59	CO_2/H_2	1.430
48	*Wu*	3	1535	−5.70	−0.59	CO_2/H_2	1.427
49	Fe_2O_3	5	1472	−6.28	−0.63	CO_2/H_2	1.426
50	Fe_2O_3	5	1469	−6.31	−0.63	CO_2/H_2	1.426
51	*Wu*	5	1469	−6.31	−0.63	CO_2/H_2	1.425
52	*Wu*	5	1444	−6.55	−0.65	CO_2/H_2	1.427
53	Fe_2O_3	5	1444	−6.55	−0.65	CO_2/H_2	1.428
54	Fe_2O_3	4	1598	−5.38	−0.78	$CO_2/CO/H_2O$	1.386
55	*Wu*	4	1598	−5.38	−0.78	$CO_2/CO/H_2O$	1.382
56	Fe_2O_3	0.4	1633	−5.11	−0.79	$CO_2/CO/H_2O$	1.392
57	*Wu*	4	1633	−5.11	−0.79	$CO_2/CO/H_2O$	1.392
58	Fe_2O_3	18	1428	−7.68	−1.64	H_2O/H_2	1.267
59	*Wu*	18	1428	−7.68	−1.64	H_2O/H_2	1.273
60	Fe_2O_3	4	1605	−6.23	−1.69	H_2O/H_2	1.250
61	*Wu*	4	1605	−6.23	−1.69	H_2O/H_2	1.245
62	*Wu*	3.25	1600	−6.36	−1.78	CO_2/H_2	1.227
63	Fe_2O_3	3.25	1600	−6.36	−1.78	CO_2/H_2	1.227
64	*Wu*	18	1500	−7.22	−1.82	CO_2/H_2	1.227
65	Fe_2O_3	18	1500	−7.22	−1.82	CO_2/H_2	1.230
66	Fe_2O_3	5.5	1395	−8.23	−1.88	CO_2/H_2	1.241
67	*Wu*	5.5	1395	−8.23	−1.88	CO_2/H_2	1.238
68	*Wu*	6	1575	−6.96	−2.19	CO_2/CO	1.169
69	Fe_2O_3	4	1575	−6.96	−2.19	CO_2/CO	1.169
70	Fe_2O_3	6	1450	−8.11	−2.26	CO_2/CO	1.178
71	Fe_2O_3	5	1403	−8.58	−2.31	CO_2/CO	1.183
72	Fe_2O_3	23	1500	−8.48	−3.08	CO_2/CO	1.086
73	*Wu*	72	1479	−8.68	−3.09	CO_2/CO	1.088
74	*Wu*	75	1445	−9.01	−3.12	CO_2/CO	1.091
75	Fe_2O_3	48	1395	−9.52	−3.16	CO_2/CO	1.097
76	*Wu*	41	1383	−9.64	−3.18	CO_2/CO	1.096

Notes: *Wu* is wüstite.

[1] f_{O_2} values were calculated from the composition of gas mixture (Darken and Gurry, 1946, Table 1) using the thermodynamic data of Deines et al. (1974). [2] ΔQFM is the difference between experimental f_{O_2} and the value for the quartz–fayalite–magnetite buffer according to O'Neill (1987).

Table 2. Correlations for the expression $\log(R\mathrm{Fe}) = k\log f_{\mathrm{O}_2} + h/T(\mathrm{K}) + s$

Model	RFe	Model details	k	1σ	h	1σ	s	1σ	R^2
1	$X_{\mathrm{Fe_2O_3}}/X^2_{\mathrm{FeO}}$	all 76 points at fixed $k = 0.5$	0.500	–	31300	2497	–15.33	0.49	0.680
2	$X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}}$	all 76 points at fixed $k = 0.25$	0.250	–	10883	690	–5.07	0.14	0.771
3	$X_{\mathrm{Fe_2O_3}}/X^2_{\mathrm{FeO}}$	all 76 points	0.238	0.002	6456	292	–2.83	0.04	0.995
4	$X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}}$	all 76 points	0.183	0.003	4563	422	–1.89	0.05	0.986
3a	$X_{\mathrm{Fe_2O_3}}/X^2_{\mathrm{FeO}}$	57 points, oxidized glasses (ΔQFM > –0.8)	0.230	0.001	6268	201	–2.75	0.02	0.998
3b	"	19 points, reduced glasses (ΔQFM < –1.6)	0.346	0.006	10362	251	–4.23	0.01	0.995
4a	$X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}}$	57 points, oxidized glasses (ΔQFM > –0.8)	0.168	0.001	4551	158	–1.92	0.01	0.998
4b	"	19 points, reduced glasses (ΔQFM < –1.6)	0.322	0.006	9646	247	–3.75	0.01	0.995
5	$X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}}$	all 76 points, nonideal mixing*	0.250	–	5478	418	–2.54	0.06	0.959
5a	"	71 points (all except for five most reduced), nonideal mixing*	0.250	–	5897	275	–2.80	0.04	0.983
6	$X_{\mathrm{FeO_{1.437}}}/X_{\mathrm{FeO}}$	all 76 points	0.218	0.002	5940	308	–2.36	0.04	0.995
6a	$X_{\mathrm{FeO_{1.434}}}/X_{\mathrm{FeO}}$	71 points (all except for five most reduced)	0.217	0.002	6271	197	–2.53	0.02	0.998

Notes: The experimental data of Darken and Gurry (1946) given in Table 1 were used.
* The equation contains the additional term $w\,X_{\mathrm{FeO}}/T$, where w is 1348 ± 74 for model 5 and 1472 ± 48 for model 5a.

In the oxidized region, the slope of $\log(X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}})$ versus $\log f_{\mathrm{O}_2}$ (k_{ox}) is 0.168 ± 0.001 (1σ), which is 33% lower than the ideal value of 0.25 but only 15% lower than $k = 0.1967$ obtained in one of the most recent empirical equations describing equilibrium (2) in natural basaltic melts (Jayasuriya et al., 2004). The temperature slope for the same oxidized glasses is $h_{\mathrm{ox}} = 4551 \pm 158$, which is only slightly lower than $h = 5394$ obtained for natural melts (Jayasuriya et al., 2004).

In the reduced region, $k_{\mathrm{red}} = 0.322 \pm 0.006$ (1σ), which is 29% higher than the expected ideal value of 0.25. In experiments with natural basalts, k almost never exceeded the theoretical value. The temperature slope for reduced glasses is $h_{\mathrm{red}} = 9646 \pm 247$, which is considerably higher than $h = 5394$ obtained for natural melts (Jayasuriya et al., 2004).

The inflection of the $\log(X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}})$ dependence on $\log f_{\mathrm{O}_2}$ in liquid iron oxides can be visualized by normalizing all experimental data to a single temperature, for instance, 1500°C (Fig. 3), using the corresponding temperature slopes for the oxidizing (h_{ox}) and reducing (h_{red}) experiments.

T-f_{O_2} Equations for the Boundary between the Fields of Oxidized and Reduced Melts

Thus, for the slags discussed here, the oxidized and reduced compositions are divided at an f_{O_2} level of approximately 1.2 log units below QFM. These slags were obtained at an average experimental temperature of ~1560°C. However, ΔQFM must not be the same at much lower temperatures characteristic of terrestrial basaltic magmatism.

Let the behavior of $\mathrm{FeO_{1.5}/FeO}$ be known within the whole T-f_{O_2} interval. As an example, Fig. 4 shows values for two temperatures, $T_2 > T_1$. In the oxidized and reduced regions, the $\log(X_{\mathrm{FeO_{1.5}}}/X_{\mathrm{FeO}}) - \log f_{\mathrm{O}_2}$ lines have slopes of k_{ox} and k_{red}, respectively, and the distance between the lines for temperatures of T_2 and T_1 depends on h_{ox} and h_{red}. In any point at the boundary of the oxidizing and reducing regions (line AB), the following relation holds:

$$k_{\mathrm{ox}}\log f_{\mathrm{O}_2} + h_{\mathrm{ox}}/T + s_{\mathrm{ox}} = k_{\mathrm{red}}\log f_{\mathrm{O}_2} + h_{\mathrm{red}}/T + s_{\mathrm{red}}, \quad (9)$$

which yields after transformations the equations of a line (in the $\log f_{\mathrm{O}_2} - 1/T$ coordinates) separating the oxidizing and reducing regions:

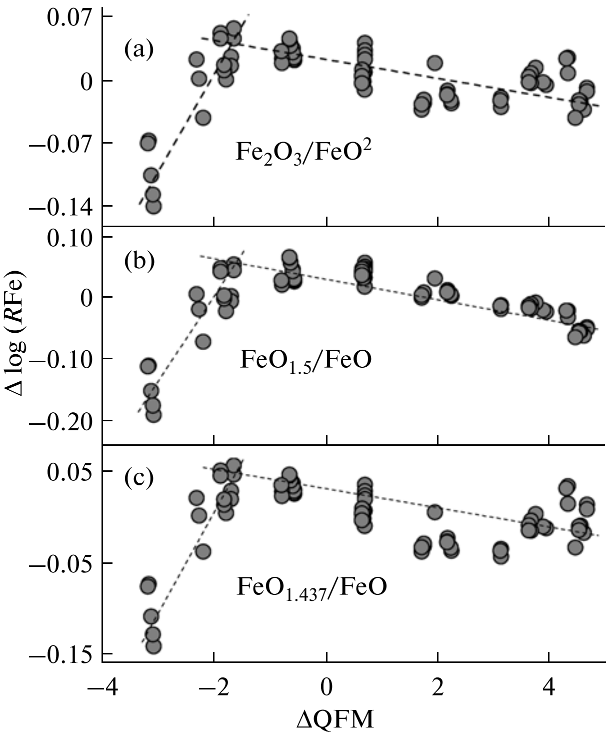

Fig. 2. Difference between the experimental and calculated $\log(R\mathrm{Fe})$ values as a function of ΔQFM ($R\mathrm{Fe} = X_{Fe_2O_3}/X^2_{FeO}$, $X_{FeO_{1.5}}/X_{FeO}$, and $X_{FeO_{1.437}}/X_{FeO}$ corresponding to models 3, 4, and 6 in Table 2, respectively). The input data are from Darken and Gurry (1946).

$$\log f_{O_2} = -(h_{red} - h_{ox})/(k_{red} - k_{ox})1/T(\mathrm{K}) - (s_{red} - s_{ox})/(k_{red} - k_{ox}). \quad (10)$$

Using the k_i, h_i, and s_i parameters from models 3a and 3b, we obtain

$$\log f_{O_2} = -33050/T(\mathrm{K}) + 11.8. \quad (11)$$

The standard deviations of the numerator for the temperature term and the constant term are ±1620 and ±0.1 (1σ), respectively. The oxygen fugacity defined by Eq. (11) will be designated as $f_{O_2}^{\mathrm{break}}$, because it corresponds to a break in the $\log(X_{FeO_{1.5}}/X_{FeO})$ versus $\log f_{O_2}$ line at any given temperature.

Reduced Melts in Nature and Experiments

Dependence (11) is not parallel to most oxygen buffers used in petrology (QFM, NiNiO, IW, etc.). The $f_{O_2}^{\mathrm{break}}$ value is lower than the QFM buffer by 1.4 orders of magnitude at 1500°C and 2.2 orders of magnitude at 1200°C. This is fortunate, because, even if the inflection exists in natural silicate melts relatively poor in iron (compared with the pure iron oxides considered here), the f_{O_2} of terrestrial basaltic magmatism is probably always higher than QFM-2 (Christie et al., 1986). Moreover, most experiments with natural melts used for the calibration of empirical relations similar to Eq. (7) were performed at oxygen fugacities from air to only slightly below QFM. In other words, empirical models calibrated on the basis of this data set (from that of Sack et al., 1980 to that of Jayasuriya et al., 2004) are plausible with respect to the form of equation, which involves no break in the slope of $\log(X_{FeO_{1.5}}/X_{FeO})$ at some $\log f_{O_2}$ value.

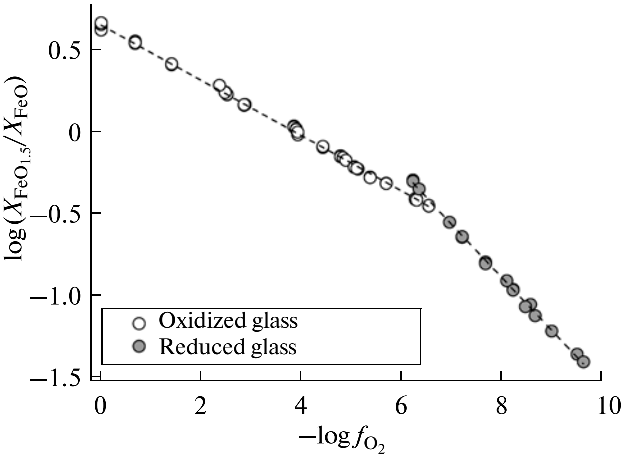

Fig. 3. Diagram of $X_{FeO_{1.5}}/X_{FeO}$ as a function of $\log f_{O_2}$.

All data were normalized to a temperature of 1500°C using different temperature slopes for oxidized and reduced experiments (h_{ox} and h_{red}, respectively). The input data are from Darken and Gurry (1946).

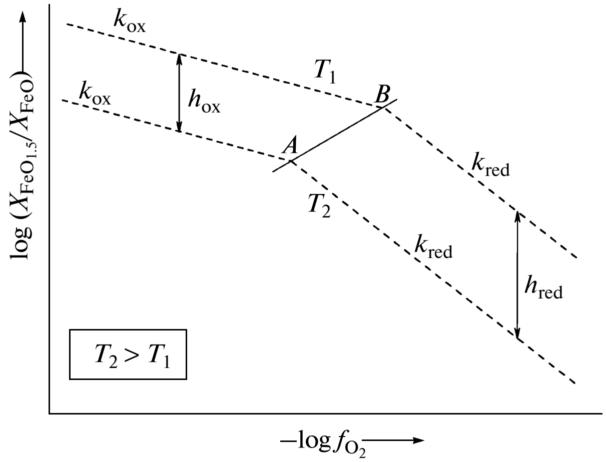

Fig. 4. Schematic diagram illustrating the determination of the boundary line between oxidized and reduced glasses (see text for detail).

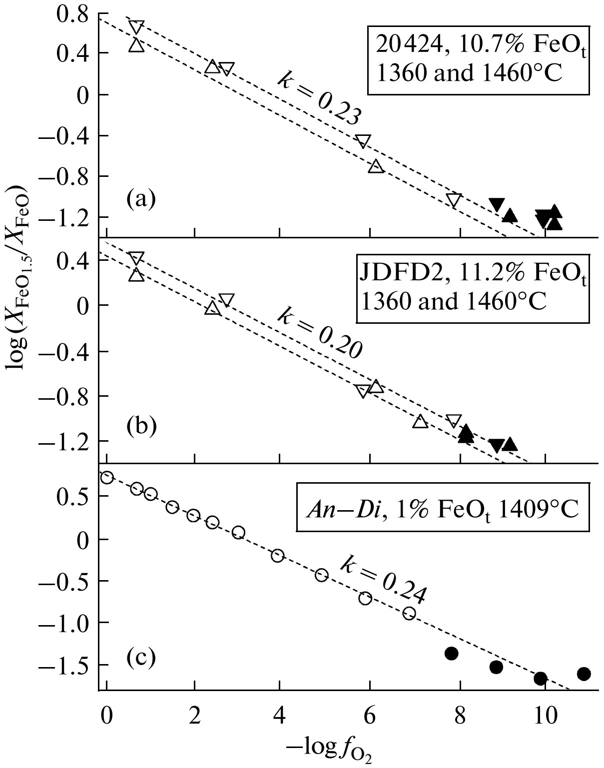

Fig. 5. Oxidized (unfilled symbols) and reduced (filled symbols) melts from experimental studies: (a) composition 20424 at 1360 (upper line) and 1460°C (lower line) (Kress and Carmichael, 1988); (b) composition JDFD2 at 1360 (upper line) and 1460°C (lower line) (Kress and Carmichael, 1988); and (c) eutectic composition in the *Di–An* system at 1409°C (Jayasuriya et al., 2004).

The slope of the lines (*k*) was determined on the basis of oxidized experiments only.

Among all of the aforementioned experiments with natural melts, only several runs of Kress and Carmichael (1988) were carried out at oxygen fugacities below $f_{O_2}^{\text{break}}$. Two compositions (20424 and JDFD2) corresponding to the highest numbers of reduced (in accordance with our classification) glasses are shown in Fig. 5 together with data for the eutectic composition in the anorthite–diopside system (DA) with 1% FeO$_t$ (Jayasuriya et al., 2004). In the latter case, Mössbauer spectroscopy was used to determine Fe^{3+}/Fe^{2+}. All the compositions from the reduced region show no sharp increase in slope against $\log f_{O_2}$, similar to that observed in Fig. 3. Moreover, the reduced basalt glasses are likely to deviate somewhat upward relative to the line obtained for the oxidized glasses, which is especially clear for composition 20424. In our opinion, this is related to problems in the determination of Fe^{3+}/Fe^{2+} in reduced glasses. Remember that the routine method of the analysis of experimental glasses of natural compositions (e.g., Sack et al., 1980) includes the determination of FeO content by colorimetry, electron microprobe analysis of FeO$_t$, and calculation of Fe_2O_3 from the difference. In such a case, even a small systematic overestimation of FeO$_t$ relative to the real content will result in the asymptotic approach of Fe^{3+}/Fe^{2+} to some fictive value with increasing degree of glass reduction, when the real fraction of Fe^{2+} becomes negligible.

Correlations Based on the Model of Solid Solutions

According to many authors, the problem of the deviation of the slope of Eq. (7) (*k*) from the theoretical value of 1/4 can be solved by accounting for the nonideal behavior of iron oxides in the melt (see discussion in Jayasuriya et al., 2004).

Let the excess Gibbs free energy of reaction (2) be specified in terms of regular solid solutions, i.e., $G^{ex} = X_{FeO_{1.5}}X_{FeO}W$, where W is the interaction parameter of FeO and FeO$_{1.5}$ independent of temperature and melt composition. Remember that for regular solutions, $RT\ln\gamma_i = (1 - X_i)^2W$, where R is the universal gas constant. It can be shown that

$$RT\ln(\gamma_{FeO_{1.5}}/\gamma_{FeO}) = 2X_{FeO}W - W. \qquad (12)$$

Then, an additional term will appear in Eq. (7), and it will have the following form:

$$\log(X_{FeO_{1.5}}/X_{FeO}) = 1/4\log f_{O_2} + h/T(K) + s + wX_{FeO}/T, \qquad (13)$$

where $w = -2W/2.303R$.

The approximation of all the data by Eq. (13) results in a high R^2 of 0.959 (model 5 in Table 2). The discrepancy between the experimental and calculated $\log(X_{FeO_{1.5}}/X_{FeO})$ values for five most reduced samples ($\Delta QFM < -3$, nos. 72–76 in Table 1) is up to -4.4σ, whereas it is within $\pm 2\sigma$ for the other glasses. Therefore, these five glasses were ignored in the final fit (model 5a).

The coefficient $w = 1348 \pm 74$ was recalculated to the interaction parameter $W = -4.09 \pm 0.46$ kJ/mol and was subsequently used to determine $\gamma_{FeO_{1.5}}$ and γ_{FeO}. These values are shown in Fig. 6 for a temperature of 1500°C. The obtained activity coefficients are valid only for the pure FeO$_{1.5}$–FeO system and only at FeO$_{1.5}$/FeO from 0.18 to 3.24 (solid segments in Fig. 6). Nonetheless, these estimates may be instructive for understanding the behavior of ferrous and ferric iron at least in iron-rich silicate melts.

Correlation with Arbitrary End-Members

Kress and Carmichael (1988) supposed that redox equilibria involving ferrous and ferric iron can be more adequately described assuming the existence of Fe^{2+}-Fe^{3+} clusters in the melts. In particular, they proposed

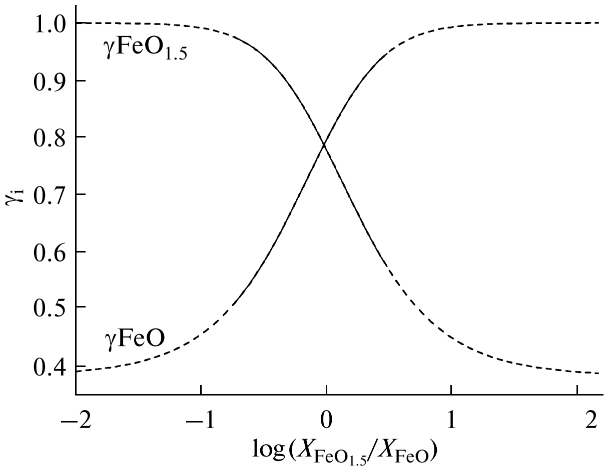

Fig. 6. Variations in $\gamma_{FeO_{1.5}}$ and γ_{FeO} in $FeO_{1.5}$–FeO oxide melts at a temperature of 1500°C.
The interaction parameter W was calculated in model 5a (Table 2) using the formalism of regular solid solutions. The solid lines correspond to the experimental interval, and the dashed lines are extrapolations.

the $FeO_{1.464}$ species instead of $FeO_{1.5}$ (which is close to the stoichiometric proportion of $Fe^{2+} \cdot 13Fe^{3+}$). Later, Jayasuriya et al. (2004) noted that Fe^{2+}-Fe^{3+} clusters can be interpreted as iron cations of fractional valences (in the above case, $Fe^{2.928+}$). Note that the existence of cations with fractional valences was previously proposed by Borisov et al. (1994) for the interpretation of palladium solubility in silicate melts. They suggested that dominant palladium speciation changes at decreasing f_{O_2} from $Pd^{4/3+}$ to Pd^{+} and further to $Pd^{2/3+}$.

Thus, a model explaining the slope $k < 1/4$ and assuming arbitrary iron oxide end-members can be constructed in the most general terms as follows. Let Fe^{2+} and Fe^{n+} $(2 < n < 3)$ coexist in a melt, which is equivalent to the coexistence of FeO and $FeO_{n/2}$. Then, instead of reaction (2), we can write

$$FeO + (n-2)/4\ O_2 = FeO_{n/2} \tag{14}$$

with the constant

$$K_{14} = a_{FeO_{n/2}}/(a_{FeO} f_{O_2}^{(n-2)/4}). \tag{15}$$

In the case of the ideal behavior of FeO and $FeO_{n/2}$ in the melt, we obtain the following relation by analogy with Eq. (7)

$$\log(X_{FeO_{n/2}}/X_{FeO}) = k \log f_{O_2} + h/T(\mathrm{K}) + s, \tag{16}$$

whose theoretical slope against $\log f_{O_2}$ is $k = (n-2)/4$. Assuming, then, that $FeO_{n/2}$ can be formed by complexation:

$$FeO_{1.5} + (3-n)/(n-2)\ FeO = 1/(n-2) FeO_{n/2}, \tag{17}$$

we obtain

$$X_{FeO_{n/2}} = 1/(n-2) X_{FeO_{1.5}}^{\mathrm{initial}}, \tag{18}$$

$$X_{FeO} = X_{FeO}^{\mathrm{initial}} - (3-n)/(n-2) X_{FeO_{1.5}}^{\mathrm{initial}}, \tag{19}$$

where $X_{FeO}^{\mathrm{initial}}$ and $X_{FeO_{1.5}}^{\mathrm{initial}}$ are the initial mole fractions of ferrous and ferric oxides, respectively, determined by redox titration or other methods. Then, manipulating n, calculating the molar fractions of $FeO_{n/2}$ and FeO, and checking the correlations of $\log(X_{FeO_{n/2}}/X_{FeO})$ with $\log f_{O_2}$ and $1/T$(K), the coefficient k is adjusted to the theoretical value $(n - 2)/4$. The desired solution of the problem is thus obtained.

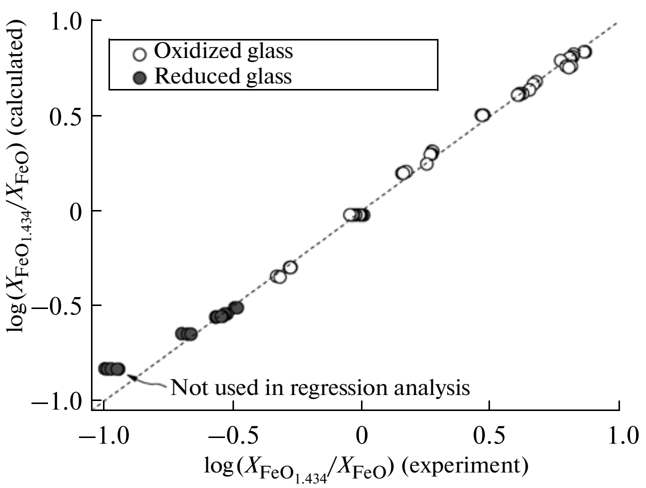

Fig. 7. Comparison of experimental and calculated $\log(X_{FeO_{1.434}}/X_{FeO})$ values (model 6a in Table 2).

The processing of all of the experimental data showed that they are best described by assuming the presence of the $FeO_{1.437}$ species (model 6 in Table 2). It was found that, similar to the case with the solid solution model, the maximum discrepancy between the experimental and calculated $\log(X_{FeO_{1.437}}/X_{FeO})$ values was obtained for five most reduced samples (ΔQFM < –3, nos. 72–76 in Table 1); the difference is up to -4.7σ for these glasses and within $\pm 2\sigma$ for the other samples. The five most reduced glasses were therefore excluded from the final regression model (6a). A comparison of model calculations with experiments is shown in Fig. 7.

Thus, almost all liquid iron oxides are excellently described ($R^2 = 0.998$) by the ideal mixing of the components FeO and $FeO_{1.434}$. The effective valence of iron in the latter is +2.867, which approximately corresponds to a complex with the stoichiometry $2Fe^{2+} \cdot 13Fe^{3+}$. The value of k in Eq. (14) is 0.217 ± 0.002, which is slightly lower than 0.232 ± 0.002 obtained for natural silicate melts by Kress and Carmichael (1988).

Additional Notes on Reduced Melts in Nature and Experiments

If the deviation of k from the ideal value of 1/4 is related to the interaction of Fe^{2+} and Fe^{3+} in liquid oxides (models 5, 5a, 6, and 6a), the separation of melts into oxidized and reduced ones at some $f_{O_2}^{break}$ value is meaningless. However, Fig. 2c shows that even complex models (in particular, model 6) are not perfect and show different relationships to oxidized and reduced melts. It cannot be excluded that the kink in Fig. 2c reflects a change of the dominant iron species. It is worth remembering that Borisov et al. (1994) explained the change of the valence state of palladium in melt from $Pd^{4/3+}$ to Pd^{+} and further to $Pd^{2/3+}$ by the appearance of appropriate complexes dissolved in the melt: $2Pd^{2+}Pd^{0}$, $Pd^{2+}Pd^{0}$, and $Pd^{2+}2Pd^{0}$.

The very high correlation coefficients obtained in the models tested above do not allow us to expect that the use of more sophisticated models (for instance, nonideal mixing of complex end-members, i.e., a combination of models 5 and 6) with the same data set would unambiguously demonstrate the constancy or variability of k within the whole f_{O_2} range.

Currently, it is obvious that models 5a and 6a equally well describe all of the oxidized and most of the reduced slags (Fig. 7), i.e., the compositions with $Fe^{3+}/Fe^{2+} \geq 0.169$. However, the proposed models do not fit the melts with $Fe^{3+}/Fe^{2+} \leq 0.097$ (they will be referred to as critical to distinguish them from reduced melts). It is possible that this is related to some experimental or analytical errors (all of the critical compositions were obtained in a single experimental series (A) at a constant CO_2/CO ratio of 0.376; Table 1 of Darken and Gurry, 1946), but this suggestion is not very probable.

It is important to determine if natural silicate melts with $Fe^{3+}/Fe^{2+} \leq 0.097$ behave similarly to the critical pure iron oxides. The most reduced basaltic melt in the experiments of Shibata (1967) at 1300°C shows $Fe^{3+}/Fe^{2+} = 0.079$ but does not deviate from the dependence based on more oxidized glasses (Fig. 3 in Shibata, 1967). All of the reduced experiments shown in Fig. 5 are also critical. Despite some scatter, the critical experiments with the DA composition (Jayasuriya et al., 2004, $Fe^{3+}/Fe^{2+} < 0.045$) do not show any systematic deviation from the line obtained by the processing of oxidized samples (Fig. 5a). Critical compositions 20424 and JDFD2 (Kress and Carmichael, 1988, $Fe^{3+}/Fe^{2+} < 0.091$ and 0.070, respectively) plot significantly above the extrapolation lines obtained for more oxidized samples (Figs. 5b, 5c) rather than below them, which could have been expected by analogy with pure liquid oxides. We noted above that this could be related to problems in the determination of Fe^{3+}/Fe^{2+} in reduced glasses.

Perhaps, the problem of the possible difference of critical and reduced silicate melts from oxidized ones can be solved only on the basis of special experiments under isothermal conditions and within a wide range of oxygen fugacity. Special attention should be given in these experiments to the accurate determination of Fe^{3+}/Fe^{2+} in reduced glasses.

CONCLUSIONS

Using the experimental data of Darken and Gurry (1946), we tested various models for the description of the ferrous/ferric ratio in pure liquid oxides as a function of temperature and oxygen fugacity.

It was shown that, at any particular temperature, the melts can be divided by some $f_{O_2}^{break}$ value into oxidized and reduced ones showing different $\log f_{O_2}$ coefficients (k). It is conceivable that the dominant iron species in melt is changed at $f_{O_2}^{break}$. On the other hand, it is possible that such a separation of melts will appear illusory and related only to imperfections of the models considered.

It was shown that the problems encountered during the description of pure liquid iron oxides can most likely be ignored in relatively low-temperature natural basaltic melts, owing primarily to the fact that $f_{O_2}^{break}$ is shifted at low temperatures into the reduced f_{O_2}, region not characteristic of terrestrial basaltic magmatism.

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