

New f_{O_2} -Barometers for Quenched Glasses of Various Petrochemical Series

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Abstract—Empirical oxygen barometers like

$$\log f_{\text{O}_2} = a \log(\text{Fe}^{3+}/\text{Fe}^{2+})_L + b/T + \sum d_i X_i$$

are proposed for melts of the tholeiitic, subalkaline, and alkaline petrochemical series. Their application provides improved $\log f_{\text{O}_2}$ computation accuracy by 20–30%. Redox conditions of oceanic basalt crystallization were estimated using the barometers proposed. It is established that previously reported values of oxygen fugacity were underestimated by 0.55 log unit, on average.

INTRODUCTION

Empirical relationships of ferric–ferrous ratio versus oxygen fugacity, temperature, and magmatic melt composition are used not only for calculating the ratio of different-valence iron forms at given P – T – f_{O_2} parameters, but also for solving the inverse problem concerning the estimation of oxygen fugacity.

In a general form, these equations look like

$$\log(\text{FeO}_{1.5}/\text{FeO})_L = k \log f_{\text{O}_2} + h/T + s, \quad (1)$$

where k , h , and s are empirical parameters, which can be represented by linear functions of melt composition:

$y = \sum X_i d_i + d_0$ (X_i are the mole fractions of major oxides). Equation (1) can be transformed into a form

$$\log f_{\text{O}_2} = [\log(\text{Fe}^{3+}/\text{Fe}^{2+})_L - h/T - \sum d_i X_i]/k, \quad (2)$$

which is suitable for the redoximetry of natural basaltic glasses. Carmichael and coauthors [1] proposed to calculate the oxygen fugacity relative to an NNO buffer [2] for MORB at arbitrary chosen temperature of 1200°C:

$\Delta\text{NNO} = \log f_{\text{O}_2}^{(\text{sample})} - \log f_{\text{O}_2}^{(\text{buffer NNO})}$. Such an approach is determined by the fact that lines of equal $\text{Fe}^{3+}/\text{Fe}^{2+}$, computed according to [3], are virtually parallel to the NNO buffer straight line in coordinates $1/T$ – $\log f_{\text{O}_2}$.

Christie and coauthors [4] have subsequently computed ΔNNO for 44 quenched MORB glasses. Fairly reducing crystallization conditions for MORB (1–2 log

units below QFM buffer) were inferred from the results obtained [4].

Further development of this research is aimed at improving the accuracy of empirical relationships proposed for the description of available experimental data on redox equilibria of ferric and ferrous components in silicate melts. Two approaches to the problem are known at present.

The first one consists in an attempt to describe the bulk of experimental data by a single equation. Advocates of this approach [3, 5–9] followed the way of expanding the experimental data sample and complicating relationship (1).

The main point of our alternative approach [10] envisages the application of the simplest form of equation (1):

$$\log(\text{Fe}^{3+}/\text{Fe}^{2+})_L = a \log f_{\text{O}_2} + b/T + \sum d_i X_i, \quad (3)$$

which is calibrated against a petrochemical series of limited compositional range and in a narrowed range of oxygen fugacity. The method proposed is more powerful for calculating the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio under certain T – f_{O_2} conditions for a melt of a given composition.

However, it should be noted that the other approach does not always lead to an increase in computation accuracy as compared with the model [7], which yields the best results by systematic testing [10]. In this connection, it seems important to call attention to the fact that in a general case the regression X on Y is by no means equivalent to the regression Y on X (see, for

Table 1. Regression coefficients and their standard deviations for equation (4) calibrated against melts of the “tholeiitic” (I), “subalkaline” (II), and “alkaline” (III) petrochemical series

Series	I	II	III
$a \log(\text{Fe}^{3+}/\text{Fe}^{2+})$	3.3796(0.5274)	3.1975(0.4293)	2.1118(0.3542)
$b(1/T)$	-22 586.2(2605.4)	-23 605.0(3226.8)	27849.6(1493.7)
d_{SiO_2}	7.1877(2.3899)	11.1331(2.5008)	14.2188(2.2194)
d_{TiO_2}	-36.7447(21.9043)	-32.7928(14.9509)	2.9525(4.6872)
$d_{\text{Al}_2\text{O}_3}$	21.6554(14.9474)	7.6259(4.2295)	3.1028(6.3130)
d_{FeO^*}	25.6818(8.1466)	20.4709(9.5107)	13.2237(3.1771)
d_{MgO}	6.9643(5.0699)	17.6792(3.2868)	10.3548(3.6607)
d_{CaO}	3.5047(4.0523)	2.6448(2.5110)	10.8360(1.5809)
$d_{\text{Na}_2\text{O}}$	41.2263(20.8824)	4.5455(8.5167)	14.3319(3.7028)
$d_{\text{K}_2\text{O}}$	-71.7530(51.0166)	6.3378(16.3134)	11.2567(4.1324)
$\sigma[\log f_{\text{O}_2}]$	0.55	0.45	0.24
Nikolaev and coauthors' model [10]			
$\sigma[\log f_{\text{O}_2}]$	0.81	0.59	0.35
The Borisov–Shapkin model [7]			
$\sigma[\log f_{\text{O}_2}]$	0.71	0.61	0.36

$\sigma = (\sum(\delta_i)^2/n)^{1/2}$

Table 2. Estimate of relative oxygen fugacity ΔNNO and of oxidation state of MORB from tholeiitic and subalkaline series during the quenching

Sample	ΔNNO [1]	ΔNNO , this work	$\delta(\Delta\text{NNO})$	Quenching temperature**, °C	$\log f_{\text{O}_2}$ at quenching temperature
523-2-1*	-1.89	-1.18	0.71	1220	-8.53
526-4-1*	-1.73	-1.07	0.66	1207	-8.55
527-1-1	-2.31	-1.81	0.50	1237	-8.99
527-4-1*	-2.25	-1.37	0.88	1222	-8.70
527-6-3	-2.00	-1.65	0.35	1194	-9.28
528-4-1	-1.83	-1.81	0.02	1232	-9.04
GLJ-7	-2.11	-1.64	0.47	1201	-9.19
TR138-11D-1*	-2.58	-1.80	0.78	1212	-9.23
TR-138-8D-1*	-2.36	-1.92	0.44	1273	-8.72
972-1*	-2.03	-1.44	0.59	1231	-8.67
975-1*	-2.19	-1.61	0.58	1187	-9.31
975-5-1*	-2.17	-1.50	0.67	1201	-9.05
D6-23	-2.79	-2.25	0.45	1219	-9.62
D12-5	-2.58	-2.02	0.56	1217	-9.40

Notes: * Basalts of subalkaline series.

** Calculated from model [16].

example [11]), and because of this, the solution of a regression equation relative to a regressor is, strictly speaking, incorrect. This specific feature of regression analysis has a potential of additionally improving accuracy in oxygen fugacity calculations.

CALIBRATION OF f_{O_2} BAROMETERS

The principal approach remains the same: the simplest equation

$$\log f_{\text{O}_2} = a \log(\text{Fe}^{3+}/\text{Fe}^{2+})_L + b/T + \sum d_i X_i \quad (4)$$

is calibrated in a restricted compositional range related to a certain petrochemical series. In order to do this, the INFOREX database [12] was used, and quenched glass samples with known ferric and ferrous cation contents equilibrated at the controlled oxygen fugacity ($\log f_{\text{O}_2} < \text{NNO} + 1$) were selected. Following the “total alkali—silica” (TAS) classification, the compositions related to three petrochemical series: conventional *tholeiitic* I, *subalkaline* II, and *alkaline* III were recognized. A detailed description of data samples representing these series was reported in [10]. Parameters of a multiple regression for equations (4) were computed for every series using the least-squares method (Table 1).

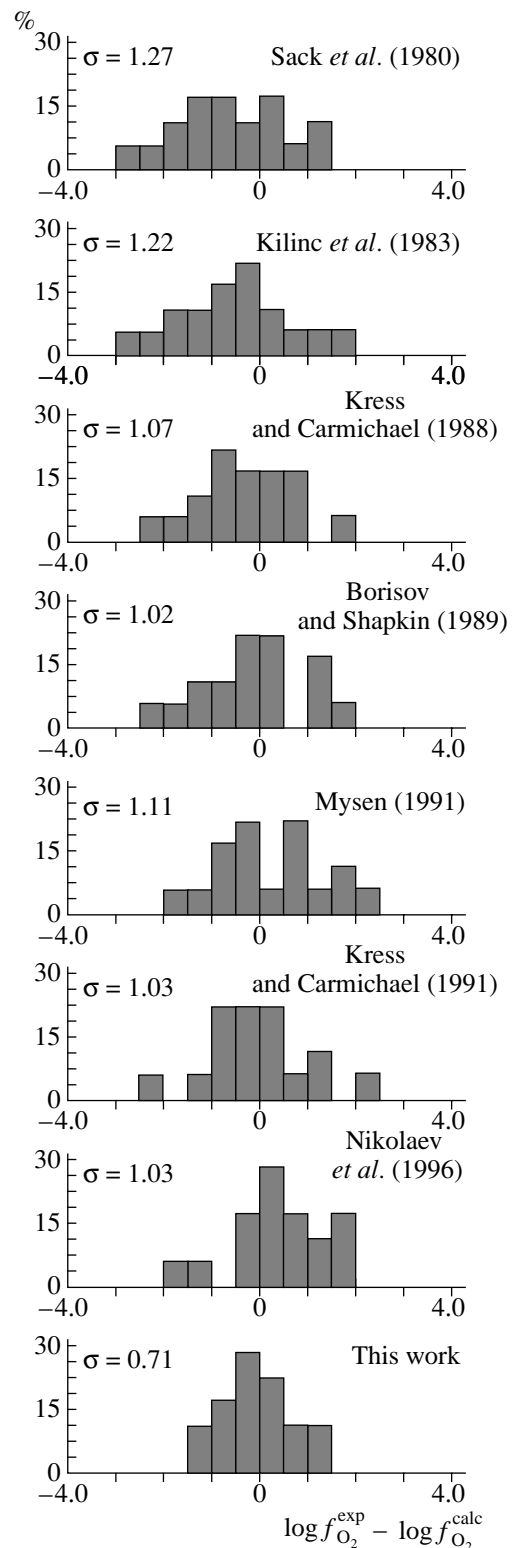
The equations of f_{O_2} -barometers for series I–III underwent the following verification. Modeling $\log f_{O_2}$ values were calculated for every composition of a respective series; then they were compared with experimental results and a difference $\delta_i = \log f_{O_2}^{\text{exp}} - \log f_{O_2}^{\text{calc}}$ was determined. After that the standard deviation $\sigma[\log f_{O_2}]$ was computed. Statistical characteristics of the calculation accuracy for the proposed f_{O_2} -barometers and for the models [7, 10] are given for comparison in the lower part of Table 1. The σ value was reduced by 20–30% depending on composition.

In addition to tests used in [10], the accuracy of $\log f_{O_2}$ determinations in the petrologically important range of low oxygen fugacities was verified by testing all the existing equations, along with the new f_{O_2} -barometer for the tholeiitic series, against 18 most reduced compositions from series I with experimental values of $\text{Fe}^{3+}/\text{Fe}^{2+} < 0.1$. The calculation results are presented in the figure as a set of bar charts; each of them is accompanied by a σ value for a given data sample. As follows from these results, the calculated oxygen fugacity values obtained from equations [3, 5] are regularly underestimated as compared with the experimental data. The bar charts indicate a marked increase in the computation accuracy when the proposed method is applied.

ESTIMATION OF REDOX CONDITIONS RELATED TO OCEANIC BASALT CRYSTALLIZATION

We have attempted to estimate the redox conditions of crystallization using representative samples of MORB glasses on the basis of new f_{O_2} -barometers for the tholeiitic and subalkaline series. Christie's data have been used for this purpose: unfortunately, we could not uniformly correlate the titration results [4] with the microprobe glass analyses [13–15] for 14 compositions only; oxygen fugacity values at 1200°C and relative oxygen fugacities ΔNNO were then computed for all of them.

Besides, the liquidus temperature for every composition, assumed to be the quenching temperature of the basaltic glasses studied, was calculated using the COMAGMAT [16] program package. The calculated oxygen fugacity values at this temperature are consistent with the redox state of magma during quenching (Table 2). The computation results show that for both the actual quenching temperature and for 1200°C, chosen in [1] as a standard temperature, the previously reported estimates of the oxygen fugacity had been underestimated by 0.55 log unit, on average. This testifies to the necessity to perform more detailed redoximetric studies that will probably lead to a revision of



Bar charts of $\delta_i = \log f_{O_2}^{\text{exp}} - \log f_{O_2}^{\text{calc}}$ for the data sample including 18 most reduced experiments ($\text{Fe}^{3+}/\text{Fe}^{2+} < 0.1$) from the tholeiitic series, after results of equation $\sigma = (\sum(\delta_i)^2/n)^{1/2}$ testing.

the current notions concerning the redox regime of oceanic magma crystallization.

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