

# Calculation of the Ferric–Ferrous Ratio in Magmatic Melts: Testing and Additional Calibration of Empirical Equations for Various Magmatic Series

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**Abstract**—The existing empirical equations for calculating the redox state of iron in natural silicate melts were tested. The best results were obtained with the Borisov–Shapkin equation (1989). None of the equations adequately describes the ferric–ferrous ratio in intermediate and acid melts. All the equations tested consistently underestimate the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  value in the petrologically important region of low oxygen fugacities. An alternative approach is proposed that improves the accuracy in calculating the redox state of iron.

## INTRODUCTION

The ferric–ferrous ratio in natural silicate melts is one of the principal parameters controlling the physical properties of magmatic liquids [1, 2] and the way in which they crystallize under open and closed conditions with respect to oxygen [3, 4]. The determination of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio is of major significance in calculating the activities of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  in the melts (on the basis of microprobe analysis of quenched glasses) and in developing mineral–melt geothermometers for olivine and pyroxenes [5–7]. It has been shown that this ratio must be included as an independent parameter when constructing empirical models of spinel–melt equilibrium based on statistical least-squares data processing [8, 9]. All this explains the importance attached to extremely accurately determining the ferric–ferrous ratio in the melts and the appearance of many experimental and theoretical works on this topic [10–20].

In general, the effect of temperature and oxygen fugacity on the ferric–ferrous ratio in silicate liquid is well studied [10–17]; however, predicting this ratio at specific  $T$ – $f_{\text{O}_2}$  conditions in melts of any given composition remains a problem. A number of empirical equations have already been proposed that relate ferric–ferrous ratio to temperature, oxygen fugacity, and composition of the liquid phase. The principal aim of this work is to estimate, on the basis of a representative sample of experimental data, the accuracy of the equations proposed by various authors, and thereby to identify both the models and the classes of igneous rocks that give the least error in determining the ferric–ferrous ratio. Moreover, in order to improve the accuracy of calculating  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in petrologic–geochemical models and the development of mineral–melt geothermometers, we propose using equations calibrated within a narrow sample that approximates the required compo-

sitional range rather than generalized equations based on the entire range of experimental glasses [10–17].

## REVIEW OF MODELS FOR CALCULATING THE FERRIC–FERROUS RATIO IN MAGMATIC MELTS

The ferric–ferrous ratio in the melt is governed by the reduction–oxidation reaction:



with the equilibrium constant

$$K = (a_{\text{FeO}_{1.5}}/a_{\text{FeO}})_L / f_{\text{O}_2}^{1/4}, \quad (2)$$

where the  $L$  index refers to the phase of the melt and  $a$  is the activity of the corresponding component. In the general case, the value of  $K$  depends on the enthalpy and entropy of reaction (1); therefore, assuming  $\gamma_{\text{FeO}_{1.5}}/\gamma_{\text{FeO}} \approx \text{const}$ , it can be easily shown that, for a given composition of the melt, the empirical relationship between the ferric and ferrous iron mole fractions, temperature, and oxygen fugacity can take the form:

$$\log(\text{FeO}_{1.5}/\text{FeO})_L = k \log f_{\text{O}_2} + h/T + s, \quad (3a)$$

or

$$\ln(\text{Fe}_2\text{O}_3/\text{FeO})_L = k \ln f_{\text{O}_2} + h_{\ln}/T + s_{\ln}, \quad (3b)$$

where  $k$ , in the ideal case, equals 0.25 (but actually is closer to 0.22 for most of the natural melts studied),  $h \geq 0$ , and  $s = \text{const}$  (see [18] for greater detail). Hereafter, in analyzing the empirical relations proposed by various authors, we will refer more frequently to form (3a), implying that expression (3b) can be transformed to (3a) by simple algebraic operations.<sup>1</sup> Let us now see

<sup>1</sup>  $h = h_{\ln} / 2.303$ ,  $s = (s_{\ln} + \log 2) / 2.303$ .

how the form of equation (3) describing the  $\text{FeO}_{1.5}/\text{FeO}(\text{Fe}^{3+}/\text{Fe}^{2+})$  ratio in a particular silicate melt can be extended to magmatic liquids of diverse compositions.

On the strength of their own data and published evidence (143 compositions of experimental glasses), Sack *et al.* [14] suggested that the  $k$  and  $h$  coefficients are constant for the entire data sample, and the influence of the melt composition on the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio is restricted to the  $s$  coefficient and can be described, in the simplest case, as a linear function of the mole fractions of major oxides  $X_i$  and empirical coefficients  $d_i$ :

$$\ln(\text{Fe}_2\text{O}_3/\text{FeO})_L = k \ln f_{\text{O}_2} + h_{\text{in}}/T + \sum d_i X_i + c. \quad (4)$$

The authors [14] pointed out that their equation was of an empirical nature and the calculated regression coefficients  $k = 0.2181$ ,  $h_{\text{in}} = 13\,185$  ( $h \sim 5700$ ), and  $d_i$  cannot be applied directly to a systematic thermodynamic description of the melt phase. Kilinc *et al.* [15] supplemented this sample with data of 49 experiments in air; using the same form of equation (4), they obtained the values  $k = 0.2185$  and  $h_{\text{in}} = 12\,670$  ( $h \sim 5500$ ).

Five years later, Borisov [18] demonstrated that, in fact, the  $h$  parameter varies over an extremely wide range, from about  $-2000$  to  $10\,000$ , for both oxidized and reduced natural magmatic melts; this brought up the question of adequately describing  $\text{FeO}_{1.5}/\text{FeO}$  for all classes of igneous rocks by means of a single equation (4) with a constant  $h$  value. Borisov and Shapkin [19] proposed a new equation in which all three parameters of equation (3a)— $h$ ,  $k$ , and  $s$ —are a function of the melt composition. In order to evaluate the corresponding regression coefficients (see table in [19]), the same set of experimental data as in [15] was used.

In 1988, Kress and Carmichael [16] conducted 63 additional redox experiments with natural basalts. Assuming that part of  $\text{FeO}$  and  $\text{FeO}_{1.5}$  in the melt form a completely associated  $\text{FeO}_{1.464}$  component, they proposed a new equation:

$$\ln(\text{FeO}_{1.464}/\text{FeO})_L = 0.232 \ln f_{\text{O}_2} - \Delta H/RT + \Delta S/R - \sum \Delta W_i X_i / RT, \quad (5)$$

where  $\Delta H$  and  $\Delta S$  are the effective enthalpy and entropy of the redox reaction,  $R$  is the gas constant, and  $\Delta W_i$  denotes the regression coefficients of the mole fractions of major oxides  $X_i$ . Comparing equation (3a) and (5) and ignoring (at least for the highly oxidized melts) the difference between the  $\text{FeO}_{1.464}/\text{FeO}$  and  $\text{FeO}_{1.5}/\text{FeO}$  ratios, we have  $h = -(\Delta H + \sum \Delta W_i X_i)/2.303R$  and  $s = \Delta S/2.303R$ . Thus, the form of equation (5) implies that the  $h$  parameter is a function of the melt composition, whereas  $s = \text{const}$  for all silicate liquids; however, this is inconsistent with the experimental data (see Fig. 5 in [18]).

Subsequently, Kress and Carmichael [17] abandoned their hypothesis of completely associated components; they conducted eight additional experiments and redetermined the compositions of eleven previously obtained experimental glasses whose chemical analyses appeared inaccurate. The new equation of these authors for 1 atm total pressure can be reduced to form (4) as well; the nonlinearity of the dependence  $\ln(\text{FeO}_{1.5}/\text{FeO})_L$  on  $1/T$  arising from the introduction of some additional terms into equation (4) (see equation (7) in [17]) was negligible within the range of the experimental temperatures.

Finally, Mysen [20] proposed an empirical equation containing (as independent variables) structural–chemical parameters of the melt  $F_i$  ( $\text{Al}/\text{Al} + \text{Si}$ ,  $\text{Fe}^{3+}/\text{Fe}^{3+} + \text{Si}$ , etc.) based on his own hypotheses concerning the structure of silicate melts:

$$\ln(\text{FeO}_{1.5}/\text{FeO})_L = k \ln f_{\text{O}_2} + h/T + \sum d_i F_i + c. \quad (6)$$

The use of this equation is complicated by the multi-stage scheme of calculating the structural–chemical parameters of the melt (the scheme varies with the ratios of the major components) and the need to construct an additional iterative cycle because ferric–ferrous iron concentrations enter the right and left sides of equation (6) simultaneously. This may explain why this model describing the dependence of the  $(\text{Fe}^{3+}/\text{Fe}^{2+})_L$  ratio on the intensive parameters of state has not found practical application in petrology. We have decided, however, to test Mysen's equation because the author claims that it shows substantially better accuracy in calculating  $\text{Fe}^{3+}/\text{Fe}^{2+}$  as compared with the relations proposed by other workers.

This brief review makes evident the difficulties encountered by the investigator attempting to compare and estimate the applicability of various equations: even for the same form of a relation, different authors used different data, and, in most cases, the standard deviations of calculating  $T$ ,  $\log f_{\text{O}_2}$ , or  $\ln(\text{Fe}^{3+}/\text{Fe}^{2+})_L$  in solving the inverse problem were not given altogether (Table 1). Thus, our plan is to test six equations proposed by various authors for calculating the ferric–ferrous ratio in natural silicate melts [14–17, 19, 20], using a single and most representative sample of the compositions of experimental glasses.

## TESTING THE EMPIRICAL EQUATIONS

To tackle this problem, we used information from the INFOREX database<sup>2</sup>, which contains a significant amount of experimental data on the compositions of

<sup>2</sup> In its recent version, INFOREX-3.0 (1996) [21, 22], the database is an information retrieval system containing data on 162 phase-equilibria studies on synthetic and natural systems carried out in 1962–1995. The database includes complete information on the conditions of 6174 experiments and contains 8311 compositions of coexisting phases, including 3197 quenched glasses.

**Table 1.** Standard deviations in calculating temperature, oxygen fugacity, and Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio and analytical errors in determining ferric and ferrous iron concentrations in silicate melts

Source*	$\sigma(t, ^\circ\text{C})$	$\sigma(\log f_{\text{O}_2})$	$\sigma(\log(\text{Fe}^{3+}/\text{Fe}^{2+}))$	$\sigma(\text{FeO}),$ wt %	$\sigma(\text{Fe}_2\text{O}_3),$ wt %
Kilinc <i>et al.</i> [15]	52	0.5	–	0.2	–
Borisov and Shapkin [19]	30–58 is a function of $h$	0.35 for $k \geq 0.2$ 0.69 for $k < 0.2$	0.09	–	–
Kress and Carmichael [16]	69	0.597	0.126	–	–
Kress and Carmichael [17]	–	–	–	0.21	0.42

\* Data for [14, 20] are absent.

quenched glasses with the known contents of ferric–ferrous iron: 298 runs representing seven experimental studies [11–17]. We excluded from consideration the results of experiments on simple synthetic systems (25 runs) and runs conducted under the most oxidizing ( $\log f_{\text{O}_2} > \text{NNO} + 1$ ) conditions.

The resultant sample included 170 glass compositions, which, in accordance with the classification proposed in [23], were divided into four series (Fig. 1): (I) the tholeiitic series (broadly) consisting of peridotites, basalts, and andesibasalts of normal alkalinity ( $n = 56$ ); (II) the subalkaline series (subalkaline picrites, trachybasalts, trachyandesibasalts, trachyandesites and trachydacites,  $n = 50$ ); (III) the alkaline series (alkaline picrites and basalts, melilitites, and melilitolites,  $n = 50$ ); and (IV) the andesite–rhyolite series ( $n = 14$ ). The distribution of these experiments over the compositions, temperatures, and oxygen fugacities is presented in Table 2.

The testing procedure was as follows. For each composition, model ferric–ferrous ratios were calculated using the equations from [14–17, 19, 20]. These ratios were compared with the experimental results by computing the values  $\delta_i = \text{Fe}^{3+}/\text{Fe}_{\text{exp}}^{2+} - \text{Fe}^{3+}/\text{Fe}_{\text{calc}}^{2+}$ . Then, for each series, the average deviations  $\Delta^{\text{av}}[\text{Fe}^{3+}/\text{Fe}^{2+}] = \sum |\delta_i|/n$  and MSWD (mean square weighed deviation)  $\sigma[\text{Fe}^{3+}/\text{Fe}^{2+}] = (\sum (\delta_i)^2/n)^{1/2}$  were calculated.

Certain difficulties arose while testing Mysen's equation. Apparently because of several misprints in the regression coefficients (see Table 4 in [20], the parameters for natural systems), we did not succeed in reproducing the author's calculations. Therefore, using the form of the equation proposed in [20], we computed the linear regression parameters ourselves; the coefficients given in the original work and the corresponding recalculated values are presented in Table 3. In this case, the sample of experimental data approximates, as well as possible, the data set of 190 compositions used by Mysen, but lacks eight experiments from [10]. This fact appears to be responsible for some minor discrepancies between most of the recalculated coefficients

and the original values. Thus, in testing the equation from [15], we used corrected regression coefficients.

Moreover, in order to determine the accuracy of calculations in the petrologically important region of low oxygen fugacities, each equation was additionally tested against the 18 most reduced compositions of the tholeiitic series having experimental values of  $\text{Fe}^{3+}/\text{Fe}^{2+} < 0.1$ .

## TEST RESULTS AND ANALYSIS

Figure 2 compares the experimental ferric–ferrous ratios with those calculated from the equations tested for the four series. Each of the horizontal rows of the plots corresponds to one glass series (I, II, III, or IV). The columns correspond to the equations tested: left column A, equations of Sack [14] and Kilinc [15]; column B, equations of Kress and Carmichael 1988 [16] and 1991 [17]; column C, equations of Borisov and Shapkin [19] and Mysen [20]. The deviations of the calculated values from the experimental ones ( $\Delta^{\text{av}}$  and  $\sigma$ ) are reported in Table 4, and average deviations of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  are also shown in Fig. 2. Analysis of the testing results leads to the following conclusions:

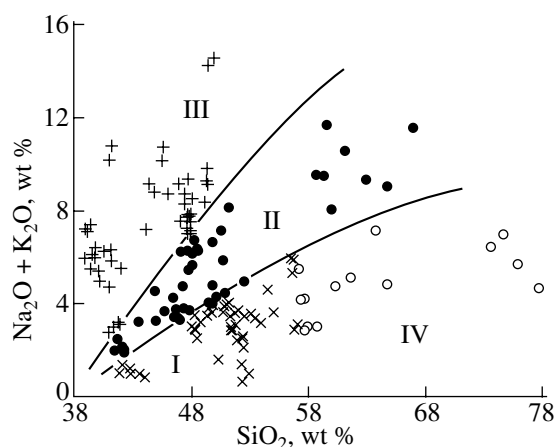
(1) The value of  $\Delta^{\text{av}}(\text{Fe}^{3+}/\text{Fe}^{2+})$  in series I, II, and III varies from 0.032 to 0.054; i.e., on the whole, the precision in estimating the ferric–ferrous ratio is comparable for all the equations.

(2) With the exception of the calculations for the andesite–rhyolite series, the best reproducibility of experimental data was observed when using the equation from [19].

(3) Despite the large amount of additional experiments involved, the equation of Kress and Carmichael [17], in the tholeiitic and subalkaline series, shows no improvement over the results obtained with the equations of Sack [14] and Kilinc [15], which have virtually the same form.

(4) None of the equations tested is capable of adequately describing data on the most acidic melts of the andesite–rhyolite series.

The results obtained clearly indicate that the consideration of the compositional dependence of the  $k$ ,  $h$ , and



**Fig. 1.** Compositions of the experimental glasses on a classification diagram alkalinity ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) vs.  $\text{SiO}_2$  [23]. I, picrites, basalts, and andesibasalts of the tholeiitic series; II, trachypicrites, trachybasalts, trachyandesites, and trachydacites of the subalkaline series; III, alkaline picrites, melilitites, melilitolites, and alkaline basalts of the alkaline series; IV, melts of the andesite–rhyolite series.

s parameters is crucial in describing the experimental values of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  by a single equation over the entire range of natural compositions [18, 19]. Furthermore, an inadequate form of empirical relation with no regard for the influence of composition on the  $k$  and  $h$  parameters leads to a situation in which additional experimental data do not improve the performance of subsequent versions of that equation, and may even deteriorate it if the new experimental data depart far from the “average” basalt.

At the same time, it should be acknowledged that single equations, even of complex form (such as in [19, 20]), poorly describe the ferric–ferrous ratio in the most acidic melts (Fig. 2, series IV). Bearing this in mind, it is desirable to conduct further experimental investigations aimed at elucidating the  $k$  and  $h$  parameters, such as were conducted in [24] with a single rhyolite.

The accuracy of predicting ferric–ferrous ratios using equations tested at low oxygen fugacities is shown on the six upper histograms in Figs. 3a–3f. These histograms represent the distribution of deviations of the calculated  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios from the experimental values for the 18 most reduced compositions (these points can also be seen in Fig. 2). Table 5 gives the  $\Delta^{\text{av}}$  values for each equation, which are as large as 36–40% of the average  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio for this sample;  $\sigma$ ; and the proportion of the experiments for which the calculated  $\delta_i$  deviations fall within  $\pm 0.02$ . These data indicate that for virtually all the equations tested, there is a consistent underestimation (up to 50%) of this ratio in the range of experimental  $\text{Fe}^{3+}/\text{Fe}^{2+}$  values  $< 0.1$ .

## ADDITIONAL CALIBRATION OF THE EQUATIONS

From a practical point of view, the above analysis of the applicability of various equations in a given range of compositions and conditions leads to another important conclusion. No matter what form of empirical relation is used in calculating the ferric–ferrous ratio in silicate melts over the complete compositional range of natural systems, it is impossible to reach a precision better than  $\pm 0.03$ . Apparently, this stems from the lack of an elaborate theory of silicate melts, so at this stage, we are unable to present more rigorous models (thermodynamically) for describing equilibrium (1). Another reason is that, in analytical determinations of ferric iron content in quenched glass, the results would differ from laboratory to laboratory, and no data processing techniques can eliminate these discrepancies.

However, without claiming to have found a fundamental solution to the problem of the ferric–ferrous ratio in silicate melts, we would like to propose an alternative approach. In essence, this approach can be described as follows. Unlike the previous workers who proceeded to extend the sample and complicate the form of the equation, we adopt the simplest form

$$\log(\text{Fe}^{3+}/\text{Fe}^{2+})_L = h/T + k \log f_{\text{O}_2} + \sum d_i X_i, \quad (7)$$

(where  $X_i$  denotes the mole fractions of major oxides), which is a slightly modified form of equation (4). This equation is calibrated within a fairly narrow range of compositions and redox conditions. It should be borne in mind, however, that the equation obtained will be correct only for the chosen range of compositions and  $f_{\text{O}_2}$ . Using the least-squares method, we processed the experimental data for the melts in each of the four series separately. The regression coefficients for the new equations are given in Table 6, and the deviations, in Table 4.

It can be seen from these data that the application of our alternative approach improved the reproducibility of the experimental data in solving the inverse problem for series I, II, and III as compared with the model described in [19]. In the case of melts of the andesite–rhyolite series, the matrix of the parameters was overdetermined and yielded no unique solution. Testing one of the new equations for the tholeiitic series (see column I in Table 6) against a sample of 18 highly reduced glasses shows that the values of  $\Delta^{\text{av}}$  and  $\sigma$  decreased to 0.020 and 0.026, respectively, and the proportion of experiments for which the  $\delta_i$  deviations lie within  $\pm 0.02$  increased to 61% (Fig. 3g).

## ESTIMATION OF OXYGEN FUGACITY AND TEMPERATURE

The presence of an empirical relation between the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio in the melt, oxygen fugacity, temperature, and composition of the silicate liquid enables not

**Table 2.** Distribution of compositions of experimental glasses over temperature and oxygen-fugacity values (the results of search in the INFOREX database)

$T, ^\circ\text{C}$	>NNO +1	NNO + 1-QFM	QFM-IM	IM-IW	<IW
>1500°C	I(4)		I(4)		
1500–1400°C	I(18); II(19) III(9); IV(5)	III(2)	I(4); II(1)	I(5)	I(2)
1400–1300°C	I(16); II(4) III(8); IV(6)	I(20); II(24) III(23); IV(13)	I(8); II(2) III(2)	II(2)	
1300–1200°C	I(10); II(4)	I(11); II(17) III(22); IV(1)			
<1200°C		I(2); II(4) III(1)			

Note: Roman numerals denote melt series (Fig. 1); arabic numerals in parentheses denote the quantity of compositions.

only the calculation of the ferric-ferrous ratio at specified  $T$ - $X$ - $f_{\text{O}_2}$  parameters, but also the solution of the inverse problems.

Equation (3a) can be transformed into the form:

$$\log f_{\text{O}_2} = [\log(\text{Fe}^{3+}/\text{Fe}^{2+})_L - h/T - s]/k, \quad (8)$$

which is convenient for solving the problems of redox relations of natural basaltic glasses at the known (from chemical analysis)  $(\text{Fe}^{3+}/\text{Fe}^{2+})_L$  ratio, temperature, and bulk composition of the melt or the corresponding quenched glass.

Using Sack's equation [14], Dmitriev *et al.* [25] were among the first to demonstrate the applicability of this approach with reference to several oceanic glasses of tholeiite composition. These studies were developed more completely by Christie *et al.* [26] who applied Kilinc's equation [15] to the compositions of 44 mid-ocean ridge glasses and concluded that the conditions of crystallization of tholeiitic magmas in seafloor spreading zones are highly reducing (1–2 log units below the QFM buffer).

Considering the importance of this petrologic problem, we have attempted to estimate the accuracy of oxygen-fugacity reproduction based on compositions of experimental glasses of various magmatic series (Fig. 1). The empirical models [14–17, 19, 20] and our equations (7) (Table 6) were reduced to form (8). Using these relations and experimental temperature values for each given composition, the model values of  $f_{\text{O}_2}$  were calculated. These were compared with the experimental oxygen-fugacity values; the average deviations  $\Delta^{\text{av}}$  and standard deviations  $\sigma$  for the three series singled out are reported in Table 4.

The main conclusion from this analysis is that, even with an experimentally specified temperature, the average accuracy of  $f_{\text{O}_2}$ -barometers varies from 0.3 to 0.8 log units, and the melts of the alkaline series typically have the least error in  $f_{\text{O}_2}$  evaluation, regardless of the model employed. This may be due not so much to the

compositional variations (e.g., with respect to the  $\text{SiO}_2$  content, Fig. 1) as to the degree of correlation between the oxidation state of iron in the melt (ferric-ferrous ratio) and oxygen fugacity within each series. The varying degrees of correlation between these parameters are reflected in the variations of the  $k$  coefficient: for the alkaline melts,  $k$  is at a maximum, and the accuracy of calculations ( $\Delta^{\text{av}}$ ) increases to 0.3–0.4 log units; in the melts of the tholeiitic series, the accuracy of  $f_{\text{O}_2}$  estimation decreases by a factor of 1.5–2. The best results in calculating redox relations in series I, II, and III were obtained when using the Borisov-Shapkin model [19]. In the case of compositions of series II and III, the accuracy of the equations proposed in this work is comparable to the model in [19], but for the tholeiitic series, our model is appreciably less precise (Table 4).

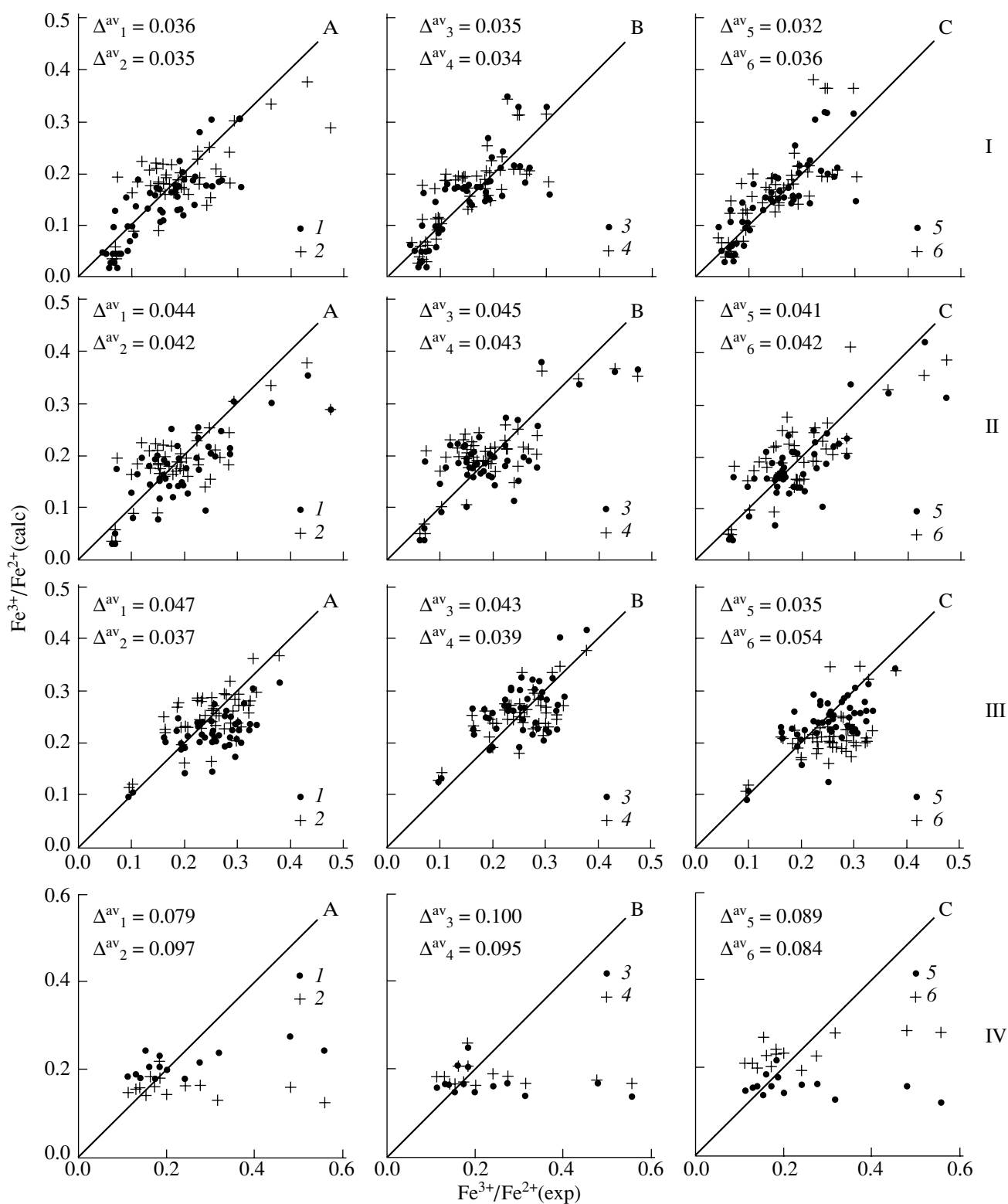
The equation (3a) can also be solved for temperature:

$$T = h/[\log(\text{Fe}^{3+}/\text{Fe}^{2+})_L - k \log f_{\text{O}_2} - s]. \quad (9)$$

**Table 3.** The values of recalculated (A) and original (B) regression coefficients for equation (14) in [15]

Coefficient	A	B
$a[\text{const}]$	4.277	4.384
$b[1/T]$	-8638.8	-0.9077*
$c[\ln f_{\text{O}_2}]$	-0.1486	-0.1420
$d[\text{Al}/(\text{Al} + \text{Si})]$	0.718	-9.875*
$e[\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Si})]$	-7.614	1.621*
$f_j[(\text{NBO}/T)_{\text{Mg}}]$	1.0142	0.8607
$f_j[(\text{NBO}/T)_{\text{Ca}}]$	-0.8295	-0.6560
$f_j[(\text{NBO}/T)_{\text{Na}}]$	-13.491	-1.194*
$f_j[(\text{NBO}/T)_{\text{Fe}^{2+}}]$	1.749	-2.310

\* Probable misprints.



**Fig. 2.** Comparison of experimental and calculated  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios for melts of various magmatic series. Roman numerals denote melt series shown in Fig. 1. Testing results for: 1, Sack *et al.*, 1980 [14]; 2, Kilinc *et al.*, 1983 [15]; 3, Kress and Carmichael, 1988 [16]; 4, Kress and Carmichael, 1991 [17]; 5, Borisov and Shapkin, 1989, [19]; 6, Mysen, 1991 [20].  $\Delta^{\text{av}}$  = average deviation of calculated ratio from experimental value:  $\text{Fe}^{3+}/\text{Fe}^{2+}_{\text{exp}} - \text{Fe}^{3+}/\text{Fe}^{2+}_{\text{calc}}$ .

**Table 4.** Statistical characteristics of deviations ( $\Delta^{\text{av}}$  and  $\sigma$ ) of the experimental values of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\log f_{\text{O}_2}$ ,  $T^\circ(\text{K})$  from those calculated by the equations for melts of various series (I–IV)

Parameter	Series	[14]		[15]		[16]		[19]		[20]		[17]		This work; coefficients in Table 6	
		$\Delta^{\text{av}}$	$\sigma$	$\Delta^{\text{av}}$	$\sigma$	$\Delta^{\text{av}}$	$\sigma$	$\Delta^{\text{av}}$	$\sigma$	$\Delta^{\text{av}}$	$\sigma$	$\Delta^{\text{av}}$	$\sigma$	$\Delta^{\text{av}}$	$\sigma$
$\text{Fe}^{3+}/\text{Fe}^{2+}$	I	0.036	0.045	0.035	0.044	0.035	0.046	0.032	0.043	0.036	0.049	0.035	0.046	0.029	0.041
	II	0.044	0.056	0.042	0.056	0.045	0.056	0.041	0.051	0.042	0.051	0.044	0.055	0.038	0.046
	III	0.047	0.058	0.037	0.045	0.043	0.050	0.035	0.045	0.054	0.065	0.039	0.046	0.032	0.041
	IV	0.079	0.113	0.097	0.159	0.100	0.156	0.089	0.123	0.084	0.109	0.095	0.147	–	–
$\log f_{\text{O}_2}$	I	0.63	0.84	0.59	0.81	0.52	0.72	0.52	0.71	0.62	0.80	0.57	0.74	0.63	0.81
	II	0.54	0.69	0.49	0.66	0.49	0.63	0.48	0.61	0.55	0.69	0.53	0.70	0.49	0.59
	III	0.40	0.49	0.31	0.39	0.34	0.40	0.26	0.36	0.52	0.62	0.36	0.44	0.27	0.35
	IV	0.63	0.75	0.83	1.19	0.81	1.10	1.05	1.39	0.91	1.03	0.87	1.15	–	–
$T^\circ(\text{K})$	I	62.5	83.9	61.7	83.5	59.6	82.5	80.0	121.0	66.5	87.4	59.2	78.8	72.3	97.1
	II	48.7	62.6	47.3	63.1	52.3	66.6	51.9	65.1	54.4	69.5	51.1	67.4	49.0	59.0
	III	35.6	43.9	29.9	37.4	34.4	40.8	22.8	31.0	47.9	55.5	34.4	42.1	22.6	29.9
	IV	58.5	69.0	73.8	102.7	83.2	108.6	n. d.	n. d.	91.2	103.8	80.2	101.7	–	–

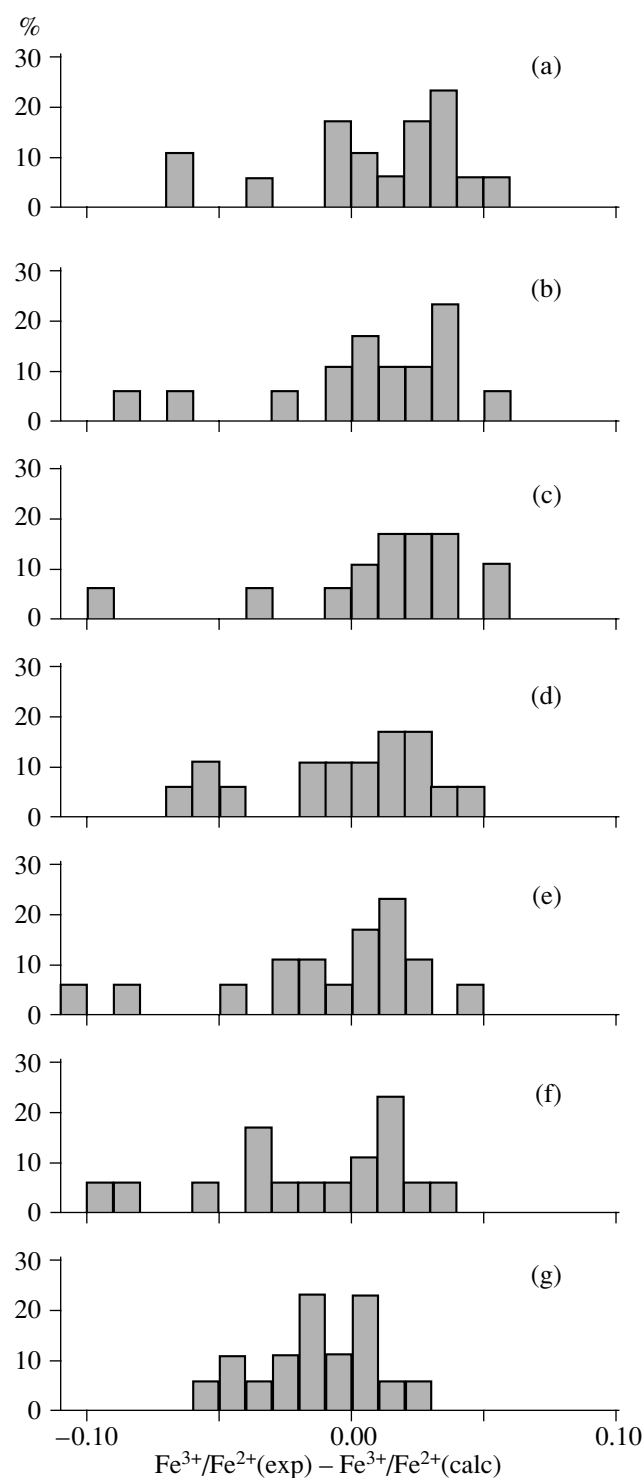
Note:  $\Delta^{\text{av}} = \Sigma|\delta_i|/n$ ;  $\sigma = (\Sigma(\delta_i)^2/n)^{1/2}$ ; u.v. = uncertain value.

**Table 5.** Results of testing the equations using a sample of 18 most reduced compositions of the tholeiitic series

Parameter	[14]	[15]	[16]	[19]	[20]	[17]	This work; coefficients in Table 6
$\Delta^{\text{av}}[\text{Fe}^{3+}/\text{Fe}^{2+}]$	0.029	0.029	0.027	0.026	0.029	0.029	0.020
$\sigma[\text{Fe}^{3+}/\text{Fe}^{2+}]$	0.035	0.036	0.036	0.031	0.037	0.040	0.026
$-0.02 < \delta_i < 0.02$	33%	38%	44%	50%	55%	50%	61%

**Table 6.** Regression coefficients and their standard deviations for equations additionally calibrated against melts of various magmatic series

Coefficient	I	II	III
$h(1/T)$	3282.2 (710.0)	4348.4 (954.2)	6447.3 (1114.4)
$k(\log f_{\text{O}_2})$	0.1395 (0.0218)	0.1817 (0.0244)	0.2228 (0.0374)
$d_{\text{SiO}_2}$	-1.4238 (0.4880)	-2.5966 (0.6024)	-3.9594 (0.8130)
$d_{\text{TiO}_2}$	-4.3585 (4.5402)	3.7652 (3.7248)	-3.6211 (1.4188)
$d_{\text{Al}_2\text{O}_3}$	-9.4488 (2.7762)	-1.3025 (1.0279)	-1.7093 (2.0388)
$d_{\text{FeO}^*}$	-0.7550 (1.8222)	-3.9708 (2.3110)	-2.2284 (1.1841)
$d_{\text{MgO}}$	-2.2326 (0.9983)	-3.9808 (0.8134)	-2.5944 (1.2363)
$d_{\text{CaO}}$	0.3404 (0.8286)	-0.4226 (0.6031)	-2.6738 (0.6282)
$d_{\text{Na}_2\text{O}}$	2.4766 (4.4047)	0.5992 (2.0352)	-2.8563 (1.3358)
$d_{\text{K}_2\text{O}}$	4.4534 (10.5676)	0.1417 (3.8959)	-1.1385 (1.4503)



**Fig. 3.** Histograms of  $\delta_i = \text{Fe}^{3+}/\text{Fe}^{2+}_{\text{exp}} - \text{Fe}^{3+}/\text{Fe}^{2+}_{\text{calc}}$  for a sample of 18 most reduced compositions of the tholeiitic series. Testing results for: (a) Sack *et al.*, 1980 [14]; (b) Kilinc *et al.*, 1983 [15]; (c) Kress and Carmichael, 1988 [16]; (d) Kress and Carmichael, 1991 [17]; (e) Borisov and Shapkin, 1989, [19]; (f) Mysen, 1991 [20]; (g) additionally calibrated equation (Table 6, column I).

We have estimated the accuracy of solving the inverse problem with respect to temperature for all the above models; the testing results are presented in Table 4. These data indicate that the average accuracy of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox thermometers is worse than 20°C and usually varies from 30 to 60°C. It is readily apparent that the application of such relations to thermometry is of no practical interest.

## CONCLUSION

We have systematically tested the empirical equations proposed in [14–17, 19, 20] for estimating the redox state of iron. When using these relations, the experimental values of the ferric–ferrous ratio in glasses of various magmatic series are reproducible to a precision of 0.03–0.05. The least errors were obtained with the equation from [19] in the melts of the tholeiitic ( $\Delta^{\text{av}} = 0.032$ ), subalkaline (0.041), and alkaline (0.035) series. Apparently, this arises from the form of the Borisov–Shapkin equation, which most adequately describes the ferric–ferrous ratio in ultramafic and mafic natural melts of different alkalinities.

All the equations tested exhibit a systematic underestimation of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  value in the petrologically important region of low oxygen fugacities: the uncertainties in calculating this ratio may exceed 50%.

None of the equations tested adequately describes data on the melts of the andesite–rhyolite series. Apparently, the ferric–ferrous ratio in acidic melts is markedly different from typical basaltlike rocks and requires further experimental study.

We proposed an alternative approach and demonstrated its efficiency. In contrast to the previous workers who expanded the sample and complicated the form of the relation, we adopted the simplest form of the equation, which was calibrated with compositions of a restricted magmatic series.

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