



# Ferric-ferrous ratio and oxygen fugacity calculations for primitive mantle-derived melts: calibration of an empirical technique

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## Summary

Several experimentally-based, empirical calibrations of the  $fO_2$  of natural silicate melts at atmospheric pressure as a function of melt composition, melt  $Fe^{2+}/Fe^{3+}$ , and crystallization temperature have been developed (e.g. Sack et al., 1980; Kilinc et al., 1983; Kress and Carmichael, 1988; Borisov and Shapkin, 1990). Cr–Al spinel is a liquidus phase of primitive mantle-derived melts, and is commonly found as inclusions in near-liquidus phenocrysts (mainly olivine). The established atmospheric pressure correlation between  $Fe^{2+}/Fe^{3+}$  values in spinel and coexisting melts over a broad range of basaltic compositions (Maurel and Maurel, 1982) can be used to calculate the  $Fe^{2+}/Fe^{3+}$  value of a melt if the composition of the equilibrium spinel is known. Compositions and crystallization temperatures of primitive melts can be determined by experimental studies of melt inclusions trapped by early-formed refractory phenocrysts. Thus, the association of spinel and melt inclusions in early liquidus phenocrysts can be used to estimate  $fO_2$  conditions at the time of their crystallization.

In this paper, we present a calibration of this method and discuss its applications. We conclude that combination of the equations of Maurel and Maurel (1982) and Borisov and Shapkin (1990) can be used to calculate  $fO_2$  with an accuracy of  $\pm 0.7$  log units, when liquidus spinels have  $TiO_2 < 2.5$  wt% and  $Cr_2O_3 > 13$  wt.%, and melt compositions are in the range from basaltic to picritic with  $H_2O$  contents  $< 6$  wt.%.

Using this technique we find  $\Delta NNO fO_2$  values of  $-0.8$  to  $-1.4$  for MORB dredged at the VEMA Fracture Zone in the Atlantic, and 0 to +1 for Tongan high-Ca boninites.

## Zusammenfassung

Die Berechnung von  $Fe^{2+}/Fe^{3+}$  und der Sauerstoff-Fugazitäten für primitive Mantel-schmelzen: Kalibration einer empirischen Methode

Empirische, auf Experimenten basierende, Kalibrationen zur Berechnung von  $fO_2$  natürlicher Silikatschmelzen bei atmosphärischem Druck in Abhängigkeit von der Schmelzzusammensetzung, des  $Fe^{2+}/Fe^{3+}$  Verhältnisses und der Kristallisationstemperatur wurden z.B. von *Sack et al. (1980)*, *Kilinc et al. (1983)*, *Kress und Carmichael (1988)* und *Borisov und Shapkin (1980)* entwickelt. Cr-Al-Spinell ist eine Liquidusphase primitiver Mantelschmelzen und kommt üblicherweise als Einschluß in "near-liquidus" Phänokristallen (hauptsächlich in Olivin) vor. Die Korrelation des Atmosphärendruckes zwischen  $Fe^{2+}/Fe^{3+}$  in Spinell und koexistierender Schmelze kann dazu verwendet werden, das Verhältnis von  $Fe^{2+}/Fe^{3+}$  der Schmelze für einen weiten Bereich basaltischer Zusammensetzungen zu berechnen, wenn die Zusammensetzung des im Gleichgewicht gebildeten Spinells bekannt ist (*Maurel und Maurel, 1982*). Die Zusammensetzungen und Kristallisationstemperaturen primitiver Schmelzen können durch experimentelle Studien von Schmelzeinschlüssen, die in früh gebildeten refraktären Phänokristallen eingeschlossen wurden, ermittelt werden. Daher lassen sich Spinelle und assoziierte Schmelzeinschlüsse in frühen Liquidus-Phänokristallen dazu benützen, die  $fO_2$ -Bedingungen während der Kristallisation abzuschätzen.

In dieser Arbeit präsentieren wir eine neue Kalibration dieser Methode und diskutieren ihre Anwendungen. Wir schlußfolgern, daß unter Kombination der verwendeten Gleichungen von *Maurel und Maurel (1982)* sowie von *Borisov und Shapkin (1990)*  $fO_2$  mit einer Genauigkeit von  $\pm 0.7 \log$  Einheiten berechnet werden kann, sofern die Liquidus-Spinelle  $< 2.5$  Gew.%  $TiO_2$  und  $> 13$  Gew.%  $Cr_2O_3$  haben und die Schmelzzusammensetzungen von basaltisch bis pikritisch, mit maximal 6 Gew.%  $H_2O$ , reichen.

Unter Verwendung dieser Technik wurden die  $\Delta NNO fO_2$  Werte für die von der VEMA Fracture Zone im Atlantik stammenden MORB Proben mit 0.8 bis - 1.4, die der High-Ca Boninite von Tonga mit 0 bis + 1 bestimmt.

## Introduction

The  $Fe^{2+}/Fe^{3+}$  ratio in basaltic melts is an important petrological parameter which, if known, can provide valuable constraints on primary melt compositions. The  $Fe^{2+}/Fe^{3+}$  value of a melt of a given composition controls the composition of equilibrium ferromagnesian silicates (usually olivine for primitive mantle derived melts). It has also been experimentally demonstrated that  $fO_2$  of natural silicate melts at atmospheric pressure can be calculated if melt composition, the  $Fe^{2+}/Fe^{3+}$  value in the melt, and crystallization temperature are known, and several empirical atmospheric pressure calibrations have been developed (e.g. *Sack et al., 1980*; *Kilinc et al., 1983*; *Kress and Carmichael, 1988*; *Borisov and Shapkin, 1990*). *Carmichael (1991)* employed this approach to demonstrate differences in  $fO_2$  between glassy lavas from several magmatic suits. However, glassy lavas which are likely to have retained the magmatic  $Fe^{2+}/Fe^{3+}$  value are usually only available for modern magmatic suits. Moreover, primitive, near-primary melts are often modified by extensive fractionation and assimilation processes en route to the surface. Thus  $fO_2$  estimates based on compositions ( $Fe^{2+}/Fe^{3+}$  values) of volcanic rocks and glasses may differ from the primary  $fO_2$  values of primitive melts.

Another possible approach to calculate  $fO_2$  uses olivine-orthopyroxene-spinel geobarometry (*O'Neill and Wall, 1987*; *Wood et al., 1990*; *Ballhaus et al., 1991*). This approach has been shown to be very useful for studies of upper mantle rocks, but its application is not straightforward to mantle-derived melts. On one hand, mantle-based calibrations are limited to highly magnesian compositions ( $Fo > 85$ ) restrict-

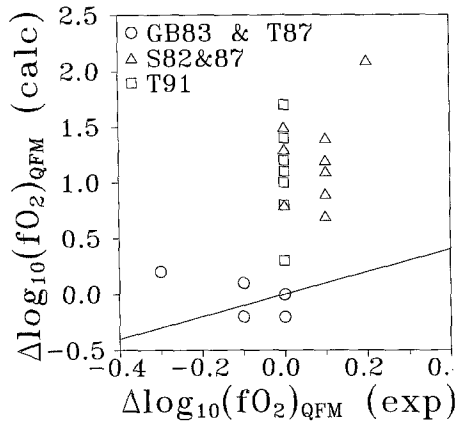


Fig. 1. Comparison between experimental oxygen fugacities and those calculated using the *Ballhaus et al. (1991)* olivine-spinel geobarometer. Tholeiitic compositions: GB83 = *Grove and Bryan (1983)*; T87 = *Tormey et al. (1987)*. Alkaline compositions: S82 = *Sack (1980)*; S87 = *Sack et al. (1987)*; T91 = *Thy et al. (1981)*. See text for discussion

ing the application of this approach to very primitive melts, which are rare among magmatic suites. On the other hand, due to the strong pressure dependence of the orthopyroxene liquidus and the typically significant difference in pressure between melt segregation and crystallization, orthopyroxene is rare in mafic melts and has only been found as an early liquidus phase in subduction-related boninite suites (e.g. *Sobolev and Danyushevsky, 1994*). However, it has been argued (*Ballhaus et al., 1991; Ballhaus, 1993*) that olivine-spinel oxygen geobarometry can still be applied to low-pressure primitive mantle-derived melts even if there is no orthopyroxene on their liquidus, and that in this case the barometer requires an insignificant (<0.2 log units) correction to the calculated  $fO_2$  values compensating for decreased  $SiO_2$  activity at low pressure. Figure 1 presents calculated  $fO_2$  using olivine-spinel geobarometry (*Ballhaus et al., 1991*) for a set of 24 available one atmospheric experiments with reported  $fO_2$  values and olivine and spinel compositions. Clearly, calculated  $fO_2$  values for experiments with tholeiitic melt compositions (*Grove and Bryan, 1983; Tormey et al., 1983*) are indeed close to the experimental  $fO_2$  values, whereas for more alkaline compositions (*Sack, 1982; Sack et al., 1987; Thy et al., 1991*) which are more undersaturated in orthopyroxene, a large correction is required. This demonstrates that the application of olivine-spinel oxygen geobarometry is limited to primitive (in equilibrium with  $FO > 85$ ) tholeiitic melts.

On the other hand,  $Fe^{2+}/Fe^{3+}$  of a melt can be calculated if the composition of the equilibrium spinel is known. Cr-Al spinel is the usual liquidus phase of primitive mantle-derived melts, and is commonly found as inclusions in early liquidus phenocrysts (mainly olivine). In general, the ferric-ferrous equilibrium between melt and spinel at low pressure can be described as:

$$\log_e((Fe_{sp}^{2+} * Fe_{melt}^{3+}) / (Fe_{sp}^{3+} * Fe_{melt}^{2+})) = -(\Delta H/R)/T + \Delta S/R$$

where  $\Delta H$  and  $\Delta S$  are enthalpy and entropy of the reaction,  $R$  is the gas constant and  $T$  is temperature.

As noted by *Ballhaus et al. (1991)*, this  $K_D$  is temperature independent (implying that the  $\Delta H$  of the above reaction is close to 0) due to similar  $T - fO_2$  relationships of spinels and silicate melts. Thus the ferric-ferrous spinel-melt equilibria can be

described as:

$$\log_e(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{sp}} = \log_e(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{melt}} + B$$

where B is a constant.

This relationship was experimentally tested by *Maurel* and *Maurel* (1982) over a broad range of basaltic compositions at atmospheric pressure. They published an empirical calibration:

$$0.764 * \log_{10}(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{melt}} = \log_{10}(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{spinel}} + 0.343$$

The melt  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values obtained can then be used to calculate  $f\text{O}_2$  using one of the existing thermodynamic models. Compositions and crystallization temperatures of primitive melts, required variables for such calculations, can either be determined by experimental studies of melt inclusions trapped by these refractory phenocrysts (*Roedder*, 1984; *Sobolev et al.*, 1989; *Danyushevsky et al.*, 1992), or can be obtained from primitive quenched glasses, if these are available (e.g. for mid-ocean ridge basalts). Thus, the association of spinel and melt inclusions in early liquidus phenocrysts can be used to estimate the  $f\text{O}_2$  of crystallization. This method is attractive because of its potential application to a wide range of mantle-derived primitive melts.

In this paper we present a calibration of this method and discuss its applications.

### Calibration

To estimate the accuracy of the proposed technique, we used 47 atmospheric pressure experiments for which  $f\text{O}_2$ , melt and spinel compositions have been reported (*Fisk and Bence*, 1980; *Sack*, 1982; *Grove and Bryan*, 1983; *Sack et al.*, 1987; *Tormey et al.*, 1987; *Thy et al.*, 1991; *Roeder and Reynolds*, 1991). From data reported by *Roeder and Reynolds* (1991), we used only spinels from the highly oxidized experiments ( $\log_{10}(f\text{O}_2) \geq -5.1$ ), as analytical problems (indicated by low totals) with spinel analyses presented in that paper most strongly affect the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values of reduced spinels. In all selected experiments, spinel compositions fall within the compositional range used by *Maurel and Maurel* (1982) to derive their correlation:  $\text{TiO}_2 < 2.5$  wt.%,  $\text{FeO}^* = 13 - 60$  wt.%,  $\text{Cr}_2\text{O}_3 > 13$  wt.%,  $\text{Al}_2\text{O}_3 > 4$  wt.%. The  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values in spinel were calculated by *Maurel and Maurel* (1982) assuming stoichiometry (3 cations for each 4 oxygens in the spinel structure). Analytical uncertainties can produce significant errors in the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values obtained by the stoichiometry calculations, if the  $\text{Fe}^{3+}$  content of spinel is very low (e.g. *Wood and Virgo*, 1989). Accordingly, experiments at very low  $f\text{O}_2$  (*Akella et al.*, 1976; *Rhodes et al.*, 1979) have not been included in the data set.

Selected experiments cover a substantial range of broadly basaltic melt compositions (from tholeiitic to alkalic), temperature (1150–1300 °C) and  $f\text{O}_2$  (from  $-2$  to  $+4.2$  log units relative to the fayalite-magnetite-quartz oxygen buffer).

The following procedure has been employed:

1.  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values of quenched experimental melts have been calculated using the correlation of *Maurel and Maurel* (1982)
2. Based on the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values obtained above,  $f\text{O}_2$  has been calculated using four different models:

Table 1. Coefficients for  $fO_2$  estimations

Coefficient				Model		
	1	2	3	D* 100	4 D1	D2* 1000
A	0.21813	0.2185	0.232	0.1735		
B	13,184.7	12,670	11,540	771.7		
C	-4.49933	-7.54	-5.54	1.914		
D <sub>SiO<sub>2</sub></sub>	-2.15036	0	0	1.647	-70.91	-1.511
D <sub>TiO<sub>2</sub></sub>	0	0	0	-53.59	816.3	0.7999
D <sub>Al<sub>2</sub>O<sub>3</sub></sub>	-8.35163	-2.24	-5900	-11.9	132.3	1.424
D <sub>FeO*</sub>	-4.49508	1.55	0	-25.2	448.4	6.92
D <sub>MgO</sub>	-5.43639	0	0	5.52	-112	2.478
D <sub>CaO</sub>	0.073113	2.96	5800	-1.685	3.876	-1.097
D <sub>Na<sub>2</sub>O</sub>	3.54148	8.42	12,760	-18.44	408.7	9.416
D <sub>K<sub>2</sub>O</sub>	4.18688	9.59	13,290	-25.14	491.6	6.207

(1) Sack et al. (1980) and (2) Kilinc et al. (1983) for which:

$$\log_e(X_{Fe_2O_3}/X_{FeO}) = A * \log_e(fO_2) + B/T + C + \Sigma(D_i * X_i);$$

(3) Kress and Carmichael (1988):

$$\log_e(X_{FeO1.464}/X_{FeO}) = A * \log_e(fO_2) + B/T + C + \Sigma(D_i * X_i)/T;$$

(4) Borisov and Shapkin (1990):

$$\log_{10}(Fe^{3+}/Fe^{2+}) = A * \log_{10}(fO_2) + B/T + C + \Sigma(D_i * X1_i) + \Sigma(D1_i * X1_i)/T + \Sigma(D2_i * X1_i) * \log_{10}(fO_2),$$

where A, B, C and D are the regression coefficients (Table 1), X = mole fraction of melt components, X1 = mole per cent of melt components.

The results of these calculations are shown in Fig. 2 and 3 and in Table 2. All four models show a close to normal distribution of differences between experimental and calculated  $fO_2$  values ( $\Delta$ ), and a good correlation exists between calculated and experimental  $fO_2$ . No systematic difference exists between data sets of different authors (Fig. 2). One particular experiment (Fisk and Bence, 1980, run #6) plots out of the main group, having the largest negative  $\Delta$  for each model, and this experiment has been excluded from the data set. Standard deviations of  $fO_2$  values calculated for the remaining 46 experiments at the 95% confidence level, are close to 0.5 (Table 2), resembling those for the models themselves ( $\sim 0.45$ , Borisov and Shapkin (1990);  $\sim 0.6$ , Kilinc et al. (1983) and Kress and Carmichael (1988)). This implies that calculation of  $Fe^{2+}/Fe^{3+}$  values in melts using the equation of Maurel and Maurel (1982) does not introduce any significant additional error. There is a systematic difference between the four models in the average  $\Delta$ . Although all four models describe the experimental data with reasonable accuracy ( $\pm 1$  log units), the model of Borisov and Shapkin (1990) best reproduces the experimental values, with an average  $\Delta$  of  $-0.21$  log units and an accuracy of  $\pm 0.7$  log units.

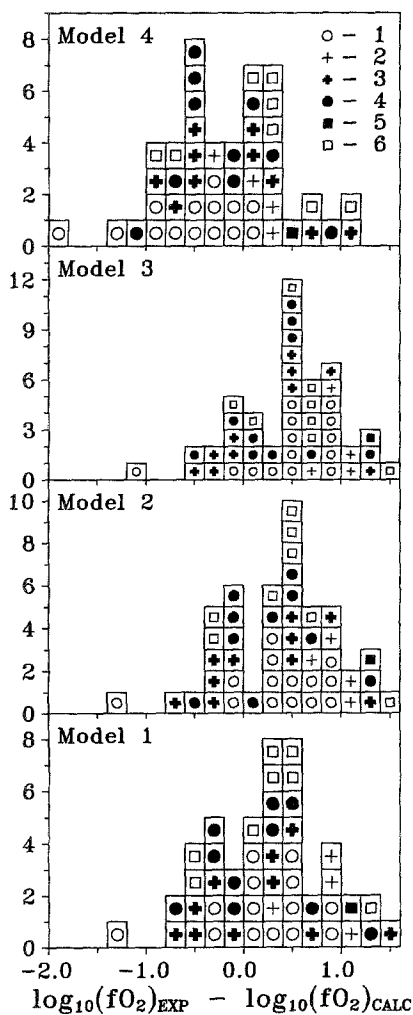


Fig. 2. Frequency histograms of differences between experimental and calculated  $fO_2$  for 47 anhydrous experiments at 1 atm with spinel  $TiO_2 < 2.5$  wt.% and  $Cr_2O_3 > 13$  wt.%. 1 data of *Fisk and Bence* (1980); 2 data of *Grove and Bryan* (1983); 3 data of *Sack* (1982) and *Sack et al.* (1987); 4 data of *Thy et al.* (1991); 5 data of *Tormey et al.* (1987); 6 data of *Roeder and Reynolds* (1991). Model 1 *Sack et al.* (1980); Model 2 *Kilinc et al.* (1983); Model 3 *Kress and Carmichael* (1988); Model 4 *Borisov and Shapkin* (1990). See text for calculation details

No correlation has been found between  $\Delta$  and  $fO_2$  values (Fig. 3) and temperature (Fig. 4) of the experiments.

To evaluate the applicability of the method to  $H_2O$ -bearing melts, we have used the available data [5 experiments of *Sisson and Grove* (1993) and *Gaetani et al.* (1994)] with spinel compositions within the range covered by *Maurel and Maurel* (1982). The results are shown in Fig. 4. The model of *Borisov and Shapkin* (1990) describes these experiments with the same accuracy as anhydrous experiments, whereas the other three models show significant negative deviations. A probable reason for this is that  $H_2O$ -bearing experiments were conducted at significantly lower temperature (Fig. 4). Models 1 to 3 have been derived from a data set consisting mainly of experiments above 1230 °C, and the possibility of negative deviations ( $\Delta > 0$ ) at lower temperatures has been discussed by *Sack et al.* (1980) and *Borisov and Shapkin* (1990). The presence of  $H_2O$  itself is not likely to affect the  $Fe^{2+}/Fe^{3+}$  equilibria, as discussed by *Carmichael* (1991).

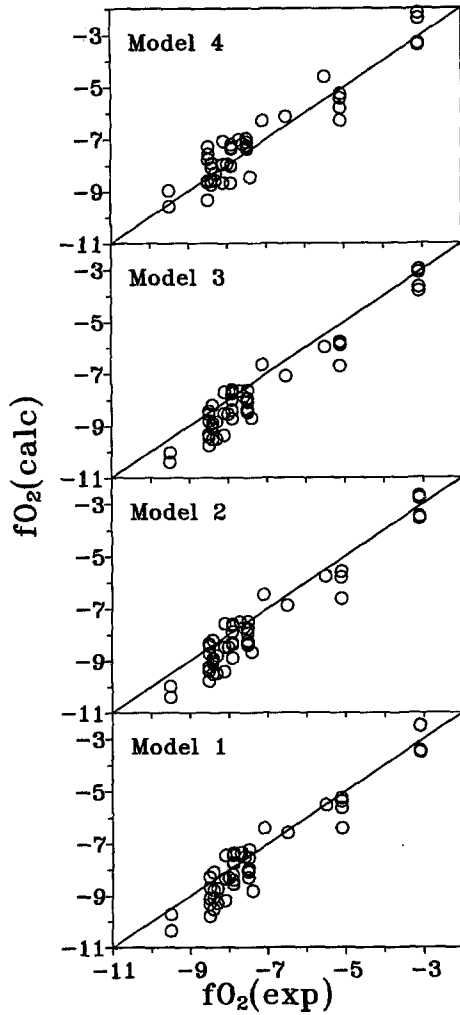


Fig. 3. Correlation between calculated and experimental  $fO_2$  for 46 anhydrous experiments at 1 atm with spinel  $TiO_2 < 2.5$  wt.% and  $Cr_2O_3 > 13$  wt.%. Solid lines show 1:1 correlation. See text for calculation details and references and Fig. 2 for model numbers

Table 2. Calibration results

Model	Aver.	Stand. dev.
1	0.28	0.54
2	0.41	0.52
3	0.49	0.49
4	-0.21	0.53

Notes: Averages and standard deviations calculated for 46 points excluding one point with maximum negative  $\Delta = \log_{10}(fO_2)_{exp} - \log_{10}(fO_2)_{calc}$  (experiment No. 6 of Fisk and Bence, 1980)

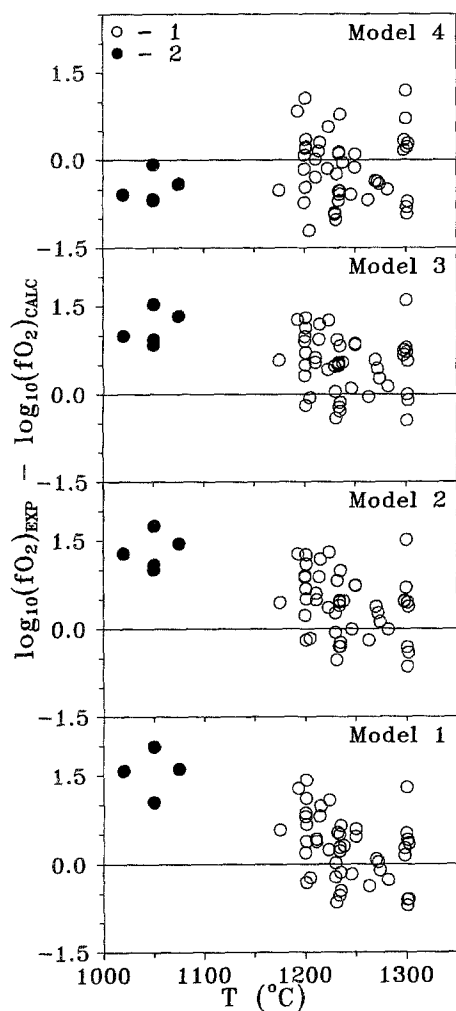


Fig. 4. Differences between experimental and calculated  $fO_2$  versus experimental temperature. 1 46 anhydrous experiments at 1 atm; 2 5  $H_2O$ -saturated experiments at 2 kbar. See text for calculation details and Fig. 2 for model numbers

Figure 5 shows the results of calculations for available experiments with spinel  $TiO_2$  contents  $> 2.5$  wt.% and  $Cr_2O_3$  contents  $> 13$  wt.%. None of the four models can reproduce these experiments, indicating that the equation of *Maurel and Maurel* (1982) cannot be extrapolated to spinel compositions with more than 2.5 wt.%  $TiO_2$ .

It is difficult to evaluate a pressure effect on either the spinel-melt equilibria or the  $fO_2$  from melt  $Fe^{2+}/Fe^{3+}$ , since both have been described for atmospheric pressure conditions only. As  $H_2O$ -bearing experiments used in this paper have been conducted at 2 kbar, we conclude that our method can be safely used up to this pressure, at least, and probably to few kbars more. However, we emphasize that application of our method to magmatic suites which may have crystallized at high-pressure conditions could lead to erroneous results.

In summary, we conclude that the combination of the equation of *Maurel and Maurel* (1982) and the model of *Borisov and Shapkin* (1990) can be used to calculate  $fO_2$  with an accuracy of  $\pm 0.7$  log units, when liquidus spinels have  $TiO_2 < 2.5$  wt.%,  $Cr_2O_3 > 13$  wt.%, melt compositions range from basaltic to picritic,  $H_2O$  contents



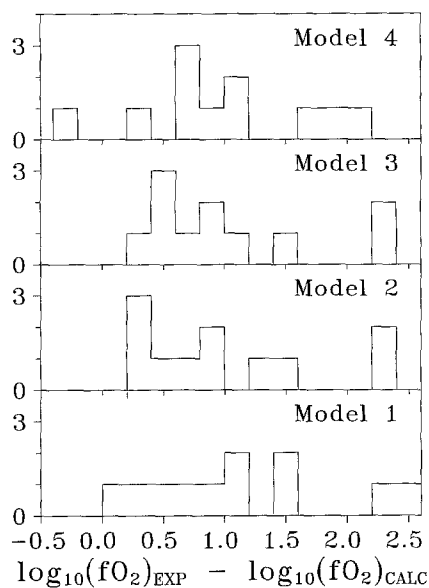


Fig. 5. Frequency histograms of differences between experimental and calculated  $fO_2$  for 11 anhydrous experiments at 1 atm with spinel  $TiO_2$  content > 2.5 wt.% and  $Cr_2O_3$  content > 13 wt.%. Data from *Sack* (1982), *Sack et al.* (1987) and *Thy et al.* (1991). See text for calculation details and Fig. 2 for model numbers

< 6 wt.%, and crystallization pressure < 2–3 kbar. Only the model of *Borisov and Shapkin* (1990) is used in the calculations below.

### Application

To apply the proposed  $fO_2$  calculation method to natural magma suites, one must establish compositions of equilibrium melt-spinel pairs. Below we present one of several possible techniques.

As olivine and spinel are common liquidus phases of primitive mantle-derived melts, and as spinels are commonly found as inclusions in olivine, it is possible to establish a correlation between forsterite (Fo) content in olivine and  $Fe^{2+}/Fe^{3+}$  values in coexisting spinels. Figure 6A presents such data for four suites from different tectonic environments. For two of these suites (mid-Atlantic ridge basalts near VEMA fracture zone, and Tongan boninites, Fig. 5A),  $Fe^{2+}/Fe^{3+}$  values in spinels do not show a significant range at any given olivine composition. For cases such as these, the correlation between Fo and  $Fe^{2+}/Fe^{3+}$  values in equilibrium melts can be established using the equation of *Maurel and Maurel* (1982) (Fig. 6B).

There are two approaches for establishing melt composition in equilibrium with a specific olivine composition. One includes the experimental study of melt inclusions (e.g. *Danyushevsky et al.*, 1992; *Sobolev and Danyushevsky*, 1994), which can provide melt compositions and crystallization temperatures, the parameters required to calculate  $fO_2$ . Another potential approach is to use the compositions of primitive quenched (e.g. pillow-rim) glasses when available (mainly for mid-ocean ridge and backarc basin basalts). The compositions of equilibrium olivine and crystallization temperatures can then be established using one of the available olivine-melt thermometers (e.g. *Ford et al.*, 1983).

Using the approaches described above, we have calculated  $fO_2$  values for the mid-Atlantic ridge basalts dredged near the VEMA fracture zone (*Sobolev et al.*,

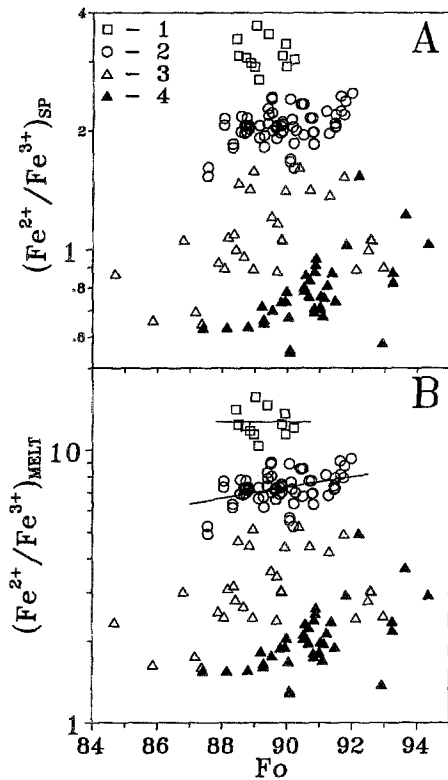


Fig. 6. **A** Correlation between forsterite content in olivine phenocrysts and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values in spinel inclusions. **B** Correlation between forsterite and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values in melt, calculated using equation of *Maurel and Maurel* (1982). Solid lines show linear best fits for two suites which spinels do not show a significant range of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values at any given olivine composition. Best fit equations are given below. 1 Mid-Atlantic Ridge basalts dredged near VEMA fracture zone (*Sobolev et al.*, 1989, and our unpublished data), average  $\text{Fe}^{2+}/\text{Fe}^{3+}$  value in melts is 12.7; 2 Tongan boninites (*Sobolev and Danyushevsky*, 1994, and our unpublished data),  $(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{melt}} = 0.3298 \cdot \text{Fo} - 22.37$ ; 3 and 4 two Cretaceous island arc picritic suites from Kamchatka, Russia (*Kamenetsky et al.*, 1995). See text for calculation details and discussion

1989), using compositions of quenched glasses and homogenized melt inclusions in olivines, plagioclases and pyroxenes, and for Tongan boninites (*Sobolev and Danyushevsky*, 1994) using compositions of homogenized melt inclusions in olivines and orthopyroxenes. All compositions used in the calculations have olivine on their liquidus, and correlations between forsterite and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  values in melt have been taken from Fig. 6B. Both suites crystallized at temperatures below 1300 °C, and  $\text{H}_2\text{O}$  contents in Tongan boninite melts is ~2 wt.% based on the measured  $\text{H}_2\text{O}$  contents of melt inclusions in olivines (*Sobolev and Danyushevsky*, 1994). Results are shown on Fig. 7.

Calculated average  $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$  for VEMA melts ( $0.073 \pm 0.006$ ) is indistinguishable from the average ( $0.0726 \pm 0.025$ ) obtained for North Atlantic glasses by *Christie et al.* (1986). However, calculated absolute  $f\text{O}_2$  values (Fig. 7A) are somewhat higher (0.6 to 1 log units) than those calculated by *Christie et al.* (1986). The reason for this discrepancy is that *Christie et al.* (1986) used the model of *Kilinc et al.* (1983) to calculate  $f\text{O}_2$ , whereas we used the model of *Borisov and Shapkin* (1990). We believe that the calibration presented in this paper indicates that the latter model yields more reliable results.

Calculated  $f\text{O}_2$  values for Tongan boninites are at or slightly above the NNO buffer (Fig. 7A), with relative  $f\text{O}_2$  ( $\Delta\text{NNO}$ ) increasing with decreasing temperature. As olivine, spinel and orthopyroxene have fractionated together over a considerable temperature interval ( $> 50$  °C, *Danyushevsky et al.*, 1992), and as equilibrium com-

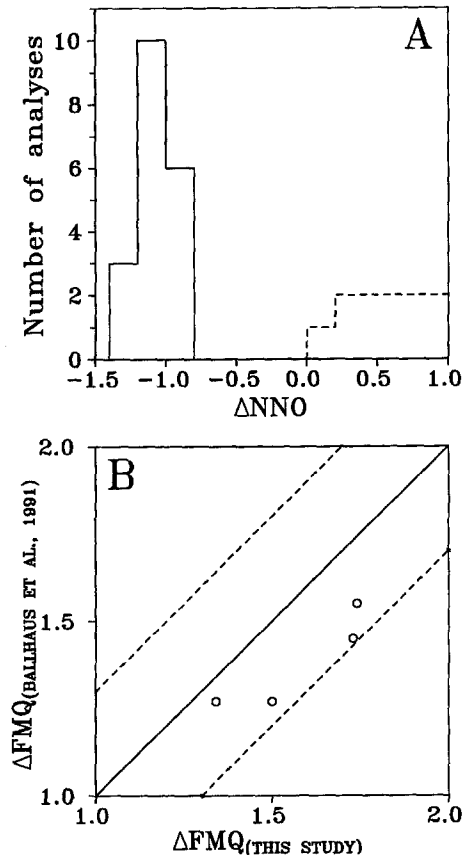


Fig. 7. **A** Frequency histograms of  $\Delta NNO = \log_{10}(fO_2)_{CALC} - \log_{10}(fO_2)_{NNO}$  for Mid-Atlantic Ridge basalts dredged near VEMA fracture zone (solid line) and Tongan boninites (dashed line). Correlations between  $Fo$  and  $Fe^{2+}/Fe^{3+}$  values in melts from Fig. 6, and melt compositions and crystallization temperatures from Sobolev et al. (1989) and Sobolev and Danyushevsky (1994) have been used for calculations. Data for the NNO oxygen buffer from O'Neill (1987a). See text for calculation details. **B** Comparison between  $\Delta FMQ = \log_{10}(fO_2)_{CALC} - \log_{10}(fO_2)_{FMQ}$  calculated for Tongan boninites by the method proposed in this study and by the olivine-orthopyroxene-spinel oxygen geobarometer (Ballhaus et al., 1991). Dashed lines show deviations of  $\pm 0.3$  log units of  $fO_2$  values. Data for the FMQ oxygen buffer from O'Neill (1987b)

positions of all three minerals have been established, an opportunity exists to compare the  $fO_2$  values obtained by our method and by the olivine-orthopyroxene-spinel oxygen geobarometer (Ballhaus et al., 1991). Results are shown on Fig. 7B. Both methods yield very similar results, with deviations being less than 0.3 log units of  $fO_2$ .

The other two suites shown on Fig. 6, both island-arc picritic suites from Kamchatka (Kamenetsky et al., 1995), demonstrate significant variations in spinel  $Fe^{2+}/Fe^{3+}$  values at any given composition of the host olivines (Fig. 6A). This results in calculated melt  $Fe^{2+}/Fe^{3+}$  values varying by a factor of 4 to 6 at any given composition of host olivines (Fig. 6B). Such variations most likely reflect the complex crystallization and cooling history of these rocks, which probably included magma mixing (Kamenetsky et al., 1995). In cases such as these, the application of our approach is not straightforward. A more detailed study is required to establish the melt compositions which crystallized olivine of the same composition at different melt  $Fe^{2+}/Fe^{3+}$  values. As such information is not available for these Kamchatka picrites, we did not perform  $fO_2$  calculations for them. We present these suites here to demonstrate that it is essential to obtain a representative set of olivine-spinel pairs, as application of this method to a single spinel analysis could lead to erroneous results.

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