

## THE DISTRIBUTION OF Cr BETWEEN BASALTIC MELT AND CHROMIAN SPINEL AS AN OXYGEN GEOBAROMETER

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### ABSTRACT

A thermodynamic model of Cr distribution between chromian spinel and basaltic melt has been developed using the Sack & Ghiorso (1991) thermodynamic model for chromian spinel and an equation analogous to that of Sack *et al.* (1980) to calculate the Cr oxidation state in the melt. The model has been calibrated using published experimental data on the composition of coexisting chromian spinel and basaltic melt. The model can be used either to calculate the oxygen fugacity,  $f(\text{O}_2)$ , of magmas saturated with chromian spinel, to predict the Cr content of the melt, or to calculate the oxidation state of Cr in the melt. The  $f(\text{O}_2)$  values calculated for a set of natural lavas (primitive MORB and a Hawaiian pumice) using the method show good agreement with  $f(\text{O}_2)$  values calculated from measured values of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in the melt. An EXCEL spreadsheet for calculating  $\log f(\text{O}_2)$  using composition of glass and chromian spinel is available from the authors upon request.

*Keywords:* chromium, chromian spinel, melt, oxidation state, primitive lavas, oxygen fugacity.

### SOMMAIRE

Nous avons développé un modèle thermodynamique de la distribution du chrome entre spinelle chromifère et liquide basaltique en utilisant le modèle thermodynamique décrivant les propriétés du spinelle chromifère de Sack et Ghiorso (1991) et une équation analogue à celle de Sack *et al.* (1980) pour calculer le niveau d'oxydation du Cr dans le liquide silicaté. Nous avons calibré notre modèle avec les données expérimentales disponibles sur la composition du spinelle chromifère et du liquide basaltique coexistant. Notre modèle peut servir soit pour calculer la fugacité d'oxygène,  $f(\text{O}_2)$ , d'un magma saturé en spinelle chromifère, pour prédire la teneur en Cr d'un magma, ou bien pour calculer le niveau d'oxydation du Cr dans un magma. Les valeurs calculées de  $f(\text{O}_2)$  selon cette méthode pour une suite de laves naturelles (basaltes de rides médio-océaniques et une ponce hawaïenne) concordent bien avec les valeurs de  $f(\text{O}_2)$  calculées d'après les valeurs mesurées du rapport  $\text{Fe}^{3+}/\text{Fe}^{2+}$  dans le liquide. Un logiciel EXCEL servant à calculer les valeurs de  $\log f(\text{O}_2)$  pour une composition de verre et une composition de spinelle chromifère données est disponible sur demande.

(Traduit par la Rédaction)

*Mots-clés:* chrome, spinelle chromifère, liquide silicaté, niveau d'oxydation, lave primitive, fugacité d'oxygène.

### INTRODUCTION

The solubility of Cr in silicate melts saturated with chromian spinel has been the subject of several studies (Hill & Roeder 1974, Irvine 1977, Maurel & Maurel 1982, Barnes 1986, Murck & Campbell 1986, Roeder & Reynolds 1991). These show a clear positive correlation between Cr content of the spinel-group mineral and melt phase. The same strong correlation can be seen in the results of other experimental studies in which the concentration of Cr in quenched glass has been carefully established (*e.g.*, Schreiber 1976, Delano 1980, Sack *et al.* 1987). One of the most striking features,

documented in a number of studies, is the strong dependence of Cr content of a basaltic melt saturated with chromian spinel on the fugacity of oxygen,  $f(\text{O}_2)$  (Fig. 1). This dependence provides a strong argument for the existence of Cr species of different oxidation state in basaltic melts under petrologically important conditions.

Our objective is to develop a quantitative model for Cr distribution between chromian spinel and basaltic melt, based on an existing thermodynamic model for chromian spinel, an adequate description of the oxidation state of Cr, and published experimental data on solubility of Cr in basaltic melts saturated with chromian

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spinel. This model can be used to calculate the oxygen fugacity of a melt in equilibrium with chromian spinel given a temperature and a careful determination of the Cr content of the melt.

#### BACKGROUND INFORMATION

The first quantitative estimates of Cr distribution between basaltic melt and chromian spinel were published by Barnes (1986) and Murck & Campbell (1986). These authors adopted a relatively simple approach to describe the influence of the composition of chromian spinel on the equilibria, since their formulations did not deal with temperature- and composition-dependent cation ordering in chromian spinel.

The formulation of Barnes (1986) made no provision for the influence of divalent cations on the equilibria, so that chromian spinel was treated as an ideal solid-solution of a sesquioxide phase. One of the major problems is the difficulty in accounting for the presence of both  $\text{Cr}^{3+}$  and  $\text{Cr}^{2+}$  (or  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  at oxidizing conditions) in the melts, with only  $\text{Cr}^{3+}$  present in chromian spinel in significant amounts (Schreiber 1976, Hanson & Jones 1998). The direct determination of oxidation state of small amounts of Cr in Fe-bearing melts is not presently possible, so that  $\text{Cr}^{3+}/\text{Cr}^{2+}$  or  $\text{Cr}^{3+}/\text{Cr}^{6+}$  can only be calculated. Barnes (1986) tried to calculate the valence state of Cr species in basaltic melt as a function of temperature and  $f(\text{O}_2)$ . In doing so, he assumed that

$\text{Cr}^{3+}$  is the only Cr species in the melt at oxygen fugacities of the extrapolated quartz – fayalite – magnetite (QFM) buffer or higher, and, he used a theoretical coefficient of 0.25 to describe the dependence of  $\log(\text{Cr}^{3+}/\text{Cr}^{2+})$  on  $\log f(\text{O}_2)$ . Roeder & Reynolds (1991) showed that the available experimental data could be better fit by accepting that both  $\text{Cr}^{2+}$  and  $\text{Cr}^{3+}$  are present at oxygen fugacities of the QFM buffer. They calibrated an equation that represents  $\text{Cr}^{2+}/\text{Cr}^{3+}$  in the melt at 1300°C for one basaltic composition as a function of  $f(\text{O}_2)$ . Poustovetov & Roeder (1994) used a similar approach to describe the Cr distribution between chromian spinel and silicate melt for a range of temperatures and melt compositions. In their study, however, they did not account for the nonideality in chromian spinel solid-solution.

Forsythe & Fisk (1994) were the first to include thermodynamically based values of the activity of spinel end-members, calculated according to the expression of Sack & Ghiorso (1991), to model chromian spinel – melt equilibria in terms of  $\text{Cr}^{3+}$  and Al distribution. However, Forsythe & Fisk ignored the influence of disorder in pure  $\text{MgAl}_2\text{O}_4$  on the value of chemical potential of  $\text{MgAl}_2\text{O}_4$  end-member. They applied the equation of Roeder & Reynolds (1991) designed for 1300°C to calculate  $\text{Cr}^{2+}/\text{Cr}^{3+}$  in melt and overlooked the important effect of temperature on the valence state of Cr in the melt.

The creation of the MELTS computer program has been a major advance in modeling element distribution among silicate melt and coexisting mineral phases (Ghiorso & Sack 1995). The program uses thermodynamically based models for solid phases calibrated using a variety of available experimental data, for example on degree of cation order, miscibility gaps, and element distribution between phases. In addition, this program utilizes a set of energy parameters for selected species in the melt phase so as to account for nonideality in silicate melts over a wide range of composition and conditions. However, Ghiorso & Sack (1995) chose to assume that all Cr in silicate melts is present in the  $\text{Cr}^{3+}$  form, even at low oxygen fugacities, thus making it inadequate for the task of modeling chromian spinel – melt equilibria. Ariskin & Nikolaev (1996) applied an empirical model and were successful in describing the distribution of Cr between high-Cr chromian spinel and melt. However, the model was not calibrated for chromian spinel with a lower Cr content, or for the melts with a Cr content typical of natural lavas (<500 ppm). In our opinion, the assumption made by Ariskin & Nikolaev (1996) about the ideality of chromian spinel solid-solution probably limits the applicability of the model to lavas containing high-Cr chromian spinel.

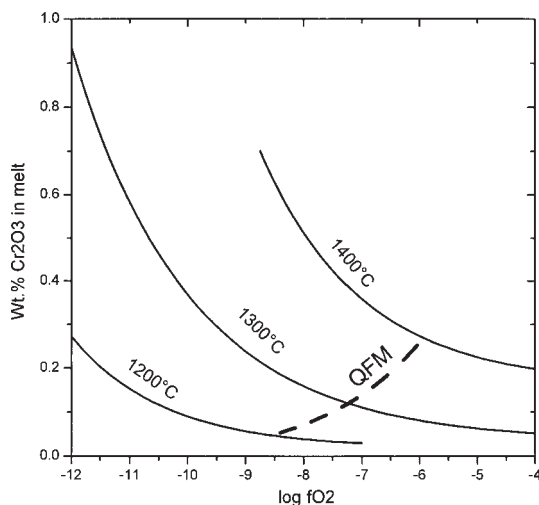


FIG. 1. The total chromium content (wt.% of  $\text{Cr}_2\text{O}_3$ ) of the chromian-spinel-saturated melt of the 401 basalt, described by Roeder & Reynolds (1991), plotted against  $\log f(\text{O}_2)$ . The curves are drawn on the basis of experimental results of Murck & Campbell (1986) and Roeder & Reynolds (1991). The four curves are for 1200°, 1300°, 1400°C and along the quartz – fayalite – magnetite (QFM) buffer.

#### ANALYTICAL PROCEDURE

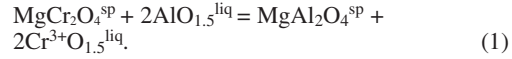
The major-element composition of the basaltic glasses and chromite used in the present study was es-

established by energy-dispersion analysis with an ARL SEMQ electron microprobe operated at 15 kV using a procedure described by Bannister *et al.* (1998). Special care was necessary in analyzing the natural glasses by electron microprobe, in view of their low (100–600 ppm) level of Cr. Wavelength-dispersion analysis for Cr was conducted at 25 kV and a beam current of 200 nA. The background was measured at three positions above and below the CrK $\alpha$  peaks, and the pulse-height analyzer was set to discriminate against interfering peaks, such as that due to vanadium. A glass rich in vanadium was used to check that vanadium does not significantly interfere with the Cr measurement. The intensity of the Cr peak was measured for 100 seconds at each of five different positions on the glass. A sample of chromian spinel (USNM 117075) was used as a standard, and a ZAF correction was applied. Glasses were prepared in an earlier study (Roeder & Reynolds 1991) from the rock powders of three well-known standards (MRG-1, W-1, and BCR-1) containing known amounts of Cr. These three glasses, two U.S. National Institute of Standards and Technology glasses (NIST 610 and 612), and eight glasses kindly provided by Dr. Geoff Thompson (Gaetani *et al.* 1995) were analyzed as unknowns. The results of these analyses conducted over a year and a half are shown in Figure 2. The same procedure was used for the unknown glasses.

#### FORMULATION OF THE MODEL FOR CR DISTRIBUTION BETWEEN SPINEL AND MELT

Any successful model describing Cr distribution between chromian spinel and silicate melt of variable compositions in the range of petrologically important conditions should: 1) account for the presence of Cr species of varying valence in the silicate melt, since distribution coefficients for these species between chromian spinel and melt are quite different (*e.g.*, Schreiber 1976, Roeder & Reynolds 1991), and 2) include terms describing the effect of the composition of the chromian spinel and associated nonideal interactions on the equilibrium. It has been shown in a number of experimental studies of geologically relevant melts (Schreiber 1976, Roeder & Reynolds 1991, Hanson & Jones 1998) that Cr<sup>3+</sup> is the only Cr species that partitions significantly into chromian spinel. In particular, no change in Cr content of chromian spinel was observed as a result of varying  $f(\text{O}_2)$  and total Cr content of melt. Thus for the purposes of the model, we assume that Cr content of chromian spinel is entirely controlled by Cr<sup>3+</sup> in the melt. This assumption would not, however, be true for the systems with very high Cr content, such as those important for metallurgy, where Cr<sup>2+</sup> can be a major component of chromian spinel (De Villiers & Muan 1992).

The following Al–Cr<sup>3+</sup> exchange reaction is used to describe Cr distribution between chromian spinel (sp) represented by magnesiochromite (MgCr<sub>2</sub>O<sub>4</sub>) and spinel (MgAl<sub>2</sub>O<sub>4</sub>) end-members, and melt (liq):



The choice of melt components is completely arbitrary and reflects the simplicity of the thermodynamic model of basaltic melt adopted (see below). At equilibrium:

$$\mu_{\text{MgAl}_2\text{O}_4}^{\text{sp}} - \mu_{\text{MgCr}_2\text{O}_4}^{\text{sp}} + 2(\mu_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}} - \mu_{\text{AlO}_{1.5}}^{\text{liq}}) = 0; \quad (2)$$

where  $\mu_j$  is the chemical potential of component  $i$  in phase  $j$  at the conditions of interest. Using the definition of activity, Equation 2 can be rewritten as:

$$\mu_{\text{MgAl}_2\text{O}_4}^{\text{sp}} - \mu_{\text{MgCr}_2\text{O}_4}^{\text{sp}} + 2(\mu_{\text{Cr}^{3+}\text{O}_{1.5}}^{\circ\text{liq}} - \mu_{\text{AlO}_{1.5}}^{\circ\text{liq}}) = -2RT \ln(a_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}}/a_{\text{AlO}_{1.5}}^{\text{liq}}). \quad (3)$$

We now introduce standard state enthalpy ( $\Delta H^\circ_{\text{CrAl}(-1)}$ ) and entropy ( $\Delta S^\circ_{\text{CrAl}(-1)}$ ) effects of the reaction in (1):

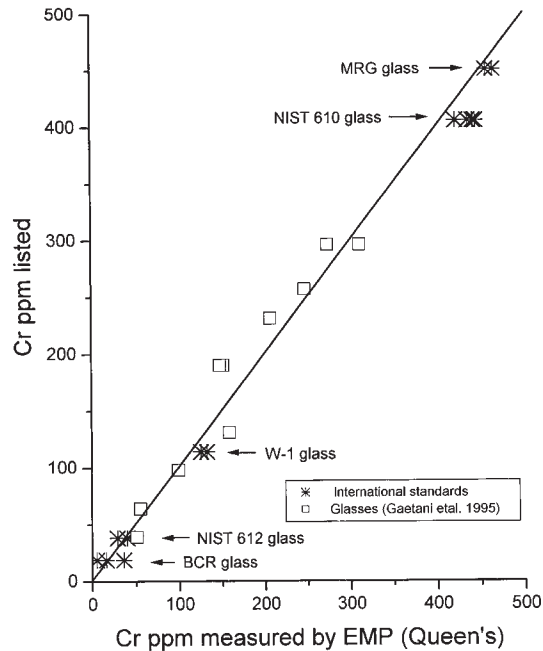


FIG. 2. The listed Cr content (see the references given below) plotted *versus* the Cr measured in glass by electron microprobe (EMP) at Queen's University. The MRG-1, W-1 and BCR-1 glasses were prepared from rock powders at Queen's University. The values listed for the rock powders are 430 ppm for MRG-1, 119 ppm for W-1 and 16 ppm for BCR-1 (Govindaraju 1994). The preferred value of NIST 610 glass is 405 ppm, and that of the NIST 612 glass is 38 ppm, as given by Pearce *et al.* (1997). The eight natural glasses were analyzed by XRF by Gaetani *et al.* (1995). The solid line represents the 1:1 line. An effective detection-limit for Cr in glass is estimated as 50 ppm.

$$G^*_{2} + 2\mu^{\circ}_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}} - G^*_{3} - 2\mu^{\circ}_{\text{AlO}_{1.5}}^{\text{liq}} = \Delta H^{\circ}_{\text{CrAl}(-1)} - T\Delta S^{\circ}_{\text{CrAl}(-1)}, \quad (4)$$

where  $G^*_{2}$  and  $G^*_{3}$  are molar vibrational free energies of  $\text{MgAl}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  end-members with fixed cation-distribution [see Sack & Ghiorso (1991) for more details], and  $\mu^{\circ}_i$  are chemical potentials of component  $i$  in its pure state. It is assumed that the ratio of activity coefficients of  $\text{CrO}_{1.5}$  and  $\text{AlO}_{1.5}$  in the melt is independent of melt composition, such that:

$$a_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}}/a_{\text{AlO}_{1.5}}^{\text{liq}} = X_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}}/X_{\text{AlO}_{1.5}}^{\text{liq}}, \quad (5)$$

where  $X_i^{\text{liq}}$ , the simple molar fraction of an oxide component in melt  $i$  based on one cation, is equal to the cation fraction. Combining Equations 3, 4, and 5 produces:

$$(\mu_{\text{MgAl}_2\text{O}_4}^{\text{sp}} - G^*_{1}) - (\mu_{\text{MgCr}_2\text{O}_4}^{\text{sp}} - G^*_{3}) + \Delta H^{\circ}_{\text{CrAl}(-1)} - T\Delta S^{\circ}_{\text{CrAl}(-1)} = -2RT \ln(X_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}}/X_{\text{AlO}_{1.5}}^{\text{liq}}). \quad (6)$$

The  $X_{\text{CrO}_{1.5}}^{\text{liq}}$  value in Equation 6 represents the cation fraction of  $\text{Cr}^{3+}$ , which is presently impossible to obtain by an analytical method (see above). We assume that the total Cr in melt (determined as  $\text{Cr}_2\text{O}_3$  by electron-microprobe analysis of the glass) at oxygen fugacities below that of QFM + 3 includes only  $\text{Cr}^{2+}$  and  $\text{Cr}^{3+}$  species, so that:

$$X_{\text{CrO}_{1.5}\text{total}}^{\text{liq}} = X_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}} + X_{\text{Cr}^{2+}\text{O}}^{\text{liq}}. \quad (7)$$

Since no general equation exists to calculate the relative proportions of  $\text{Cr}^{3+}$  and  $\text{Cr}^{2+}$  in the melt [the equation of Barnes (1986) does not compensate for the effect of melt composition on oxidation state of Cr in melt], we use an equation analogous to that of Sack *et al.* (1980) for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in order to calculate  $\text{Cr}^{3+}/\text{Cr}^{2+}$ :

$$\ln(X_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}}/X_{\text{Cr}^{2+}\text{O}}^{\text{liq}}) = a \ln f(\text{O}_2) + b/T + c + \sum d_i X_i \quad (8)$$

Equation 7 and Equation 8 can be used to define the concentration of  $\text{Cr}^{3+}$  species in melt as a function of total Cr concentration, temperature, and  $f(\text{O}_2)$ :

$$X_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}} = X_{\text{CrO}_{1.5}\text{total}}^{\text{liq}} / (1 + \exp[-b/T - a \ln f(\text{O}_2) - c - \sum d_i X_i]) \quad (9)$$

Substituting this expression for  $X_{\text{Cr}^{3+}\text{O}_{1.5}}^{\text{liq}}$  in Equation 6 results in the final equation, describing total Cr ( $X_{\text{CrO}_{1.5}\text{total}}^{\text{liq}}$ ) concentration in melt as a function of temperature, oxygen fugacity, composition of the chromian spinel and Al content in melt:

$$X_{\text{CrO}_{1.5}\text{total}}^{\text{liq}} = X_{\text{AlO}_{1.5}}^{\text{liq}} (1 + \exp[-b/T - a \ln f(\text{O}_2) - c - \sum d_i X_i]) \exp[(\mu_{\text{MgCr}_2\text{O}_4} - G^*_{3}) - (\mu_{\text{MgAl}_2\text{O}_4} - G^*_{2}) - \Delta H^{\circ}_{\text{CrAl}(-1)} + T \Delta S^{\circ}_{\text{CrAl}(-1)}/2RT]. \quad (10)$$

The calculated value of  $X_{\text{CrO}_{1.5}\text{total}}^{\text{liq}}$  can be converted to wt.% or ppm of Cr if the major-element composition of melt is known (the value of the normalizing factor is required). Re-arranging Equation 10 produces an equation used to calculate  $f(\text{O}_2)$ :

$$\ln f(\text{O}_2) = (\ln(X_{\text{CrO}_{1.5}\text{total}}^{\text{liq}}/X_{\text{AlO}_{1.5}}^{\text{liq}}) / \exp[(\mu_{\text{MgCr}_2\text{O}_4} - G^*_{3}) - (\mu_{\text{MgAl}_2\text{O}_4} - G^*_{2}) - \Delta H^{\circ}_{\text{CrAl}(-1)} + T \Delta S^{\circ}_{\text{CrAl}(-1)}/2RT] - 1) + b/T + c + \sum d_i X_i / -a \quad (11)$$

## RESULTS OF CALIBRATION

Equation 10 can be calibrated using the equilibrium composition of chromian spinel and coexisting melt from experiments at known conditions of temperature and  $f(\text{O}_2)$ . It is important that the Cr content in glass should be carefully established, since it generally amounts to just a few hundred ppm. Data used for calibration of Equation 10 are from Barnes (1986), Murck & Campbell (1986), Roeder & Reynolds (1991), and Forsythe & Fisk (1994). In these studies, the Cr content of glass from the experimental runs was carefully determined, which satisfies an important requirement for the data selection. Only data from experiments at 1 bar were used, and data from experiments performed at oxidizing conditions were excluded to eliminate the influence of  $\text{Cr}^{6+}$ . The final dataset thus only contained data for  $f(\text{O}_2)$  lower than that of QFM + 2.2. Data from the short-duration runs on K-rich bulk compositions of Murck & Campbell (1986) were not included owing to the possible difficulty in obtaining equilibrium. Values of  $\mu_{\text{MgCr}_2\text{O}_4} - G^*_{3}$  and  $\mu_{\text{MgAl}_2\text{O}_4} - G^*_{2}$  were calculated according to Sack & Ghiorso (1991). The coefficients in Equation 10 were obtained by nonlinear regression analysis of the experimental data. The coefficients  $a$ ,  $b$ , and  $d_i$  were fixed at the values reported by Sack *et al.* (1980) in order to minimize the number of regression parameters, and because of the relatively limited range of melt composition in the database used for the regression. The values for these parameters can be adjusted when direct determination of  $\text{Cr}^{2+}/\text{Cr}^{3+}$  in Fe-bearing glasses becomes possible. Meanwhile, it should be noted that any of these values cannot be changed (*e.g.*, use of the theoretical value of 0.25 for  $a$ ) without considering the effect it would have on the values of other parameters, because of the cross-correlation among these parameters. Thus the lines describing the change of  $\log(\text{Cr}^{2+}/\text{Cr}^{3+})$  with changing temperature,  $\log f(\text{O}_2)$ , or cation fraction of an element in melt are parallel to those describing  $\log(\text{Fe}^{2+}/\text{Fe}^{3+})$ . Roeder & Reynolds (1991) found that  $\log(\text{Cr}^{2+}/\text{Cr}^{3+})$  and  $\log(\text{Fe}^{2+}/\text{Fe}^{3+})$  lines are almost parallel, if plotted against  $\log f(\text{O}_2)$ . The values for the parameters obtained by the regression, together with the values of the other parameters from Equation 10, are listed in Table 1.

TABLE 1. VALUE OF PARAMETERS IN EQUATION 10

Parameter	Value, J	Standard error, J
<i>a</i>	13184.7*	
<i>b</i>	0.21813*	
<i>c</i>	-1.846	0.1008
<i>d</i> <sub>SiO<sub>2</sub></sub>	-2.15036*	
<i>d</i> <sub>Al<sub>2</sub>O<sub>3</sub></sub>	-8.35163*	
<i>d</i> <sub>FeO</sub>	-4.49508*	
<i>d</i> <sub>MgO</sub>	-5.43639*	
<i>d</i> <sub>Cr<sub>2</sub>O<sub>3</sub></sub>	0.073113*	
<i>d</i> <sub>H<sub>2</sub>O</sub>	3.54148*	
<i>d</i> <sub>Cr<sub>2</sub>O</sub>	4.18688*	
$\Delta H^\circ_{\text{CrAl}(-1)}$	223033.267**	9272.86325**
$\Delta S^\circ_{\text{CrAl}(-1)}$	62.161***	5.31634***

\* same as in Sack *et al.* (1980); \*\* values in J; \*\*\* values in J/K.

The calculated total concentration of Cr in the melt for the experimental data used in the calibration are compared to the measured Cr in Figure 3. The suggested model (values from Table 1 and equations) can be used to predict the Cr content in melt of known composition saturated with chromian spinel at the temperature and oxygen fugacity of interest. Alternatively, it can be applied to calculate the  $f(\text{O}_2)$  if the total Cr content of the melt is known, or it can be used to calculate the inferred oxidation state of Cr in a melt.

Schreiber (1976) conducted experiments at known  $f(\text{O}_2)$  on two iron-free compositions, FAS and FAD, that are in the system Ca–Mg–Al–Si–O with a small amount of added Cr. Schreiber was able to directly analyze the glasses for both Cr<sup>2+</sup> and Cr<sup>3+</sup> since the glasses con-

tained no Fe. His main method was indirect chemical redox titration, based on the assumption that Cr<sup>2+</sup> and Cr<sup>3+</sup> are the only ions that can change oxidation state. The detailed description of the procedure can be found in Schreiber (1976). The use of Equation 8 and the coefficients from Table 1 overestimate the value of Cr<sup>2+</sup>/Cr<sup>3+</sup> in the melt for these iron-free compositions. This discrepancy correlates with the results of the Cr solubility calculation for the melts using Equation 10. The inferred total Cr content is higher than that experimentally determined by Hanson & Jones (1998) and Roeder (unpublished experimental data). The disagreement suggests that the use of the equations developed in the present study should be limited to compositions of natural melts that contain iron and approach basalt in composition, such as those used in the calibration. The results of the calibration, precision, and range of the applicability of the Equation 11 for calculating  $f(\text{O}_2)$  are further discussed in the Appendix.

#### Oxidation state and Cr content of the melt from primitive natural lavas

The intrinsic  $f(\text{O}_2)$  of a primitive basaltic melt saturated with chromian spinel can be calculated with the use of Equation 11 if temperature, major-element composition of both melt and chromian spinel, and total Cr content of the melt are known. For this purpose, the Cr content of glass from primitive, chromian-spinel-saturated natural lavas was determined with an electron microprobe at Queen's University (Kingston, Ontario), and also compiled from published data. The samples include four basalts from the Mid-Atlantic Ridge, sup-

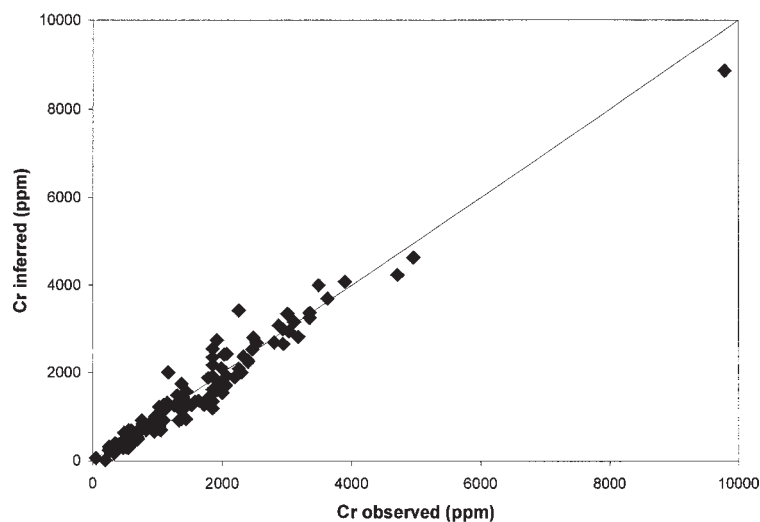


FIG. 3. Plot of calculated (according to Equation 10) total Cr content in melt versus reported values for the experiments used for the calibration.

plied by Haraldur Sigurdsson, basalt from the East Pacific Rise (EPR), provided by James Allan, and five samples of pumice from Kilauea Iki volcano on Hawaii, supplied by Rosalind Helz. In addition, data on a set of MORB-like lavas from the Blanco Fracture Zone (north-eastern Pacific), including the Cr content of glasses, also were considered. The samples chosen had been previously analyzed for both FeO and Fe<sub>2</sub>O<sub>3</sub> by bulk analysis of FeO using a titration technique and by determining the total iron in the sample or in the glass by X-ray fluorescence or an electron microprobe. The data from these samples were then used to calculate  $f(\text{O}_2)$  and to compare the values defined by FeO/Fe<sub>2</sub>O<sub>3</sub> equilibrium in the melt (Sack *et al.* 1980) and by Equation 11. The  $f(\text{O}_2)$  calculation was done for each sample using the following steps:

1. Glass and chromian spinel are analyzed for major elements with an electron microprobe (chromian spinel composition is chosen to most likely represent the equilibrium composition, see below);
2. Careful analysis of glass for its Cr content is done;
3. Temperature of quenching is estimated or calculated from the composition of glass in equilibrium with olivine using the Beattie (1993) equation;
4. The values of chemical potentials of MgAl<sub>2</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> end-members of the chromian spinel solid-solution are calculated using the Sack & Ghiorso (1991) thermodynamic model;
5. The  $f(\text{O}_2)$  value is calculated using Equation 11.

An EXCEL spreadsheet used to perform steps 3–5 is available from the authors upon request. The choice of chromian spinel composition for the calculations is

in some cases complicated by within-sample variability in spinel composition (*e.g.*, Allan *et al.* 1988). The composition of the rim of chromian spinel beside glass usually was chosen. Data necessary for the calculations and the results are listed in Table 2.

The calculated values of the temperature of quenching and  $f(\text{O}_2)$  are plotted on Figure 4. The difference between  $\log f(\text{O}_2)$  values, calculated using known Fe<sup>3+</sup>/Fe<sup>2+</sup> of the glass, and those calculated with Equation 11 is no more than 1 unit, and can generally be explained by an analytical error in the electron-microprobe measurements of the total Cr content in glass (Fig. 4).

There seems to be good agreement between the  $\log f(\text{O}_2)$  calculated by the method suggested in the present study and the  $\log f(\text{O}_2)$  calculated from the Fe<sup>3+</sup>/Fe<sup>2+</sup> analyzed from the bulk sample. The limited range of oxygen fugacities of the samples used to check the technique, as shown in Figure 4, is due to the limited number of natural samples available to the authors where the oxygen fugacity could be independently calculated. One advantage of the suggested method is that it can be used for the volcanic glass directly, whereas to measure the Fe<sup>3+</sup>/Fe<sup>2+</sup> of the glass, one should also analyze it for FeO using a titration technique, in addition to the analysis for the total iron. The suggested method is quite dependent on careful analysis of the glass for Cr and will not work well at a  $f(\text{O}_2)$  much higher than QFM because the amount of inferred Cr<sup>2+</sup> becomes very low. The method should, however, work much better at lower  $f(\text{O}_2)$  because of the strong dependence of Cr solubility on  $f(\text{O}_2)$  below QFM, as shown in Figure 1.

TABLE 2. THE COMPOSITION OF GLASS, CHROMIAN SPINEL, AND CALCULATED LOG( $f(\text{O}_2)$ ) OF SELECTED PRIMITIVE LAVAS

Setting	Mid-Atlantic Ridge				Hawaii	Eastern Pacific			Blanco Trough						
Sample	1D	2D	11D	16D	IKI-22	F2-2	F2-1	vg172	vg345	vg347	vg348	vg356	vg360	vg373	vg376
T <sup>o</sup> C	1200	1190	1211	1195	1248	1216	1215	1195	1210	1200	1226	1187	1177	1222	1184
Log $f(\text{O}_2)$ (Fe) <sup>2</sup>	-9.61	-8.57	-9.1	-8.6	-7.77	-8.57	-8.77	-9.65	-8.97	-9.46	-8.74	-9.74	-8.75	-9.33	-9.51
Log $f(\text{O}_2)$ (Cr) <sup>3</sup>	-9.2	-9.1	-8.9	-8.9	-8.4	-8.8	-8.6	-9.1	-8.5	-8.5	-8.4	-9.2	-8.9	-8.6	-9.2
SiO <sub>2</sub>	50.71	51.53	50.62	50.40	49.08	48.79	48.40	49.80	49.30	48.80	48.09	49.70	50.40	48.20	49.90
TiO <sub>2</sub>	1.26	1.27	1.13	1.26	2.48	0.83	0.86	2.20	1.58	1.66	0.90	1.98	2.60	0.79	2.00
Al <sub>2</sub> O <sub>3</sub>	15.46	15.53	16.02	16.30	12.48	17.50	17.38	15.10	16.10	16.10	17.41	15.20	14.70	17.36	15.33
Fe <sub>2</sub> O <sub>3</sub>	0.67	1.21	0.77	1.13	1.59	0.86	0.81	0.89	0.93	0.89	0.93	0.87	1.67	0.72	0.96
FeO	8.07	7.68	7.57	7.77	10.05	7.45	7.60	9.90	8.66	10.00	9.56	9.52	10.40	9.70	9.14
MgO	8.41	8.19	8.88	8.23	10.20	9.50	9.44	7.64	8.66	8.02	9.22	7.50	6.90	9.11	7.42
CaO	11.46	12.44	11.93	12.05	11.05	12.87	13.16	10.68	11.67	11.20	11.50	11.08	10.30	11.60	11.10
MnO	ND <sup>4</sup>	ND	ND	ND	0.18	ND	ND	0.21	0.19	0.20	0.22	0.20	0.22	0.17	0.16
Na <sub>2</sub> O	2.30	2.54	2.80	2.66	2.04	2.13	2.18	3.15	2.81	2.88	2.60	2.96	2.90	2.53	2.93
K <sub>2</sub> O	0.08	0.03	0.00	0.12	0.48	0.02	0.02	0.31	0.12	0.19	0.09	0.25	0.43	0.07	0.30
Source	2	2	2	2	3	6	6	5	5	5	5	5	5	5	5
Cr, ppm	390	380	402	354	540	313	289	332	319	270	272	323	234	285	293
Al <sub>2</sub> O <sub>3</sub>	27.82	23.25	30.99	25.96	16.34	42.79	42.90	21.70	32.20	31.60	46.20	22.40	17.70	45.00	24.30
TiO <sub>2</sub>	0.67	0.76	0.46	0.64	2.91	0.31	0.22	2.30	0.69	1.00	0.24	1.64	3.73	0.25	1.61
Cr <sub>2</sub> O <sub>3</sub>	35.83	40.10	33.55	36.33	39.73	21.57	21.84	34.50	31.90	29.80	19.90	36.50	32.00	20.20	34.60
FeO	12.88	14.14	9.35	13.32	14.86	7.43	7.71	17.00	13.70	15.00	11.80	17.10	21.10	12.30	16.70
Fe <sub>2</sub> O <sub>3</sub>	5.53	7.25	6.34	8.40	11.43	6.73	6.05	11.60	6.39	8.11	4.57	9.44	13.80	3.79	8.73
MgO	15.30	14.49	17.88	14.97	14.14	20.29	19.95	13.20	15.60	14.80	18.10	12.80	10.60	17.30	13.00
MnO	0.32	0.00	0.26	0.38	0.59	0.15	0.16	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Source	4	1	4	1	1	6	6	5	5	5	5	5	5	5	5
$\mu_{\text{Cr}(\text{Al})}$ <sup>5</sup>	-37982	-35095	-39050	-37991	-31580	-49795	-49376	-39153	-41842	-43810	-52847	-38054	-40162	-52071	-39569

<sup>1</sup> Temperature calculated after Beattie (1993). <sup>2</sup>  $\log f(\text{O}_2)$  from FeO/Fe<sub>2</sub>O<sub>3</sub> using Sack *et al.* (1980). <sup>3</sup>  $\log f(\text{O}_2)$  using Equation 11. <sup>4</sup> ND: not determined. <sup>5</sup>  $\mu_{\text{Cr}(\text{Al})} = (\mu_{\text{MgCr}_2\text{O}_4} - G^*_7) - (\mu_{\text{MgAl}_2\text{O}_4} - G^*_7)$  (J, Sack & Ghiorso 1991). Sources: 1: this study, 2: Colton (1986), 3: Murata & Richter (1966), 4: Sigurdsson (unpubl. data), 5: Gaetani *et al.* (1995), 6: Allan *et al.* (1988).

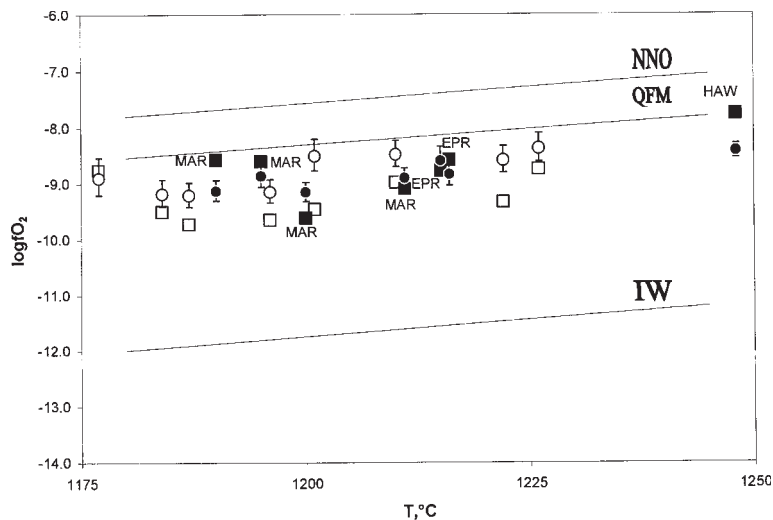


FIG. 4. Plot of calculated values of  $\log f(\text{O}_2)$  versus temperature for selected natural lavas. Squares show the  $f(\text{O}_2)$  calculated from known  $\text{Fe}^{3+}/\text{Fe}^{2+}$  using equation by Sack *et al.* (1980). Circles refer to  $f(\text{O}_2)$  calculated using the method described in the present study (Equation 11). Temperature is calculated using Beattie (1993) equation for olivine–melt equilibria. Solid symbols correspond to the samples where the glass was analyzed for total Cr at Queen's University, and open symbols are used for the samples studied by Gaetani *et al.* (1995). Labels indicate source of the sample: MAR: Mid-Atlantic Ridge, EPR: East Pacific Rise, HAW: Hawaii (all open symbols represent samples from Blanco Trough). Error bars show the error associated with the calculation of  $f(\text{O}_2)$  due to estimated analytical error of Cr analysis,  $\pm 20$  ppm.

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#### APPENDIX. PRECISION AND RANGE OF APPLICABILITY

Equation 10 was calibrated using the results of experiments ( $1150 < T < 1500^{\circ}\text{C}$ ,  $-5.5 < \Delta\text{QFM} < +2.2$ ,  $P = 1$  bar) on melts of broadly basaltic composition (*e.g.*, tholeiitic, alkali basalts, ankaramite, komatiite, boninite). The difference in  $\log f(\text{O}_2)$  calculated using Equation 10 and the  $\log f(\text{O}_2)$  of the experiments is shown in Figure 5 to be a strong function of the amount of Cr measured in the glass. The large variability of the calculated  $\log f(\text{O}_2)$  for experiments with a low Cr content in the melt phase is thought to be due to the difficulties of analyzing quenched experimental melts for Cr at low concentrations and of achieving Cr equilibrium at the low temperatures and high  $f(\text{O}_2)$  where Cr is in low concentration in the melt. The analytical problem of measuring a low concentration of Cr in high- $f(\text{O}_2)$  and lower-temperature runs is exacerbated by the presence in these runs of many small (less than 5  $\mu\text{m}$ ) crystals of chromite that may cause secondary fluorescence of Cr radiation by Fe in the glass. There is also the increased potential for variable Cr volatility in experimental charges with a high surface-area that are run at higher  $f(\text{O}_2)$  (Schreiber 1976). Most of the above-mentioned problems are considered to be experimental problems not present when dealing with natural samples. These contain larger and fewer crystals of chromian spinel and are not expected to show variable Cr volatility. However, it is recommended that Equation 10 not be used for oxygen fugacities much higher than QFM.



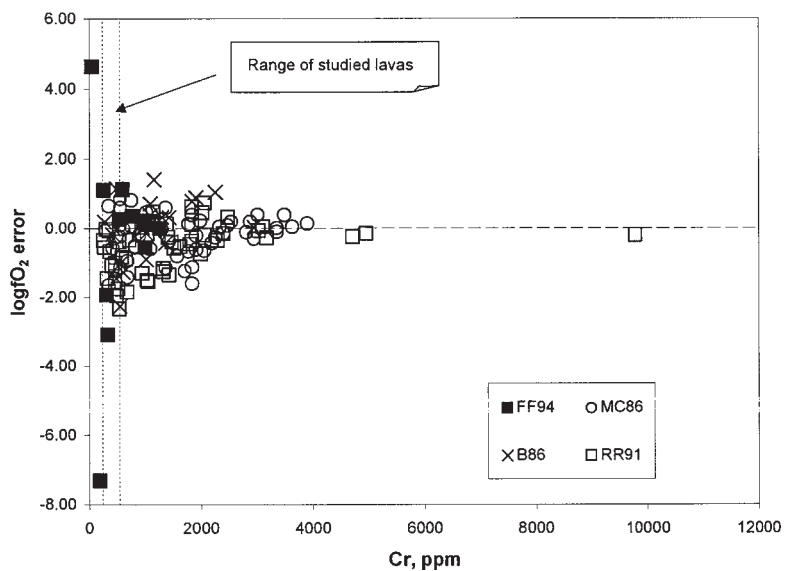


FIG. 5. Plot of the difference between the values of  $\log f(\text{O}_2)$  calculated using Equation 11 and Table 2 for the experimental data using for calibration, and the reported values as a function of total Cr in glass. Data are from: MC86: Murck & Campbell (1986), B86: Barnes (1986), RR91: Roeder & Reynolds (1991), FF94: Forsythe & Fisk (1994).

