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A pressure-independent geothermometer for primitive mantle melts

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Abstract. Phase equilibrium data from the CaO-MgO-Al_2O_3-SiO_2, CaO-MgO-Al_2O_3-SiO_2-Na_2O, and CaO-MgO-Al_2O_3-SiO_2-FeO systems on the melting behavior of plagioclase, spinel, and garnet lherzolite, are used to determine the molar partition coefficient of MgO between olivine and melt, $D^{ol/liq}_{MgO*}$, as a function of temperature, pressure, and composition. The data sets cover the pressure range 0.1 MPa to 5 GPa and temperatures of 1225°–1830°C. It is shown that the trend of $D^{ol/liq}_{MgO*}$ is little affected by the transitions between different lherzolite assemblages and that one empirical equation, which has reciprocal temperature (in Kelvin) and mole fraction of $NaO_{0.5}$ in the melt as independent variables, describes the variation of $D^{ol/liq}_{MgO*}$ in pressure, temperature, and composition space and has the form $\ln D^{ol/liq}_{MgO*} = (4723/T) + 2.566 C^{liq}_{NaO_{0.5*}} - 1.729$. This expression is tested by using it to calculate the temperatures of melting experiments containing olivine-saturated basalt and picrite melts and is shown to yield good results for multiply saturated melts, consistent with the fact that the observed simple trend of $D^{ol/liq}_{MgO*}$ is dictated by low-variance phase relations. With fewer phases present, the equation systematically predicts temperatures that are too high. If the value of $K^{ol/liq}_{DFe^{2+}/Mg}$ (K_D) is known, the value of $D^{ol/liq}_{MgO*}$ can be calculated from $D^{ol/liq}_{MgO*} = 0.6667 / (C^{liq}_{FeO*} K_D + C^{liq}_{MgO*})$, and hence the mole fractions of MgO, FeO, and $NaO_{0.5}$ can be used to calculate the equilibrium temperature of multiply saturated olivine-bearing melts. This geothermometer is mainly applicable to primitive tholeiitic and mildly alkalic basalt and picrite melts, with small amounts of volatiles only, in the 1150°–1800°C temperature range.

1. Introduction

Low-variance phase relations in simplified systems can provide important insights into natural melting processes that may not be apparent from higher-variance experiments on natural compositions. This is because melting can generally be treated in a more rigorous way in simple systems and also because different effects that can become obscured in the more complex systems can be investigated in isolation in simple systems. Phase relations in the simplified CaO-MgO-Al_2O_3-SiO_2 (CMAS), CaO-MgO-Al_2O_3-SiO_2-Na_2O (CMASN), and CaO-MgO-Al_2O_3-SiO_2-FeO (CMASF) systems resemble phase relations in the mantle closely enough to allow detailed prediction of the melting behavior of the mantle. Data on the melting relations of simplified lherzolite in the CMASN [*Walter et al.*, 1995], CMAS [*Gudfinnsson and Presnall*, 1996], and CMASF [*Gudfinnsson and Presnall*, 2000] systems have, for example, been used to obtain melting reactions for mantle lherzolite that are very similar to melting reactions obtained from experiments on natural peridotite compositions. However, it has been possible to extract certain details of melting reactions from the simplified systems that are not evident from studies of natural peridotites. In this paper, we use data on the melting relations of model lherzolite in the CMAS, CMASN, and CMASF systems to determine the pressure, temperature, and compositional dependence of the molar partition coefficient of MgO between olivine and melt, $D^{ol/liq}_{MgO*}$, at 0.1 MPa to 5 GPa pressure and in the 1225°–1830°C temperature range. We demonstrate that the resulting expression can be used as a pressure-independent geothermometer for multiply saturated, primitive mantle melts. To minimize the effect of errors introduced by using different experimental and analytical methods, setups, and calibrations, we use data from one laboratory only; and in all cases except two (one 1-atm experiment and one multianvil experiment) the experiments were performed using piston-cylinder presses with similar assemblies. In addition, all the experiments contained a large amount of melt, which facilitated equilibration.

Following a brief review of the evidence for the temperature dependence of $D^{ol/liq}_{MgO*}$ and modeling of this relationship, we derive equations for the temperature dependence of $D^{ol/liq}_{MgO*}$ from the experimental data in the CMAS, CMASN, and CMASF systems, where the relationship between temperature and $D^{ol/liq}_{MgO*}$ is constrained by low-variance phase relations. The equations thus derived are then tested by using them to calculate temperatures of experimental liquids saturated with olivine and comparing the calculated temperatures to the measured temperatures in the experiments. Finally, the equations are modified and extended so that the composition of liquid alone is enough to calculate $D^{ol/liq}_{MgO*}$ or temperature, and olivine compositions are no longer required. Notations in this paper follow the recommendations of *Beattie et al.* [1993], where D_* indicates a partition coefficient calculated on a molar basis.

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2. Theoretical Aspects of the Temperature Dependence of $D^{ol/liq}_{MO*}$

It is well established that the molar partition coefficients of MgO and FeO between olivine and melt, $D^{ol/liq}_{MO*}$, where M is either Mg or Fe^{2+}, correlate inversely with temperature at a fixed pressure and that there is a near-linear positive correlation between ln $D^{ol/liq}_{MO*}$ and

$1/T$ [*Roeder and Emslie*, 1970; *Roeder*, 1974; *Leeman*, 1978; *Longhi et al.*, 1978]. This relationship can be predicted from the temperature dependence of the equilibrium constant, which at a fixed pressure can be expressed as

$$\ln K = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}, \tag{1}$$

where K is the equilibrium constant, T is the temperature, R is the gas constant, and ΔG, ΔH, and ΔS are the Gibbs free energy, enthalpy, and entropy of the reaction, respectively. This relationship holds if ΔH and ΔS are constant over the temperature and compositional range of interest. Hence expressions of the form

$$\ln D^{\mathrm{ol/liq}}_{MO^*} = \frac{A}{T} + B, \tag{2}$$

where A and B are constants and T is the temperature in Kelvin, have commonly been adopted to describe the temperature dependence of the partition coefficients. Data from 0.1 MPa experiments have been used to derive the coefficients for these expressions [*Roeder and Emslie*, 1970; *Roeder*, 1974; *Leeman*, 1978; *Longhi et al.*, 1978; *Nielsen and Dungan*, 1983], and the expressions can then be used as geothermometers for olivine-bearing lavas or to demonstrate equilibrium between olivine and melt. In other cases [e.g., *Ramsay et al.*, 1984; *Helz and Thornber*, 1987; *Montierth et al.*, 1995], temperature has simply been expressed as a function of MgO content of the melt. If pressure P is also variable, the equilibrium constant can be expressed as

$$\ln K = \frac{-\Delta G}{RT} - \frac{(P-P_0)\Delta V}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} - \frac{(P-P_0)\Delta V}{RT}, \tag{3}$$

which is valid if ΔH, ΔS, and ΔV remain constant over the temperature, pressure, and compositional range of interest. As an example, *Ulmer* [1989] conducted melting experiments on calc-alkaline compositions to determine the partitioning of Mg and Fe^{2+} between olivine and melt at up to 3.0-GPa pressure, and to describe the pressure and temperature dependence of the partition coefficients, he employed an equation of the form

$$\log D^{\mathrm{ol/liq}}_{MO^*} = A + \frac{B}{T} - \frac{CP}{T} + DP, \tag{4}$$

where A, B, C, and D are constants.

Formulations of the kind shown above usually yield good results only for relatively narrow compositional ranges because the partition coefficients are sensitive to changes in melt composition [*Roeder*, 1974; *Herzberg*, 1979; *Leeman*, 1978; *Longhi et al.*, 1978; *Takahashi*, 1978; *Ulmer*, 1989]. *Longhi et al.* [1978] found systematic differences in the partition coefficients for low-Ti and high-Ti lunar basalts and proposed that the equilibrium of Mg and Fe^{2+} between olivine and melt could be described by a reaction of the form

$$\underset{\text{liquid}}{2MO} + \underset{\text{liquid}}{\mathrm{SiO_2}} = \underset{\text{olivine}}{M_2\mathrm{SiO_4}}, \tag{5}$$

whereby $D^{\mathrm{ol/liq}}_{MO}$ becomes dependent on silica activity in the melt. They used an activity model for the melt to calculate a modified partition coefficient for MgO and FeO between olivine and melt that includes silica activity, whereas *Nielsen and Dungan* [1983] used a different melt model that also takes into account the activity of silica in the melt. *Ariskin et al.* [1993], *Beattie* [1993], and *Sisson and Grove* [1993] all used different activity models that include pressure terms in equations for the temperature and pressure dependence of the partition coefficient of MgO. The thermodynamic MELTS program [*Ghiorso and Sack*, 1995] can also be used for geothermometric calculations involving liquid and olivine equilibrium. *Roeder* [1974], *Herzberg* [1979], and *Leeman* [1978] noted the strong effect of alkalis on $D^{\mathrm{ol/liq}}_{\mathrm{MgO}}$, and Leeman's activity model for the melt phase partly accounts for this effect. The strong effect of Na on the partition coefficient will become clearer from the discussion in section 3. In addition to thermodynamically based geothermometers, purely empirical melt geothermometers [e.g., *Grove and Juster*, 1989; *Sisson and Grove*, 1993] and hybrids of the two kinds [e.g., *Kinzler and Grove*, 1992] have also been invented, generally for narrow compositional ranges or for multiply saturated melts.

3. Temperature, Pressure, and Compositional Dependence of $D^{\mathrm{ol/liq}}_{\mathrm{MgO^*}}$ in the CMAS, CMASF, and CMASN Systems

In the CMAS system the lherzolite phase assemblage (ol + opx + cpx + an/sp/gt, where ol is olivine, opx is orthopyroxene, cpx is clinopyroxene, an is anorthite, sp is spinel, and gt is garnet) coexisting with melt is isobarically invariant. These phase relations have been determined by *Presnall et al.* [1979] (0.1 MPa to 2.0 GPa), *Milholland and Presnall* [1991] (3.0 GPa), and *Gudfinnsson and Presnall* [1996] (2.4–3.4 GPa) using piston-cylinder presses (except at 0.1 MPa), and the 5.0-GPa point was determined in a multianvil experiment by *Weng* [1997]. The glass analyses in the CMAS and CMASN systems used here, other than those of the 2.4–3.4-GPa and the 5.0-GPa points, are from *Walter and Presnall* [1994]. Olivine in the CMAS system is almost pure end-member forsterite, but is estimated to contain up to ~0.4 wt % CaO and 0.3 wt % $\mathrm{Al_2O_3}$ [*Gudfinnsson and Presnall*, 1996]. *Gudfinnsson and Presnall* [2000], using Fe capsules, conducted piston-cylinder experiments at 0.7–2.8 GPa to determine the same phase relations with FeO added to the CMAS system. In this case, as in the CMASN system, the phase assemblage is isobarically univariant.

Because the lherzolite assemblage in equilibrium with melt is univariant in P-T space in the CMAS system, the partition coefficient for MgO between olivine and melt can be rigorously described as a function of only one variable in the CMAS system, but different functions might be expected to be necessary for the plagioclase, spinel, and garnet lherzolite stability fields. In the CMASF system, the same assemblages being isobarically univariant, one would expect that two independent variables would be needed to describe the variation of $D^{\mathrm{ol/liq}}_{\mathrm{MgO^*}}$ in P-T space. However, on a diagram of $\ln D^{\mathrm{ol/liq}}_{\mathrm{MgO^*}}$ plotted against reciprocal temperature (in Kelvin) (Figure 1), apart from slight divergence of the CMAS and CMASF data sets at the lower temperatures, the two data sets form a single well-defined linear trend, as a goodness of fit of 0.98 supports (Table 1). Apparently, the introduction of FeO to the CMAS system has little influence on the partitioning of MgO between olivine and liquid. Furthermore, the transitions from plagioclase to spinel lherzolite and spinel to garnet lherzolite do not seem to have a discernible effect on the trend of the partition coefficient. Regression of the two data sets yields an equation for the temperature dependence of $\ln D^{\mathrm{ol/liq}}_{\mathrm{MgO^*}}$ in the alkali-free systems as

$$\ln D^{\mathrm{ol/liq}}_{\mathrm{MgO^*}} = \frac{4440}{T} - 1.556, \tag{6}$$

where the temperature is in Kelvin. The regression parameters and errors are listed in Table 1.

The phase relations of model lherzolite in the CMASN system at 0.7–3.5 GPa, with up to 5.5 wt % $\mathrm{Na_2O}$ (mole fraction of $\mathrm{NaO_{0.5}}$ of 0.094) in the melt, were determined by *Walter and Presnall* [1994], and the analyses used here are from that paper. As in the CMASF system, the lherzolite assemblage in equilibrium with melt

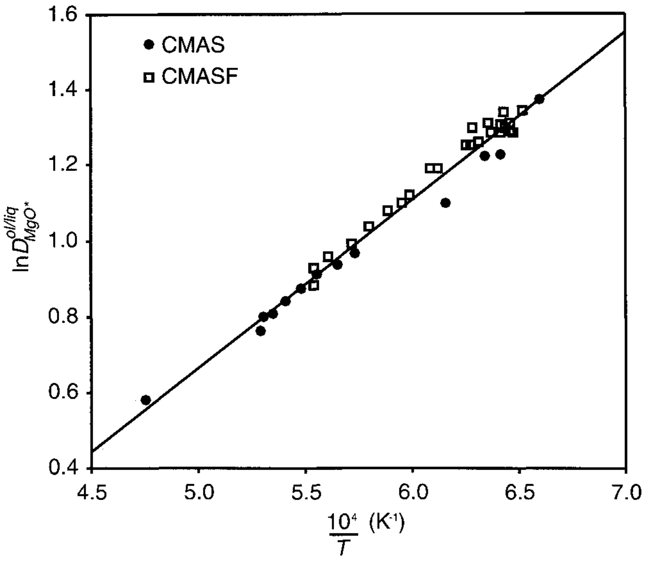

Figure 1. Temperature dependence of the molar partition coefficient of MgO between olivine and melt derived from the CMAS and CMASF data sets, plotted as ln $D^{ol/liq}_{MgO*}$ versus reciprocal temperature. The line shown is a regression fit to the data sets (see Table 1).

is isobarically univariant in the CMASN system, and $D^{ol/liq}_{MgO*}$ can be described as a function of two independent variables. On a diagram of ln $D^{ol/liq}_{MgO*}$ plotted against reciprocal temperature (Figure 2) the CMASN data are generally offset from the trend of the CMAS and CMASF data sets, but the deviations are clearly systematic. At similar temperatures, in agreement with the findings of *Leeman* [1978], the partition coefficient is larger in the CMASN experiments. This means, since the olivine composition can be treated as nearly constant in the CMAS and CMASN systems, that the Na-bearing runs have less Mg in the melt phase at identical temperatures than do the Na-free runs. As mentioned in section 2, some of the earlier studies have attempted to account for the compositional effect on $D^{ol/liq}_{MgO}$ by employing activity models for silica in the melt. Even with a pressure term, such models turn out to yield considerably worse fits to the CMAS, CMASF, and CMASN data than the empirical approach we have chosen, which involves regressing all the data to an equation that has a term with the mole fraction of $NaO_{0.5}$ in the melt, $C^{liq}_{NaO_{0.5}*}$. The resulting best fit equation is

$$\ln D^{ol/liq}_{MgO^*} = \frac{4723}{T} + 2.566 C^{liq}_{NaO_{0.5}*} - 1.729, \tag{7}$$

where the temperature is in Kelvin. The fit of this equation to the regression data is excellent as indicated by the goodness of fit (R^2 = 0.98) and other regression statistics (Table 1). The difference in the first and third constants of (7) and the constants of (6) reveals a slight misfit in the trend of $D^{ol/liq}_{MgO*}$ between the data sets. Figure 3 shows how well the equation recovers $D^{ol/liq}_{MgO*}$ determined in the experiments.

4. Application of the CaO-MgO-Al_2O_3-SiO_2-Na_2O-FeO (CMASNF) Geothermometer to Natural Melt Compositions

The CMAS, CMASN, and CMASF systems lack components, such as TiO_2 and K_2O, that could affect $D^{ol/liq}_{MgO*}$ in natural systems. One measure of the utility of (7) is its ability to predict temperatures of natural olivine-saturated melts. A large amount of data on olivine-bearing melting experiments has been published. In our evaluation of the expression we restrict the comparison to experiments on relatively primitive tholeiitic or mildly alkalic basaltic or picritic melt compositions because they are most closely related to the experimental liquid compositions from which the expression was derived. To this end, the selection is limited to experiments that have glasses with Mg/(Mg + Fe) $\geq$ 0.5 (cation fractions), $Na_2O \leq 4.0$ wt %, and, in light of the predicted strong effect of K_2O on the partitioning of MgO between olivine and melt [*Herzberg*, 1979], $K_2O \leq 0.5$ wt %. The comparison is restricted to volatile-free experiments, because H_2O and CO_2 are known to have a strong effect on the structure of silicate melts [*Mysen*, 1976; *Mysen et al.*, 1980]. Also, experiments are only included if glass totals are 99.0 wt % or higher. As a test for equilibrium, it is required that $K^{ol/liq}_{D_{Fe/Mg*}}$ of the experiments be within ±0.03 of the same parameter calculated according to the method of *Kushiro and Walter* [1998]. In Figure 4 we have plotted measured against calculated temperatures for a large number of melting experiments that fit these criteria. These data are from experiments conducted using 1-atm furnaces, gas pressure vessels, piston-cylinder presses, and multianvil presses, at pressures from 0.1 MPa to 7 GPa and temperatures from 1150° to 1950°C (see Figure 4 caption for sources). The data have been divided into runs containing olivine (±spinel) as the only crystalline phase and runs containing more crystalline phases. The data form a cluster around the 1:1 line, but there are some significant deviations from a perfect fit, so a closer look at the data is warranted. Despite the fact that temperature measurements in high-pressure experiments are more uncertain than those in experiments at 0.1 MPa, the CMASNF geothermometer at all pressures tends to predict temperatures of multiply saturated experiments better than temperatures of experiments with olivine as the sole crystalline phase, where the geothermometer tends to give temperatures that are too high. From Figure 5, which contains only the multiply saturated data and where the experiments are distinguished according to the phase assemblage present, it can be seen that the CMASNF geothermometer generally predicts the temperature of multiply saturated experiments quite well, but for melts with only olivine or olivine and spinel present, it consistently yields temperatures that are too high.

Thus, consistent with the phase relations represented by the CMAS, CMASN, and CMASF data, the CMASNF geothermometer tends to yield good results for primitive melts in equilibrium with three or more crystalline phases. When only two crystalline phases are present, it generally works best when, in addition to olivine, the melt is saturated with plagioclase or clinopyroxene or orthopyroxene, but it consistently predicts temperatures that are too high when olivine and melt coexist only with spinel. The CMASF experiments were conducted in equilibrium with metallic Fe, which imposes a somewhat lower fO_2 than that generally prevailing during generation of upper mantle melts [*Christie et al.*, 1986;

Table 1. Regression Parameters for Temperature-Dependent Expressions of $D^{ol/liq}_{MgO*}$

Data Sets	Dependent Variable	Intercept	SE	Independent Variables				
				1/T (K^{-1})	SE	$C^{liq}_{NaO_{0.5}*}$	SE	R^2
CMAS and CMASF	$D^{ol/liq}_{MgO*}$	−1.556	0.065	4440	107			0.980
CMAS, CMASF, and CMASN	$D^{ol/liq}_{MgO*}$	−1.729	0.058	4723	97	2.566	0.150	0.980

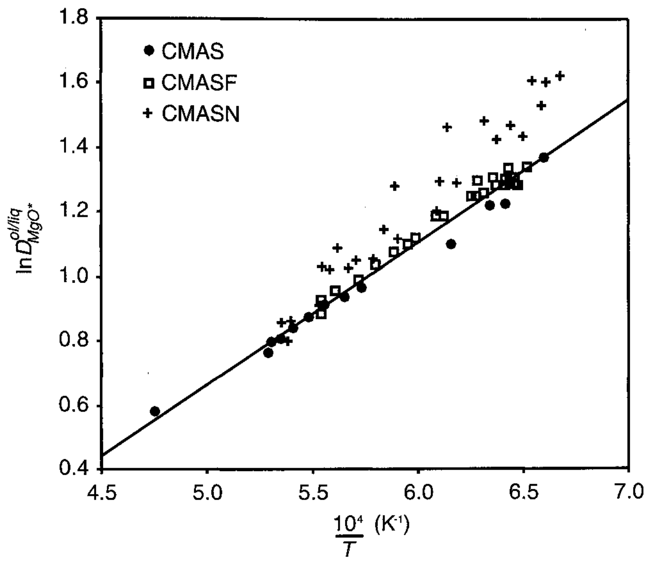

Figure 2. Temperature dependence of the molar partition coefficient of MgO between olivine and melt in the CMAS, CMASF, and CMASN data sets, plotted as $\ln D^{\mathrm{ol/liq}}_{\mathrm{MgO}^*}$ versus reciprocal temperature. The line shown is a regression fit to the CMAS and CMASF data sets only.

Bryndzia et al., 1989; *Ballhaus and Frost*, 1994]. Almost all the high-pressure experiments on natural compositions were performed with the samples confined in graphite capsules, which restricts the fO_2 close to the relatively reduced conditions of the C-CO-CO_2 (CCO) buffer. However, in the experiments at 0.1 MPa the fO_2 was generally fixed at the fayalite-magnetite-quartz (FMQ) buffer, but was as low as iron-wüstite (IW) and as high as Ni-NiO (NNO). These variations in redox conditions do not seem to affect the accuracy of the geothermometer. Moreover, the amount of TiO_2 in the glasses ranges from 0.21 to 4.15 wt %, but within this range there is no apparent correlation between TiO_2 content of the experiments and the difference between the measured and predicted temperatures. Nevertheless, since the geothermometer is derived from Ti-free experiments, we do not recommend its use for high-Ti melt compositions. It should also be kept in mind that the geothermometer is not well constrained at temperatures above ~1600°C.

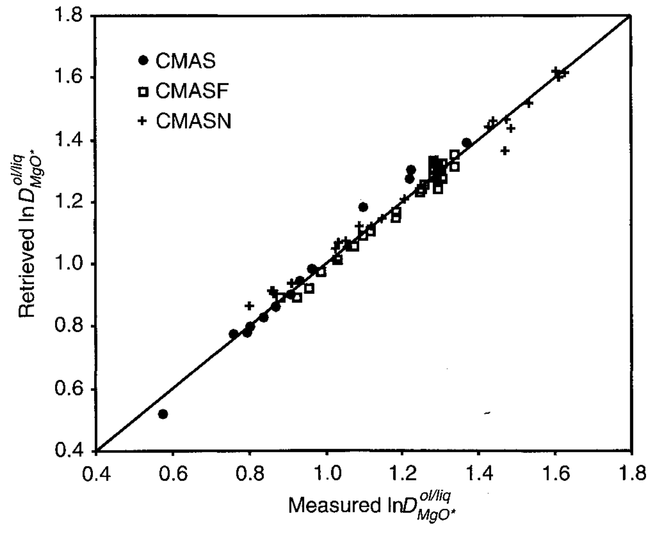

Figure 3. Calculated $\ln D^{\mathrm{ol/liq}}_{\mathrm{MgO}^*}$ using equation (7) in comparison with measured $\ln D^{\mathrm{ol/liq}}_{\mathrm{MgO}^*}$ in the CMAS, CMASF, and CMASN data sets. The diagonal line indicates perfect agreement.

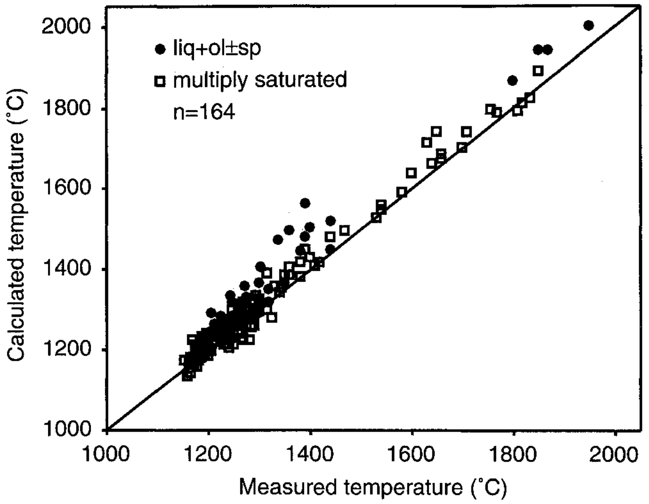

Figure 4. Temperatures calculated by using equation (7) compared to measured values in melting experiments containing olivine-bearing basalt and picrite melts. The line denotes perfect agreement. Here, liq is liquid, ol is olivine, and sp is spinel. The sources of experimental data are as follows: *Weill and McKay* [1975], *Delano* [1977], *Bender et al.* [1978], *Grove and Vaniman* [1978], *Stolper* [1980], *Grove et al.* [1982, 1990, 1992], *Fujii and Bougault* [1983], *Grove and Bryan* [1983], *Takahashi and Kushiro* [1983], *Elthon and Scarfe* [1984], *Kinzler and Grove* [1985, 1992], *Tormey et al.* [1987], *Longhi and Pan* [1988], *Sato* [1989], *Dunn and Stringer* [1990], *Bartels et al.* [1991], *Draper and Johnston* [1992], *Eggins* [1992], *Baker and Stolper* [1994], *Montierth et al.* [1995], *Thy* [1995], *Yang et al.* [1996], *Kinzler* [1997], and *Walter* [1998].

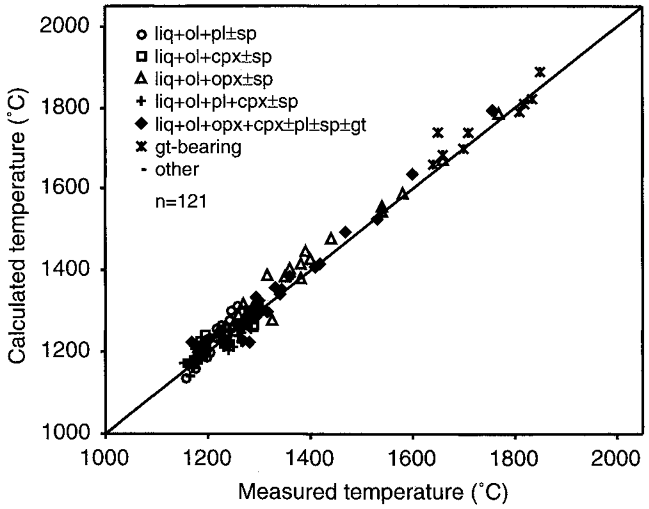

Figure 5. Temperatures in multiply saturated experiments calculated by means of equation (7) compared to measured temperatures of the experiments. The line denotes perfect agreement. This is a subset of the experiments in Figure 4 that have one or more crystalline phases in addition to olivine ± spinel. The type of symbol indicates the phase assemblage present in the experiment. liq is liquid, ol is olivine, pl is plagioclase, sp is spinel, cpx is clinopyroxene, opx is orthopyroxene, and gt is garnet.

5. Mg-Fe^{2+}-Na Melt Geothermometer

The CMASNF geothermometer requires the compositions of melt and the coexisting olivine. Generally, however, the composition of the equilibrium olivine can be inferred from the composition of the melt, and hence a geothermometer that requires only the mole fractions of MgO, FeO, and $NaO_{0.5}$ in the melt as input can be derived. The composition of olivine in basalts and picrites can, to a good approximation, be described as a pure Mg_2SiO_4-Fe_2SiO_4 solid solution. This means that if FeO/MgO of the olivine is known, the concentration of MgO can be calculated from the stoichiometry of olivine. Assuming that the exchange coefficient of Fe^{2+} and Mg between olivine and melt, $K_{D_{Fe^{2+}/Mg^*}}^{ol/liq}$ (K_D), is constant, then the mole fraction of MgO in olivine can be calculated from K_D and the mole fractions of FeO and MgO in the coexisting melt can be calculated as follows [*Langmuir and Hanson*, 1980]:

$$C_{MgO*}^{ol} = 0.6667 C_{MgO*}^{liq} / (C_{FeO*}^{liq} K_D + C_{MgO*}^{liq}). \tag{8}$$

Correspondingly, the molar partition coefficient of MgO between olivine and melt can be expressed as

$$D_{MgO*}^{ol/liq} = 0.6667 / (C_{FeO*}^{liq} K_D + C_{MgO*}^{liq}), \tag{9}$$

which can be substituted into (7) to calculate temperature from the mole fractions of MgO, FeO, and $NaO_{0.5}$ in the melt alone. Implicit is the assumption that the melt was multiply saturated, with olivine being one of the crystalline phases. Temperatures calculated in this fashion are not particularly sensitive to the value of K_D; analysis of the literature data shows that differences in temperatures obtained using $K_{D_{Fe/Mg^*}}^{ol/liq}$ of 0.30, on the one hand, and 0.35, on the other, are ~25°C at 1100°C, 13°C at 1400°C, and 8°C at 1800°C. This expansion of the CMASNF geothermometer can in many cases be useful because analyses of olivine are not always available or, when available, have a range of compositions indicating that not all the olivine crystals are in equilibrium with the coexisting melt.

6. Discussion

Table 2 contains a comparison of the accuracy of the geothermometers presented in sections 3 and 5 and several published geothermometers when applied to our data set. The accuracy is measured by the standard deviations of the difference between measured and predicted temperatures. All the other geothermometers contain pressure terms and hence, unlike the CMASNF geothermometer, require more information than the phase compositions only. Not surprisingly, some of the other geothermometers yield better results than the CMASNF geothermometers when applied to the whole data set, because the data set also contains information from experiments that were not multiply saturated. When used for multiply saturated experiments only, the CMASNF geothermometer provides better results than the other geothermometers except for one, that of *Sisson and Grove* [1993], apparently because of improved prediction of temperatures in high-pressure runs. It should be noted that a few of the experimental runs from our data set are at higher pressures than the calibration ranges for some of the other geothermometers. However, the accuracies of the CMASNF geothermometer and the geothermometer of *Sisson and Grove* [1993] are comparable, and importantly, the CMASNF geothermometer is the only one that does not require knowledge of pressure.

The comparison above reaffirms that the CMASNF geothermometers are applicable to multiply saturated liquids and that the phase relations in the CMAS, CMASN, and CMASF systems closely approach those of primitive basaltic and picritic melts in nature. It appears that in such melts the effects of additional components, such as Cr_2O_3, TiO_2, K_2O, and P_2O_5, on the phase relations are generally minor. The analysis of the phase relations involving four-phase lherzolites in equilibrium with melt in the CMASNF system indicates that the partitioning of MgO between olivine and liquid closely approaches divariant behavior. In theory, one could then use any two variables, composition or pressure or temperature, to describe the partitioning, but the preferred choice of using temperature and $NaO_{0.5}$ content of the melt as independent variables is based on best fit criteria. The fact that the CMASNF geothermometer does not include a pressure term is commonly an advantage, because when estimating the temperatures of naturally occurring melts, the pressure of equilibration is sometimes highly uncertain.

7. Conclusions

Phase relations involving the plagioclase, spinel, or garnet lherzolite phase assemblage coexisting with melt in the CMAS system are univariant, and correspondingly, the variation in $D_{MO*}^{ol/liq}$ can be described as a function of one variable in P-T space. With FeO added to the CMAS system the same phase relations become divariant. Nevertheless, the temperature variation of $D_{MgO*}^{ol/liq}$ in the two chemical systems is very similar, such that ln $D_{MgO*}^{ol/liq}$ is a nearly linear function of reciprocal temperature and is little affected by the transitions between different lherzolite phase assemblages. In contrast, with the lherzolite phase assemblage and melt present in the CMASN system, as the phase equilibria dictate, $D_{MgO*}^{ol/liq}$ must be described as a function of two variables. The combined CMAS, CMASF, and CMASN data are used to derive a pressure-independent empirical expression for the variation of $D_{MgO*}^{ol/liq}$ in pressure, temperature, and composition space (equation (7)). Use of this

Table 2. Comparison of the Temperature Retrieval of Different Geothermometers for Olivine-Saturated Basaltic Melts[a]

Data Set	CMASNF-1	CMASNF-2	*Ariskin et al.* [1993]	*Beattie* [1993]	*Sisson and Grove* [1993]	*Sugawara* [2000] Geothermometer 1	*Sugawara* [2000] Geothermometer 2
All data[b]	41	42	73	53	26	32	29
Multiply saturated	27	26	71	54	22	32	28
0.1 MPa	23	23	16	9	19	14	17
High pressure	28	28	89	68	24	39	33

[a] Standard deviations of the difference between measured and calculated temperatures using different geothermometers. Calculated as $\sqrt{\sum_{i=1}^{n}(x_i - X_i)/n}$, where n is the number of data and x_i and X_i are the measured and calculated temperatures. CMASNF-1 and CMASNF-2 temperatures were calculated from equation (7), CMASNF-1 incorporating $D_{MgO*}^{ol/liq}$ calculated from published olivine and glass (or quench) compositions and CMASNF-2 using $D_{MgO*}^{ol/liq}$ calculated from equation (9) where $K_{D_{Fe/Mg^*}}^{ol/liq}$ was calculated according to the method of *Kushiro and Walter* [1998]. Other geothermometers are from *Ariskin et al.* [1993], *Beattie* [1993], *Sisson and Grove* [1993], and *Sugawara* [2000]. The Sugawara geothermometers 1 and 2 are equations (3) and (4) of *Sugawara* [2000], respectively.

[b] "All data" are the data set used in Figure 4. The "multiply saturated" data set is the subset of "all data" used in Figure 5. The "0.1 MPa" and "high pressure" data sets are subsets of the "multiply saturated" data set that include 0.1-MPa pressure experiments and experiments at pressures higher than 0.1 MPa, respectively.

expression to predict temperatures of experimental olivine-bearing basaltic and picritic melt compositions shows that the expression works best for multiply saturated melts, whereas it yields temperatures that are systematically too high when the state of the system is constrained by fewer phases. The effectiveness of the CMASNF geothermometer in predicting temperatures of primitive experimental basalt and picrite liquids indicates that components other than CaO, MgO, Al_2O_3, SiO_2, Na_2O, and FeO are in sufficiently small amounts to have little influence on $D_{\mathrm{MgO}*}^{\mathrm{ol/liq}}$ of most primitive mantle melts. If the value of K_D is known, the concentration of Mg in olivine can be calculated from the Fe^{2+} and Mg concentrations of the coexisting melt, hence yielding a geothermometer for primitive mantle melts that uses the mole fractions of MgO, FeO, and $NaO_{0.5}$ in melt as input. We recommend the use of the CMASNF geothermometer for relatively primitive multiply saturated olivine-bearing melts of tholeiitic or mildly alkalic composition, for melts with only small amounts of volatiles, for temperatures of ~1150°–1800°C, and whenever the pressure is not known.

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