THERMOBAROMETRY OF MANTLE PERIDOTITES: CALIBRATION BASED ON EXPERIMENTAL AND NATURAL DATA

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INTRODUCTION

Most of the thermometers and barometers currently available for use with mantle peridotites have been calibrated using the results of experiments performed at relatively high T/P conditions in compositionally simple systems. Mutually inconsistent P-T results are often revealed when these calibrations are applied to naturally occurring, compositionally complex peridotite xenoliths. These inconsistencies can partly be attributed to incomplete equilibration of products in calibration experiments, as evidenced by compositional heterogeneity of run products. In contrast, natural peridotitic minerals are often fairly homogeneous and well equilibrated. The compositions of coexisting natural phases have been used for the refinement of the thermodynamic properties of minerals (e.g., Holland and Powell, 1990) and construction of empirical thermobarometers (e.g., Witt-Eickschen & Seck, 1991; Griffin et al., 1989). The use of natural data for such purposes is complicated by the poorly constrained P-T conditions of equilibrium. They can be calculated from some other independent equilibria but this approach inevitably increases the ambiguity of results. Girnis et al. (1999) used natural compositions of mineral inclusions in diamonds to refine the thermodynamic mixing properties of peridotitic minerals in the FMASCr system. Their approach did not require the preliminary knowledge of the P-T conditions of mineral equilibrium, because these parameters were refined together with the thermodynamic properties of minerals. The idea of such processing is based on the fact that the number of mineral reactions in a multiphase natural assemblage is usually higher than two, and, in principle, the two unknown parameters (temperature and pressure) can be excluded from the system. In this contribution, we extend this approach including data on clinopyroxene-bearing compositions and a large data set of natural mineral compositions from mantle xenoliths.

THERMODYNAMIC FORMALISM

There is a fundamental difference between experimental and natural mineral equilibrium data, which defines their different treatment in a single optimization scheme. Experimental data are always obtained at known pressure and temperature (ignoring for the moment uncertainty in experimental parameters), but the equilibrium may be not attained. A number of contrivances have been proposed to circumvent the sluggishness of reactions between solid phases, but in most cases, the experiments yield only one-sided bounds (half-brackets) to the equilibrium compositions. Reversal experiments with different compositions of starting materials are used to obtain full brackets under given P-T parameters. The advantage of natural minerals is the high degree of equilibration and large sizes and homogeneity of grains (or parts of grains), which can be accurately analyzed. In addition to the unknown temperature and pressure of equilibrium, there is another problem arising at the use of natural minerals: they always contain many minor components, which can influence thermodynamic relations. This problem is not addressed in this contribution. We selected the compositions of natural minerals with negligible concentrations of minor components. However, this complication is not fundamental, because any additional component can be readily incorporated in the model.

The general thermodynamic equilibrium condition for reaction *i* is:

$$\Delta G(i) = 0 = \Delta H_0(i) - T\Delta S_0(i) + P\Delta V_0(i) + RT\ln K(i) + \Delta G^{ex}(i), \qquad (1)$$

where ΔG is the Gibbs free energy change of the reaction; ΔH is the enthalpy change; ΔS is the entropy change; ΔV is the volume change; K is the equilibrium constant; ΔG^{ex} is the change of excess mixing free energies; P is pressure; and T is temperature. Using this relation, the following system of equalities and inequalities can be written for a set of experimental and natural data. Experimental data provide the following inequality constraints for each reaction considered:

$$(\Delta H_0 - T\Delta S_0 + P\Delta V_0 + RT\ln K + \Delta G^{ex})q < \sigma \qquad (2)$$

where q is either +1 or -1 depending on the direction of approach to equilibrium, and the term σ accounts for errors in experimental P, T and compositions. Each natural assemblage *k* yields at least three (i=1,2,3…) equations:

$$\Delta G(i)^{nat} = \Delta H_0(i) - T\Delta S_0(i) + P_k\Delta V_0(i)$$
$$+ RT_k\ln K(i) + \Delta G^{ex}(i) = 0 \qquad (3)$$

Note that unlike eq. 2, the values P_k and T_k in eq. 3 are not known (though can be constrained to lie within some reasonable limits) and must be calculated. The set of unknown parameters includes the Gibbs free energies of reactions, thermodynamic mixing properties of phases, and equilibrium P-T parameters of natural assemblages. These values can be found by the minimization of the nonlinear target function $Z = \Sigma(\Delta G(i)^{nat})^2$ under constraints given by eq. 2 for experimental data.

The compositions of minerals were projected onto the system $Na_2O-CaO-FeO-MgO-Al_2O_3-Cr_2O_3-SiO_2$. Because of this, the main limitation used in the selection of input data was low Ti content of spinel, garnet and pyroxenes (TiO_2 in spinel < 1 wt %) and low degree of iron oxidation in spinel and garnet. The following independent reactions were considered:

1. $1/2Fe_2SiO_4^{Ol} + MgAl_2O_4^{Sp} = 1/2Mg_2SiO_4^{Ol} + FeAl_2O_4^{Sp}$
2. $Mg_2SiO_4^{Ol} + Fe_2Si_2O_6^{Opx} = Fe_2SiO_4^{Ol} + Mg_2Si_2O_6^{Opx}$
3. $1/2Mg_2SiO_4^{Ol} + CaFeSi_2O_6^{Cpx} = 1/2Fe_2SiO_4^{Ol} + CaMgSi_2O_6^{Cpx}$
4. $3Mg_2SiO_4^{Ol} + 2Fe_3Al_2Si_3O_{12}^{Grt} = 3Fe_2SiO_4^{Ol} + 2Mg_3Al_2Si_3O_{12}^{Grt}$
5. $CaMgSi_2O_6^{Cpx} + Mg_2Si_2O_6^{Opx} = Mg_2Si_2O_6^{Cpx} + CaMgSi_2O_6^{Opx}$
6. $3CaMgSi_2O_6^{Cpx} + Mg_3Al_2Si_3O_{12}^{Grt} = 3Mg_2Si_2O_6^{Cpx} + Ca_3Al_2Si_3O_{12}^{Grt}$
7. $MgAlAlSiO_6^{Cpx} + MgAlCrSiO_6^{Opx} = MgAlCrSiO_6^{Cpx} + MgAlAlSiO_6^{Opx}$
8. $2MgAlAlSiO_6^{Opx} + Mg_3Cr_2Si_3O_{12}^{Grt} = 2MgAlCrSiO_6^{Opx} + Mg_3Al_2Si_3O_{12}^{Grt}$
9. $2MgAlAlSiO_6^{Opx} + MgCr_2O_4^{Sp} = 2MgAlCrSiO_6^{Opx} + MgAl_2O_4^{Sp}$
10. $MgAlAlSiO_6^{Opx} + Mg_2Si_2O_6^{Opx} = Mg_3Al_2Si_3O_{12}^{Grt}$
11. $MgAlAlSiO_6^{Cpx} + Mg_2Si_2O_6^{Cpx} = Mg_3Al_2Si_3O_{12}^{Grt}$
12. $CaMgSi_2O_6^{Opx} = CaMgSi_2O_6^{Cpx}$
13. $Mg_2SiO_4^{Ol} + Mg_3Al_2Si_3O_{12}^{Grt} = Mg_2Si_2O_6^{Opx} + MgAl_2O_4^{Sp}$

The excess mixing functions of the olivine solid solution were approximated by the regular solution model. Garnet, spinel, and pyroxenes were considered as two-site solid solutions with independent mixing on two sites. Their excess mixing functions included same-site and cross-site terms (e.g., Powell and Holland, 1993). Asymmetrical (subregular) models were used for mixing on spinel and garnet sites, and quaternary symmetrical (i.e., second-degree) models were used for the M1 and M2 positions of ortho- and clinopyroxene. Ordering of Fe and Mg between M1 and M2 was ignored, i.e. it was assumed that $Mg/(Mg+Fe)^{M1} = Mg/(Mg+Fe)^{M2}$. All Margules parameters were taken to be pressure and temperature independent. Sodium admixture in orthopyroxene was ignored, thus, the only Na-bearing phase was clinopyroxene. Note that clinopyroxene from mantle xenoliths often contains more than 1 wt % of Na_2O, which cannot be ignored because of the possible effect on the solubility of Cr and Al (as jadeite and cosmochlore end-members).

INPUT DATA

The experimental database included the results for Fe-Mg exchange between silicates and spinel (von Seckendorff & O'Neill, 1993; Hackler & Wood, 1989; and others), Al solubility in orthopyroxene coexisting with garnet (Lee and Ganguly, 1988; Perkins et al., 1981; and others), Cr-Al distribution between garnet, spinel, and pyroxenes (Brey et al., 1999; Klemme & O'Neill, 2000a), two-pyroxene equilibrium in the CMAS system (Nickel et al., 1985; Perkins & Newton, 1980; Klemme & O'Neill, 2000b), and reaction (13) in the MAS system (Danckwerth & Newton, 1978; Perkins et al., 1981). The natural database comprised 162 spinel- and garnet-bearing lherzolite and websterite xenoliths, mainly from kimberlites of southern Africa, Yakutia, and North America and several xenoliths from alkali basalts from various localities. In all these samples, olivine, orthopyroxene, clinopyroxene, garnet and spinel were analyzed and mineral relationships suggested their equilibrium character. The compositions of phases used for model calibration vary within a wide range covering a substantial portion of the compositional field of natural peridotite minerals (Table 1).

Table 1: Summary of natural mineral compositions used in the model calibration

Parameter	Average	Min	Max
Mg/(Mg+Fe) Ol	0.913	0.84	0.936
Mg/(Mg+Fe) Sp	0.627	0.42	0.833
$Cr/(Cr+Al+Fe^{3+})$ Sp	0.553	0.018	0.811
$Mg/(Mg+Fe^{2+}+Ca)$Grt	0.69	0.537	0.763
$Ca/(Mg+Fe^{2+}+Ca)$Grt	0.139	0.089	0.212
Cr/(Cr+Al) Grt	0.098	0	0.267
X_{Ca}^{M2} Opx	0.013	0.005	0.082
X_{Al}^{M1} Opx	0.024	0.005	0.123
X_{Cr}^{M1} Opx	0.008	0.001	0.017
Mg/(Mg+Fe) Opx	0.924	0.833	0.944
X_{Ca}^{M2} Cpx	0.823	0.621	0.96
X_{Al}^{M1} Cpx	0.152	0.024	0.362
X_{Cr}^{M1} Cpx	0.040	0.001	0.111
Mg/(Mg+Fe) Cpx	0.933	0.832	0.964

RESULTS

The minimization procedure yielded a set of mutually consistent expressions for ΔG of 13 independent end-member reactions and excess mixing energies of solid solutions. The Margules parameters for the majority of phases were similar to values accepted in the recent literature (e.g., Berman & Aranovich, 1996). Olivine and orthopyroxene show slightly nonideal Fe-Mg mixing. The orthopyroxene Al-Cr, Mg(Fe)-Cr, and Mg(Fe)-Al mixing terms are large (20-80 kJ) and of different signs. These large values cancel each other and result in a small total nonideality within the compositional range of experimental and natural orthopyroxenes. The reason of such a behavior is that all orthopyroxene compositions lie close to the $Mg_2Si_2O_6$ end-member, while the model accounts for the complete range of solid solution. In addition, there are a number of oversimplifications including ignoring Mg-Fe site ordering, Cr incorporation in the tetrahedral positions (Klemme and O'Neill, 2000) and possible pressure and temperature effect on mixing parameters. The model parameters for clinopyroxene are much smaller because of the larger compositional range used in the model calibration. Garnet shows small Cr-Al nonideality ($W_{CrAl}^{Grt} \sim 4$ kJ) consistent with the thermochemical data of Wood & Kleppa (1984). The obtained parameters will be used for the derivation of practical thermobarometers for mantle peridotites.

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