# MINERAL CHEMISTRY OF SILICATE AND OXIDE PHASES FROM FERTILE PERIDOTITE EQUILIBRATED WITH A C-O-H FLUID PHASE – A LOW fO₂ DATA SET FOR THE EVALUATION OF MINERAL BAROMETERS, THERMOMETERS AND OXYGEN SENSORS.

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To determine which particular mineral thermometer and barometer formulations provide the most accurate calibrations for natural spinel or garnet peridotite assemblages, one method is to test them against independent experimental data from multicomponent (natural-system) compositions (e.g. Carswell and Gibb, 1987a). Oxygen sensor formulations, involving ilmenite- or spinel-olivine-orthopyroxene equilibria, may be tested in a similar fashion (e.g. Ballhaus et al., 1990). This approach, however, is limited by the quality of the experimental data. In some older experimental studies, mineral chemical data is of questionable quality because of problems with Fe-loss to noble metal capsules, and unknown or variable $Fe^{3+}$ contents of phases due to uncontrolled $fO_2$. Knowledge of $Fe^{3+}$ levels, in particular, is important in evaluating thermometers based on Mg-Fe exchange equilibria.

In this paper we present new mineral compositional data from thirty-five $fO_2$-controlled experiments on fertile peridotite (mg# 87, Hawaiian pyrolite composition) that can be used to evaluate geothermometers, geobarometers and oxygen sensors. [Original references for all of the thermometers and barometers quoted below can be found in either Carswell and Gibb (1987a) or Finnerty and Boyd (1987)]. All experiments were C-O-H fluid saturated and were run under conditions of P = 0.9 to 3.5 GPa, T = 1050 to 1260°C and $fO_2$ ~ IW+1 log units (see Taylor and Green, 1988). Improvements to experimental techniques, such as the use of graphite inner capsules, have eliminated Fe-loss problems allowing longer runs times (~50 hours at 1050°C to ~10 hours at 1200°C) and hence better approach to equilibrium. Microprobe analyses of mineral phases were carefully screened on compositional criteria to exclude overlapped and non-stoichiometric analyses. Subsolidus phase assemblages are $TiO_2$-saturated and consist of olivine, orthopyroxene, clinopyroxene, garnet or spinel, ilmenite, chromian rutile, amphibole and/or phlogopite. Amphibole and phlogopite persist to ~20°C above the solidus, but ilmenite and rutile are absent in above-solidus assemblages. Because $fO_2$s are controlled to very low levels, just above the IW buffer, silicate phases contain negligible $Fe^{3+}$ contents, and spinel and ilmenite have $Fe^{3+}/\Sigma Fe$ ratios that are similar to those of spinels and ilmenites associated with diamond. Pyroxenes have unusually high $TiO_2$ levels compared with those of mantle origin: an average of 0.5 wt% in orthopyroxenes (with positive temperature dependence in the subsolidus) and an average of 1.3 wt% in clinopyroxene.

For the pressure range investigated (i.e. to 3.5 GPa), we found that the Wells (1977) orthopyroxene-clinopyroxene solvus thermometer gives the most accurate (to within ±50°C) and precise (i.e. least scatter) temperature estimates as shown in the $T_{calc}$-$T_{expt}$ plot in Fig. 1. The absence of a pressure correction term, however, is believed to reduce the accuracy of the Wells thermometer at pressures greater than ~3.5 GPa (Carswell and Gibb, 1987a). The Harley (1984) garnet-orthopyroxene thermometer also yields satisfactory temperature estimates but slightly more scatter is evident in the $T_{calc}$-$T_{expt}$ plot compared with the Wells thermometer. Other orthopyroxene-clinopyroxene thermometers such as those

of Lindsley and Dixon (1974), Finnerty and Boyd (1987) or Bertrand and Mercier (1985) yield temperature underestimates for pyroxenes equilibrated at <2.0 GPa and overestimates for >2.0 GPa pyroxenes. The O'Neill and Wood (1979) garnet-olivine and Powell (1985) garnet-clinopyroxene thermometers yield consistent temperature overestimates of ~100°C and ~50°C, respectively. Although these two thermometers were recommended by Carswell and Gibb (1987b), it is also evident from their xenolith data that these thermometers have a tendency to overestimate temperatures by some 50-100°C relative to the Harley (1984) thermometer, particularly at T>1100°C. We therefore cannot recommend the O'Neill and Wood (1979) or Powell (1985) thermometers for garnet peridotites xenoliths equilibrated at T>1100°C.

Of the garnet-orthopyroxene geobarometers, we recommend a modified version of the Nickel and Green (1985) formulation. Because our orthopyroxene compositions are rich in $TiO_2$, with up to 0.2 Ti atoms per Al atom, large pressure overestimates result when the proportion of Al in the M1 site is calculated with the equation suggested by Nickel and Green (1985) i.e. $X_{Al}(M1) = (Al-Cr-2Ti+Na)/2$. This equation implies Ti substitution in orthopyroxene via $MgTiAl_2O_6$-type molecules. We instead recommend calculation of Al in M1 by the equation $X_{Al}(M1) = (Al-Cr+Ti+Na)/2$ which implies a different Ti substitution mechanism, possibly with Ti present in the tetrahedral site; there is no stoichiometric evidence for the presence of $Ti^{3+}$ in these pyroxenes as is a possibility at low experimental $fO_2$s, although existence of $Ti^{3+}$ cannot be ruled out. The modified Nickel and Green (1985) barometer yields P estimates all within ±0.5 GPa. The Perkins and Newton (1980) and Wood (1974) modification'C' barometers also yield satisfactory pressure estimates (within ±0.6 GPa). The Harley(1982) barometer tends to consistently underestimate pressure by 0.2-0.3 GPa while the MacGregor (1974) barometer consistently overestimates pressure by 0.5 GPa. The Bertrand (1986) barometer is more erratic but there is a tendency to underestimate pressure by ~0.4 GPa.

Because our experiments were controlled within the $fO_2$ range IW+0.5 to IW+1.5 log units by the WCWO buffer (Taylor and Foley, 1989), spinel and ilmenite compositions may be used to evaluate oxygen sensor formulations. Despite the low $Fe^{3+}$ contents in our experimental spinels (which must be calculated from stoichiometry and are therefore subject to relatively large errors), we find that both the O'Neill and Wall (1987) and the Ballhaus et al. (1990) formulations of the spinel oxygen sensor yield $fO_2$s within 1 log unit of the experimentally predicted values. At high spinel Cr/Cr+Al ratios (>0.6), however, there is a tendency for the Ballhaus et al. sensor to overestimate $fO_2$ by ~0.5-1.0 log units and for the O'Neill and Wall sensor to underestimate $fO_2$ by a similar amount. Since Cr-rich spinels are potentially important indicators of $fO_2$ in the diamond source region, recalibration of these sensor formulations for high Cr compositions may be necessary. The Ballhaus et al. (1990) spinel-olivine Mg-Fe thermometer yields very satisfactory temperature estimates except for very high Cr/Cr+Al spinels. The Mattioli and Wood (1988) oxygen sensor formulation yields erratic $fO_2$ over- and underestimates. The ilmenite oxygen sensor of Eggler(1983) overestimates experimental $fO_2$s by ~1.5 log units and is not recommended.

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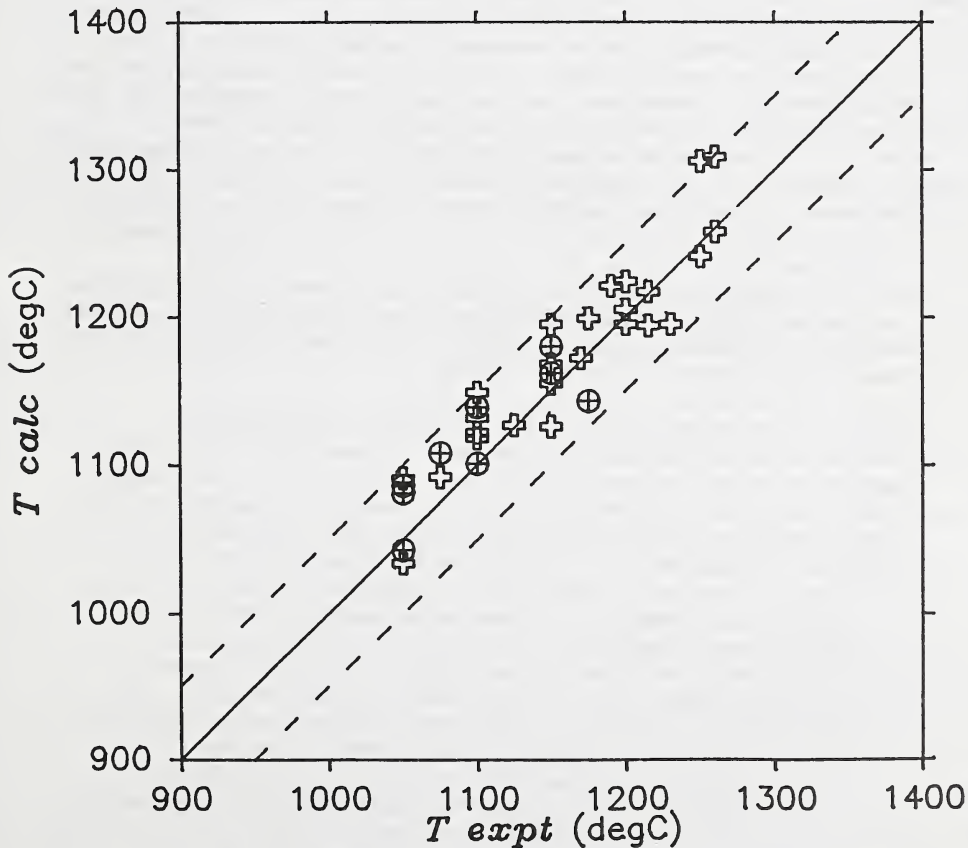
Figure 1. $T_{calc}$-$T_{expt}$ plot for the Wells (1977) thermometer. Cross symbols = P>2 GPa experiments; Circles with cross = P<2 GPa experiments.