Temperatures and pressures of mineral equilibration in peridotite xenoliths: Review, discussion, and implications

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Abstract—Pressures and temperatures have been calculated to compare thermobarometers for peridotite assemblages, as part of a review of methods, kinetic constraints, and applications. The comparisons use analyses of minerals in xenoliths, many selected to optimize the probability that they represent equilibrated assemblages. A combination of two-pyroxene thermometry plus orthopyroxene-based barometry is preferred for most garnet peridotites above about 900°C, and the accuracy of the combination is best established in the range 900–1100°C and 2–5 GPa. Above this range, it is difficult to confirm accuracy of temperatures and pressures for samples with mineral chemistries different from those in calibration experiments. Below 900°C, the thermometers potentially the most accurate are based on Ca and Al in orthopyroxene, but additional calibrations are needed. Experiments and characterizations of gradients establish that diffusion rates for relevant cations in peridotite minerals cover a range of at least 4 orders of magnitude at single temperatures, and so mineral rims are more likely to represent equilibrium assemblages than cores. The range in diffusion rates is an asset for interpretations of rock histories. Xenoliths that record temperatures above about 1200°C commonly sample mantle volumes affected by melt percolation and heat advection, and although geotherm inflections are not certainly defined, their presence is consistent with the dynamic processes recorded by compositional zonation of minerals. Samples that record temperatures in the range 900–1100°C typically appear to have equilibrated at ambient conditions just before eruption, and calculations for these rocks accurately constrain mantle geotherms. Xenoliths that record temperatures below 800°–900°C may not have equilibrated to ambient conditions except very near grain contacts, if equilibration depended upon diffusion. Comparisons of temperatures calculated by methods with different kinetic responses can be used to test if mineral assemblages in xenoliths represent equilibrium, although such comparisons may be inconclusive because of uncertainties in thermobarometer calibrations. The Al-Cr-in-orthopyroxene plus Ca-in-orthopyroxene pair of thermometers is a particularly promising pair to test for equilibrium in spinel peridotite, as documented by xenoliths from the Siberian craton. Further progress will depend both on additional calibrations and on more texturally-related analyses that characterize mineral homogeneity.

INTRODUCTION

CALCULATED PRESSURES and temperatures for peridotite xenoliths have been integral to studies of the upper mantle following the pioneering work of BOYD (1973). FINNERTY and BOYD (1984, 1987), CARSWELL and GIBB (1987a, b), FINNERTY (1989) and CARSWELL (1991) reviewed calculation methods prior to publication of important experiments on natural peridotite compositions by BREY *et al.* (1990). BREY and KOHLER (1990) and others have proposed new thermobarometers and assessed older ones. Contrasts between temperatures for single xenoliths calculated by different methods may document mantle histories (FRANZ *et al.*, 1996a, b), if the methods are mutually consistent. In this review, methods and kinetic constraints are discussed, and mutual consistencies of procedures are evaluated to investigate how accurately xenolith data constrain mantle conditions.

The best approaches to pressure-temperature calculations for mantle xenoliths may not be the same as for crustal rocks. The more complex mineral assemblages of crustal metamorphic rocks can be evaluated with respect to internally consistent thermodynamic databases to make average P-T assignments consis-

tent with multiple mineral reactions (POWELL and HOLLAND, 1994). Mantle peridotite has a limited assemblage of minerals, however, and so reactions involve only a few phases. Ranges of calculated temperature and pressure exceed 700°C to 1500°C and 1 to 7 GPa, much greater than those common for crustal metamorphism, and some methods are likely to be more accurate than others in parts of those ranges. Although CARSWELL and GIBB (1987a) have advocated use of average values of a few preferred methods, uncertainties are more clearly defined when single methods are used. In addition, comparisons between methods with contrasting kinetic responses can yield insights into mantle histories.

MINERAL CHEMISTRIES AND SITE ASSIGNMENTS

Five minerals are abundant in peridotite xenoliths – olivine, orthopyroxene, clinopyroxene, garnet, and spinel. Two types of uncertainties in compositions of these minerals are particularly troublesome in calculations of pressure and temperature. First, uncertainties in Fe^{3+}/Fe^{2+} in pyroxene, spinel, and garnet can cause large errors in temperatures calculated from

reactions dependent upon Fe-Mg partitioning and possibly significant errors in temperatures based on other methods. Second, ambiguities in site assignments of Al in pyroxenes lead to uncertainties in calculated pressures and temperatures.

Ferric/ferrous iron in the pyroxenes is particularly difficult to assess by electron probe analysis. Orthopyroxene and clinopyroxene mg values [100*Mg/(Mg + Fe)] lie mostly in the range 85 to 94. Relative abundances of ferric and ferrous Fe calculated from charge balance and stoichiometry are commonly so uncertain as to be almost meaningless for such Fe-poor pyroxenes, because of uncertainties of more abundant cations such as Si (GIARAMITA and DAY, 1990). Mössbauer analyses of pyroxene have found Fe^{3+}/Fe^{total} from 0.12 to 0.36 for clinopyroxene and 0.04 to 0.14 for orthopyroxene in spinel peridotite (DYAR et al., 1989; LUTH and CANIL, 1993; CANIL and O'NEILL, 1996). In garnet peridotite, CANIL and O'NEILL (1996) found Fe^{3+}/Fe^{total} from 0.07 to 0.41 for clinopyroxene and 0.06 to 0.10 for orthopyroxene.

Mössbauer analyses of peridotite garnets (LUTH et al. 1990; CANIL and O'NEILL, 1996) yield Fe^{3+}/Fe^{total} from 0.02 to 0.12. CANIL and O'NEILL (1996) found that garnet in high-temperature peridotites had Fe^{3+}/Fe^{total} from 0.07 to 0.12, whereas in low-temperature peridotites the range was 0.02 to 0.07. CANIL and O'NEILL (1996) found that formula calculation for garnets resulted in errors so large that the results were not useful for this compositional range, because of propagation of uncertainties from cations such as Si. Although Fe^{3+} could also be calculated by assuming complete tetrahedral occupancy by Si, implications of that assumption for thermometry have not been well explored.

Spinel is a more tractable phase for determination of ferric/ferrous ratios from electron probe analyses, although the necessary assumption of stoichiometry has been shown to be invalid for Cr-rich spinels by KAMPERMAN et al. (1996). BALLHAUS (1991a, 1993) considered electron probe analyses to be sufficient for meaningful calculations of temperatures and oxygen fugacities, although WOOD and VIRGO (1989) advocated calibration by analysis of Mössbauer-analyzed standards. CANIL and O'NEILL (1996) found ferric iron abundance in spinel calculated from electron probe analysis to have similar uncertainty to that measured by Mössbauer spectroscopy.

The most widely used methods to calculate pressures of garnet peridotite rely upon Al contents of orthopyroxene, and directly or indirectly upon the assignment of that Al to sites within the pyroxene structure, specifically to the $MgAl_2SiO_6$ component. Orthopyroxene in garnet peridotite xenoliths typi-cally has 0.7 to 2 wt% Al_2O_3, and orthopyroxene with as little as 0.36 wt% Al_2O_3 has been reported by BOYD et al. (1997). This lowest value corresponds to 0.014 cations Al for a 4-cation pyroxene formula. Allocation of Al to sites and to the $MgAl_2SiO_6$ component depends critically upon other minor constituents and upon some choices that now must be somewhat subjective, as noted by BOYD (1973), and as emphasized by CARSWELL (1991). Ferric iron is among the components that increase uncertainties in proper allocation of Al (CANIL and O'NEILL, 1996). TAYLOR (1998) has discussed the effect of Ti upon Al-based pressure calculations and has formulated an empirical correction for Ti. Accuracies of activity models for orthopyroxene are limited by these uncertainties.

MAJOR ELEMENT THERMOBAROMETERS

Compositions of minerals have been compiled to assess mutual consistency of some important thermobarometers. All Fe in olivine, garnet, and pyroxene was treated as ferrous in these calculations, but ferrous and ferric iron were calculated for spinel by assuming stoichiometry. One problem with any such compilation is that analyses may not represent equilibrium assemblages, and so many of the data were selected to minimize that problem. Garnet peridotite xenoliths are represented by two sets of analyses that were acquired with close attention to possible compositional heterogeneity. These two sets are the rim analyses of minerals in kimberlite-hosted samples from Siberia (BOYD et al., 1997; available at http://probe.ciw.edu/) and from southern Africa (SMITH and BOYD, 1992; available at http://www.geo.utexas.edu/DougSmith/). The Siberian samples come from a single intrusion, the Udachnaya kimberlite (BOYD et al., 1997). In contrast, the garnet peridotite xenoliths from southern Africa are from many different kimberlites, as described in notes accompanying the analyses. For spinel peridotites, the data include those for Siberian samples of BOYD et al. (1997) and for about 120 Cr-diopside xenoliths from a variety of locations in southwestern North America. Most of the analyses for lower-temperature spinel peridotites represent Grand Canyon xenoliths and were selected by RITER and SMITH (1996) as probable equilibrated compositions. Pressures and temperatures have been calculated with the FORTRAN program TP98. The compilations of analyses, the notes, and a text file of a version of the program are available from a web address (http://www.geo.utexas.edu/DougSmith/).

Combined clinopyroxene-based two-pyroxene thermometry and orthopyroxene barometry for garnet lherzolites

Calibrations of clinopyroxene-based two-pyroxene thermometry are based on many experimental studies, including the important early contribution of BOYD and SCHAIRER (1964) for the system CaO-MgO-SiO$_2$. Within that system, changes in pyroxene composition with temperature at 2 GPa are guides to the sensitivity of the thermometer; CARLSON and LINDSLEY (1988) calculated that Ca/(Ca + Mg) in diopside changes from 0.462 to 0.446 from 900°C to 1000°C, but from 0.372 to 0.324 from 1300° to 1400°C. The ratio Ca/(Ca + Mg) in clinopyroxene, the basis of the thermometer, thus is three times more sensitive to temperature from 1300°C to 1400°C than from 900°C to 1000°C. Effects of one additional component, ferrous iron, are well-studied, and phase relationships for compositions in the system CaO-MgO -FeO-SiO$_2$ can be reproduced accurately by models such as that of SACK and GHIORSO (1994). The influence of Al, Cr, Ti, and other minor constituents are less well-known. Concentrations of Al and Cr in clinopyroxene are lower in garnet peridotite than in spinel peridotite, and so clinopyroxene-based thermometry is particularly suitable for high-temperature garnet peridotites.

The most recently formulated, widely used clinopyroxene-based thermometer for peridotites is that of BREY and KOHLER (1990) (TBKN). The TBKN formulation is based on experimental data in the simpler systems and the experiments of BREY *et al.* (1990) on natural peridotite compositions at 1 to 6 GPa and 900 to 1400°C. Differences between two-pyroxene thermometers were discussed by BREY and KOHLER (1990), and they showed that TBKN best reproduced the experimental results. Accuracies for xenoliths are still in dispute, however, and use of techniques of FINNERTY and BOYD (1987), BERTRAND and MERCIER (1985), and WELLS (1977) is also common in recent literature. The thermometer of WELLS (1977) does not consider pressure effects, although diopside-enstatite equilibria have a slight pressure dependence, and so other formulations should be considered for the extended pressure range recorded by garnet peridotite xenoliths. The new two-pyroxene thermometer proposed by TAYLOR (1998) specifically for fertile lherzolite and websterites has not been tested for the garnet peridotite database in this review.

The potential of using the pressure-sensitive solubility of Al in orthopyroxene as a barometer was shown by the experiments of MACGREGOR (1974) and by many subsequent investigations. The most commonly applied formulations of the barometer to mantle rocks are by BREY and KOHLER (1990) (PBKN) and by FINNERTY and BOYD (1984) (PMC74). More recent experiments include those of ARANOVICH and BERMAN (1997), who recommend their calibration for 0.2–2 GPa and 600–1000°C, and hence it is not designed for application to garnet lherzolites. TAYLOR (1998) has presented new experimental results for fertile, Ti-rich mantle compositions and proposed a correction scheme to account for effects of Ti upon orthopyroxene barometry. It is also possible to determine pressure by comparison to thermodynamic calculations for the phases involved and appropriate bulk compositions, as discussed by SCHMADICKE and EVANS (1997).

P-T values calculated using the PMC74-TFB86 combination of FINNERTY and BOYD (1984, 1987) are inconsistent in detail with those based on the PBKN-TBKN combination of BREY and KOHLER (1990) (Fig. 1), although the pressure-temperature arrays span similar ranges. Differences are accentuated near the extremes of those ranges. At high pressures and temperatures (Fig. 1C, D), TBKN values for Siberian xenoliths scatter near 1300°C, but TFB86 temperatures plot in a more linear array, as pointed out by BOYD *et al.* (1997). In contrast, calculations for most African samples in this database yield in relatively coherent arrays with both thermobarometers. Even though the African samples are from many different kimberlites, the PMC74-TFB86 array for these rocks appears to be fit by two line segments intersecting at a "kink" (Fig. 1A), whereas no "kink" is obvious in the PBKN-TBKN array for the same data (Fig. 1B). Differences between TBKN and TFB86 vary systematically with temperature (Fig. 1E). Most TFB86 temperatures are about 50° to 100°C cooler than TBKN in the range 900 to 1200°C. From 1200° to 1400°C, TFB86 values approach TBKN with increasing temperature, and they are hotter above 1400°C.

Garnet-olivine thermometry

The Fe-Mg exchange thermometer between garnet and olivine formulated by O'NEILL and WOOD (1979) and O'NEILL (1980) (TOW) has received wide use. The simplicity of the olivine solid solution contributes to the success of the formulation. CANIL and O'NEILL (1996) found that differences between TOW values can exceed 200°C for comparisons in which either all Fe in garnet is treated as ferrous, or ferrous iron is determined by Mössbauer spectroscopy. The comparison in Fig. 2B confirms the general concordance of this olivine-garnet thermometer with the TBKN temperatures for the African xenoliths with all
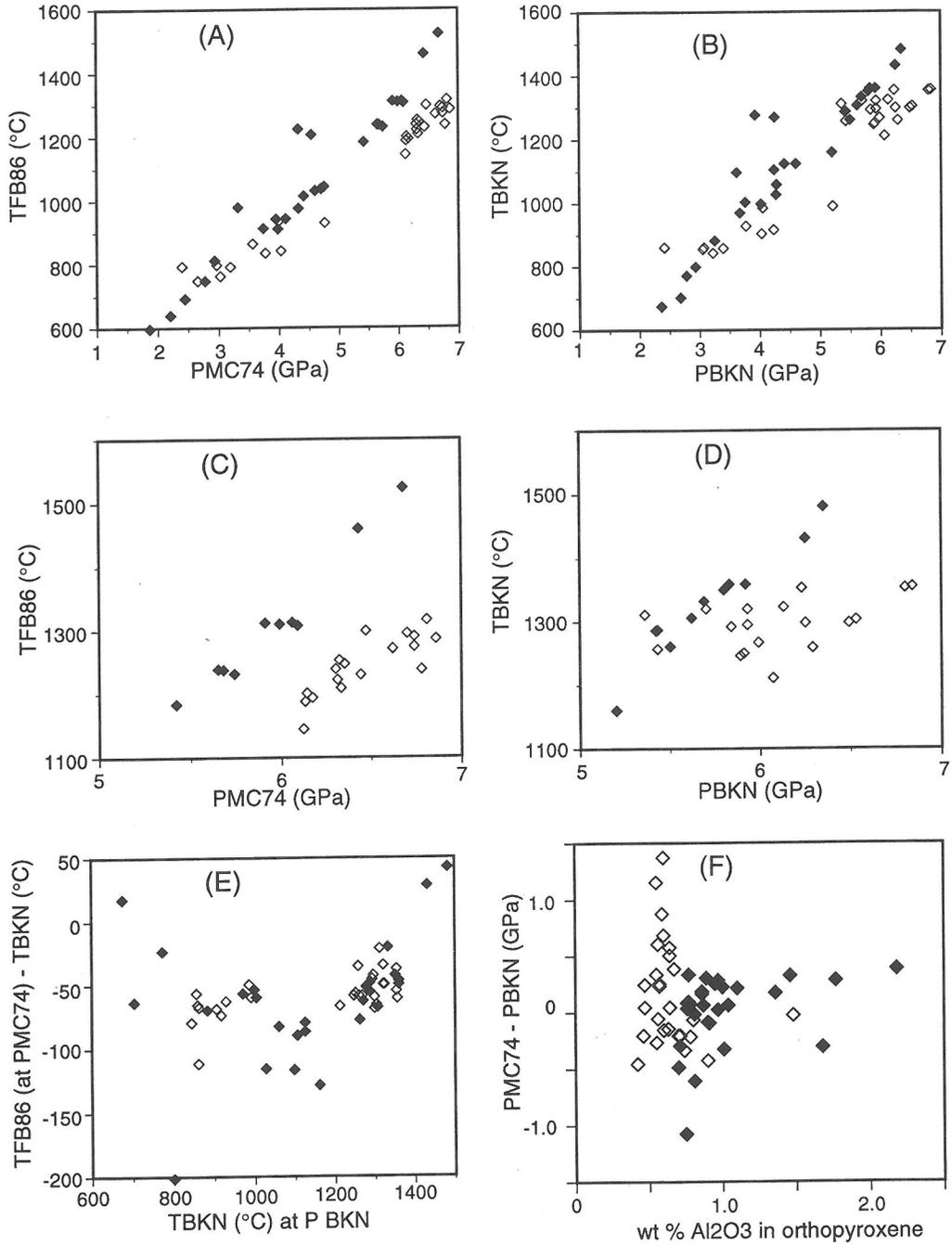
FIG. 1. Temperatures and pressures calculated for garnet peridotite xenoliths with the TFB86-PMC74 pair of FINNERTY and BOYD (1987) and the TBKN-PBKN pair of BREY and KOHLER (1990). Each pair includes clinopyroxene-based two-pyroxene and Al-in-orthopyroxene equilibria. Filled symbols are for xenoliths from a number of kimberlites in southern Africa (SMITH and BOYD, 1992). Open symbols are for xenoliths from the Udachnaya kimberlite in Siberia (BOYD et al., 1997). Analyses of rim compositions are used for zoned minerals.

Fe ferrous, as noted by BREY and KOHLER (1990). Agreement is less satisfactory for the Siberian suite. Possible contributing factors include disequilibrium, wider ranges of and more abundant ferric iron in the Siberian garnets (BREY, 1989), and possible inaccuracies in pressures calculated for the Siberian rocks with consequent effects on the combined P-T solutions.

Garnet-clinopyroxene thermometry

Fe-Mg exchange thermometry between garnet and clinopyroxene is applicable to a wide range of bulk compositions and temperatures. Application to eclogites and some crustal rocks is complicated by uncertainties in thermodynamic mixing models for garnets and pyroxenes (ALAOUI et al., 1997; GUIRAUD and POWELL, 1996). Some of these uncertainties are minimized in lherzolites, because these mantle rocks have a restricted range of mg values, and Ca/(Ca + Fe + Mg) in Cr-free garnet is restricted to values near 0.12 by equilibration with orthopyroxene plus clinopyroxene (BOYD, 1970). The presence of Cr complicates applications based on Cr-free systems, however, as Cr is significant in many lherzolite garnets and is correlated with Ca (SOBOLEV, 1977). Moreover, the uncertainties in calculated ferrous/ferric ratios of clinopyroxene and garnet are substantial in magnesian rocks. CANIL and O'NEILL (1996) found that differences between garnet-clinopyroxene temperatures calculated with either Mössbauer-determined ferrous iron or total iron can exceed 300°C in peridotite xenoliths.

The formulation of KROGH (1988) (TKr) is widely used, and BREY and KOHLER (1990) found that temperatures calculated with that formulation reproduced their experimental conditions within ± 62°C. Likewise, for the African samples in the database, differences between TKr and TBKN temperatures are within about 80°C for most samples with no apparent systematic difference, but for the Siberian samples with TBKN temperatures below 1000°C, all TKr temperatures are systematically lower by 50 to 150°C (Fig. 2A). Additional calibrations have been proposed by AI (1994), BERMAN et al. (1995), and GANGULY et al. (1996). That of AI (1994) is more sensitive to pressure than that of KROGH (1988), and combined solution with the PBKN barometer yields unreasonably high temperatures for the highest-pressure xenoliths. The formulation of BERMAN et al. (1995) (TBer) in conjunction with the PBKN barometer yields plausible results for both garnet peridotite data sets, with temperatures systematically lower than TBKN above 1100°C (Fig. 2C). GANGULY et al. (1996) noted their algorithms are valid only if cli-

nopyroxene has X_{Ca} = 0.40 to 0.45 and should be used for eclogites only if equilibration temperatures exceed 1000°C; their cautionary note indicates the hazards in using any one thermobarometer over the range of conditions sampled by mantle xenoliths.

Orthopyroxene-garnet thermometry

The Fe-Mg exchange thermometer commonly applied to garnet-orthopyroxene pairs in peridotites is that of HARLEY (1984a) (THar), and it can be applied with the independent orthopyroxene barometer of HARLEY (1984b) (PHar) as corrected by FITZSIMMONS and HARLEY (1994). BREY and KOHLER (1990) concluded that THar yielded slight overestimates at low temperature and underestimates at high. As expected from their analysis, comparison to TBKN for the two garnet peridotite suites demonstrates near concordance at 800°–900°C, with higher THar below 800°C and markedly lower THar above 1000°C (Figs. 2E, F). Comparisons with TBKN are similar, whether THar values are calculated at PHar (Fig. 2E) or at PBKN (Fig. 2F). FRANZ et al. (1996 a, b) reported similar relative results for other African xenoliths. At high temperatures THar and TBKN typically are more disparate for Siberian samples than for African ones, just as the case for TOW (olivine-garnet) and TBKN. TAYLOR (1998) compared conditions of experiments at 1050° to 1260°C with THar temperatures and reported agreement within 70°C for most instances. The garnet-orthopyroxene thermometer of GANGULY et al. (1996) (TGang96) yields temperatures within about 100°C of TBKN above 1000°C for most of the xenoliths considered here, but it yields markedly hotter values below 1000°C (Fig. 2D).

Orthopyroxene-based two-pyroxene thermometry

The Ca content of orthopyroxene equilibrated with clinopyroxene provides an alternative pyroxene thermometer. The diopside content in clinopyroxene decreases by only 3 relative percent from 900 to 1000°C, whereas the diopside content in orthopyroxene increases by 67 relative percent, according to the enstatite-diopside equilibrium values at 2 GPa calculated by CARLSON and LINDSLEY (1988). Hence, if Ca contents are measured adequately, an orthopyroxene-based thermometer is potentially more precise and accurate for temperatures below ~1000°C than the more widely used formulations based on Ca in clinopyroxene. In addition, orthopyroxene contains less Al, Cr, Na, and Ti than coexisting clinopyroxene, and so orthopyroxene-based thermometry may be less affected by bulk compositional variations, as empha-
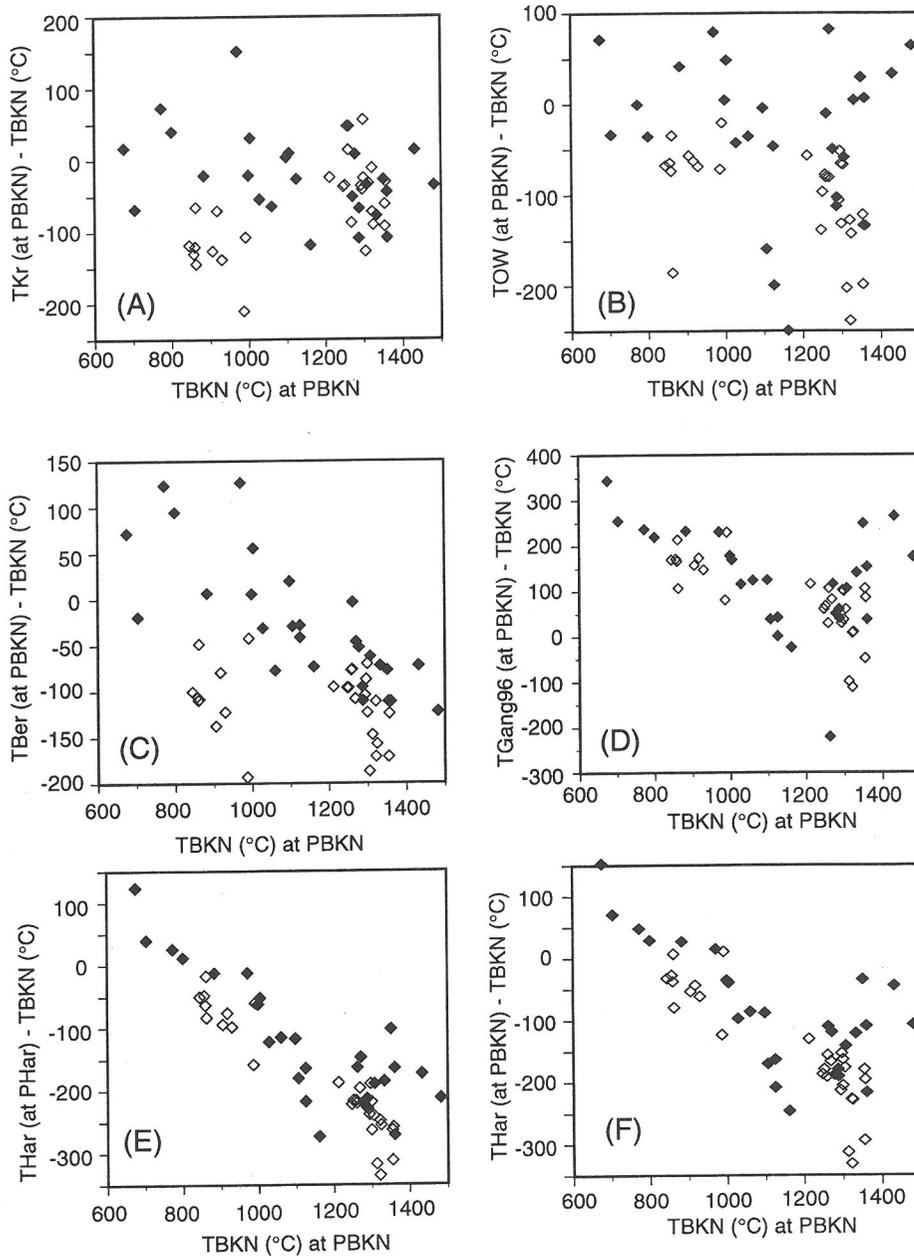
FIG. 2. Temperatures for garnet peridotite xenoliths calculated from Fe-Mg exchange equilibria compared to those calculated with the two-pyroxene TBKN thermobarometer of BREY and KOHLER (1990). Filled symbols are for xenoliths from a number of kimberlites in southern Africa (SMITH and BOYD, 1992). Open symbols are for xenoliths from the Udachnaya kimberlite in Siberia (BOYD et al., 1997). Pressures for each temperature calculation utilize the PBKN Al-in-orthopyroxene barometer of BREY and KOHLER (1990), except for the comparison in (E). (A) TKr temperatures from garnet-clinopyroxene equilibria (KROGH, 1988) at PBKN. (B) TOW temperatures from garnet-olivine equilibria (O'NEILL and WOOD, 1979) at PBKN. (C) TBer temperatures from garnet-clinopyroxene equilibria (BERMAN et al., 1995) at PBKN. (D) TGang96 temperatures from garnet-orthopyroxene equilibria (GANGULY et al., 1996) at PBKN. (E) THar temperatures from garnet-orthopyroxene equilibria (HARLEY, 1984A) at pressures based on HARLEY (1984B). (F) THar temperatures from garnet-orthopyroxene equilibria (HARLEY, 1984A) at PBKN.

sized by SACHTLEBEN and SECK (1981) and WITT-EICKSCHEN and SECK (1991).

BREY and KOHLER (1990) calibrated a Ca-in-orthopyroxene thermometer from the experiments of NICKEL and BREY (1984) and found that it satisfactorily reproduced temperatures in the experiments of BREY et al. (1990). They recommended caution in application to peridotites, however, because of uncertainties in the effects of Na, Al, and other minor components. The BREY and KOHLER (1990) formulation (TBKopx) is compared to TBKN for garnet peridotite in Fig. 3A and for spinel peridotite in Fig. 3B. The comparisons for spinel and garnet peridotites are similar. TBKopx exceeds TBKN below about 900°C, but systematic differences are negligible at about 900°–1000°C. With increasing temperature TBKopx becomes progressively less than TBKN, and differences typically are 100 to 150°C at TBKN of 1150°C; above about 1200°C, no systematic differences were observed. BREY and KOHLER (1990) and FRANZ et al. (1996a, b) show differences for other African garnet peridotites similar to those in Figs. 3A, B.

Al-in-opx thermometry for spinel peridotite

WITT-EICKSCHEN and SECK (1991) used the TBKopx thermometer to calibrate a thermometer (TWES) based on the Al and Cr contents of orthopyroxene equilibrated with olivine and spinel. Al-in-orthopyroxene in spinel peridotite is insensitive to pressure, unlike the case in garnet peridotite. Typical ranges for Al_2O_3 and Cr_2O_3 in orthopyroxene of spinel peridotite xenoliths are 2–5 wt% and 0.2–0.7 wt%, respectively (SMITH and RITER, 1997). These concentration ranges are sufficient for precise and accurate temperature assignments. The TWES calibration was recommended by WITT-EICKSCHEN and SECK (1991) only for a restricted range of Al and Cr.

TWES temperatures (Fig. 3C) are related to TBKN in the same fashion as TBKopx. Although TWES was calibrated from TBKopx by WITT-EICKSCHEN and SECK (1991), TBKopx temperatures are systematically slightly higher for the data used here (Fig. 3D), so the relative calibration might be improved. TWES-TBKN agreement is good at 900–1000°C, but TWES is relatively higher at cooler temperatures and relatively lower at hotter temperatures. The scatter of TWES values in the comparison (Fig. 3C) is significantly less than that of TBKopx (Fig. 3B), perhaps for kinetic reasons discussed below, and perhaps because analyses for Al in orthopyroxene are more precise than for Ca.

Olivine-spinel thermometry

The Fe-Mg exchange olivine-spinel thermometer has been the subject of repeated calibrations. BALLHAUS et al. (1991a, b) have discussed earlier work, reported experimental results, and provided the formulation (TBallhaus) that is compared to TBKN in Fig. 3E. Differences between TBallhaus and TBKN form a trend similar to those defined by the thermometers compared in Figs. 3B and C, but with more scatter. That scatter in part may be caused by the late-stage alteration to which spinel is prone (WITT-EICKSCHEN and SECK, 1991) and by errors associated with calculated apportionments of ferric and ferrous iron in electron probe analyses of spinel.

Clinopyroxene-based two-pyroxene thermometry without P correction for spinel peridotite

The clinopyroxene-based two-pyroxene thermometer of WELLS (1977) (TWells) can be applied to spinel peridotites with more confidence than to garnet peridotites, because most spinel peridotites have equilibrated at pressures between 1 and 2 GPa. TWells is compared to TBKN calculated at a fixed pressure of 1.5 GPa in Fig. 4A. Differences between the two formulations mimic but are less extreme than those between TBKopx and TBKN (Fig. 3B). For relatively Ti-rich compositions in the P-T range 1.0 – 3.5 GPa and 1050°–1260°C, TAYLOR (1998) found that TWells reproduced temperatures in experiments better than the other methods discussed above. The new two-pyroxene thermometer of TAYLOR (1998) (TA97) is compared to TBKN in Fig. 4B. Though TWells and TA97 results are broadly similar, TA97 points are somewhat more scattered relative to TBKN. TWells and TA97 also produce different relative results for the Colorado Plateau and Siberian populations, perhaps because of effects of minor elements.

Methods based on Cr in orthopyroxene, garnet, and spinel

The transition between aluminous spinel and garnet in peridotite is sensitive to pressure, temperature, and bulk composition, as documented in the experiments of O'NEILL (1981), NICKEL (1986), and WEBB and WOOD (1986). These experiments are consistent with thermobarometry of peridotites sampled from near the transition to garnet peridotite, as discussed by IONOV et al. (1993) and SUTHERLAND et al. (1994). Cr-rich spinel coexists with garnet at pressures well above those necessary to stabilize garnet peridotite, and the partitioning of Cr between garnet and spinel in the lherzolite assemblage can be used for P-T
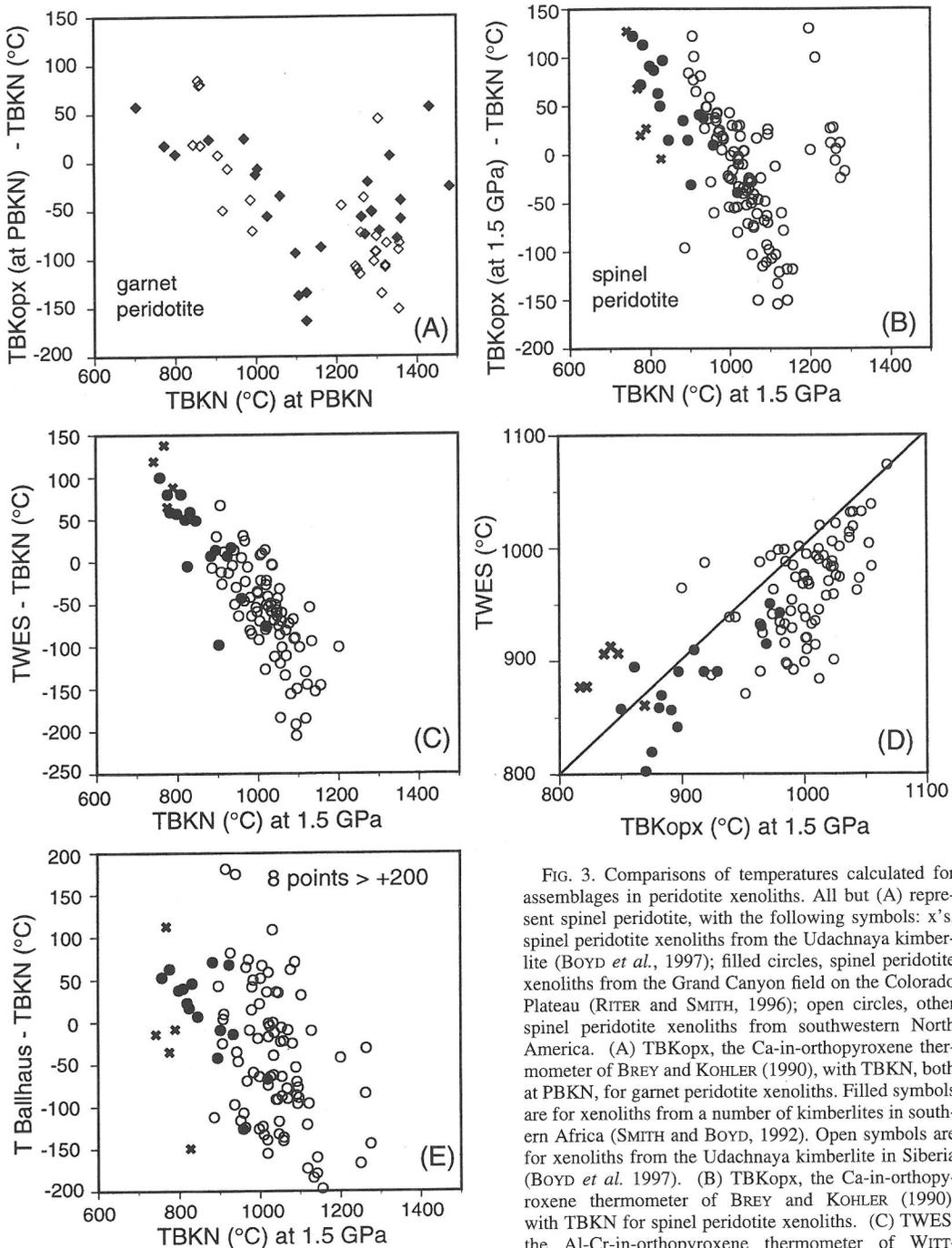
Fig. 3. Comparisons of temperatures calculated for assemblages in peridotite xenoliths. All but (A) represent spinel peridotite, with the following symbols: x's, spinel peridotite xenoliths from the Udachnaya kimberlite (BOYD et al., 1997); filled circles, spinel peridotite xenoliths from the Grand Canyon field on the Colorado Plateau (RITER and SMITH, 1996); open circles, other spinel peridotite xenoliths from southwestern North America. (A) TBKopx, the Ca-in-orthopyroxene thermometer of BREY and KOHLER (1990), with TBKN, both at PBKN, for garnet peridotite xenoliths. Filled symbols are for xenoliths from a number of kimberlites in southern Africa (SMITH and BOYD, 1992). Open symbols are for xenoliths from the Udachnaya kimberlite in Siberia (BOYD et al. 1997). (B) TBKopx, the Ca-in-orthopyroxene thermometer of BREY and KOHLER (1990), with TBKN for spinel peridotite xenoliths. (C) TWES, the Al-Cr-in-orthopyroxene thermometer of WITT-EICKSCHEN and SECK (1991), with TBKN. The points at temperatures above 1200°C present in Fig. 2B but absent here represent compositions outside the recommended range for TWES. (D) TWES (WITT-EICKSCHEN and SECK, 1991) and TBKopx (BREY and KOHLER, 1990). (E) TBallhaus, the olivine-spinel thermometer of BALLHAUS (1991), with TBKN.
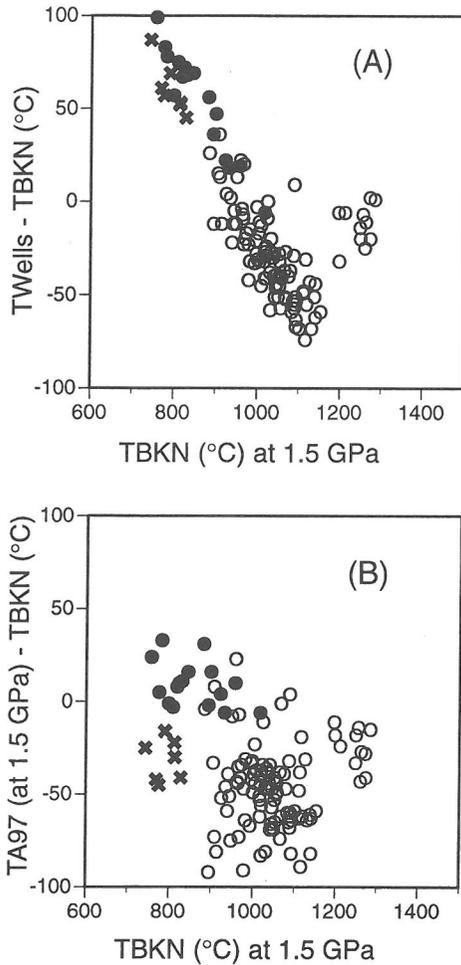
FIG. 4. Comparisons of temperatures for spinel peridotite xenoliths. Symbols are as in Fig. 3. (A) TWells, the Ca-in-clinopyroxene thermometer of WELLS (1977), with TBKN. (B) TA97, the two-pyroxene thermometer of TAYLOR (1998), with TBKN, both at 1.5 GPa.

roxenes is common (BODINIER et al., 1987; SMITH and BOYD, 1992), and because garnet rims are altered in many xenoliths, analyses may not represent equilibrated assemblages. Tests of the Cr-barometer of NICKEL (1989) by SMITH and BOYD (1992) and by FRANZ et al. (1996a, b) nonetheless indicate good correspondence with the PBKN Al-barometer of BREY and KOHLER (1990). RYAN et al. (1996) proposed a recalibration of the expression of NICKEL (1989) to provide a better fit to pressures calculated using the PMC74 Al-barometer of MACGREGOR (1974) and FINNERTY and BOYD (1984).

The ratio Ca/Cr of lherzolite garnet provides an additional tool to determine pressures. Based upon the experiments of BREY (1989), BRENKER and BREY (1997) formulated an expression relating Ca and Cr in garnet to P and T. They applied the expression to investigate metamorphism of an alpine peridotite and found confirmation of Al-in-orthopyroxene barometry.

TRACE-ELEMENT THERMOBAROMETERS

KOHLER and BREY (1990) calibrated a thermobarometer based on concentrations of Ca in olivine in lherzolite and discussed earlier work on the method. They noted that the equilibrium provides a barometer applicable to spinel peridotite and that, due to the rapid diffusion of Ca in olivine, the calibration could provide information on thermal histories. Applications have been limited by analytical problems at the low Ca concentrations of olivine, by the rapid diffusion of Ca, and by the sensitivity of Ca-in-olivine to both T and P. O'REILLY et al. (1997) used a proton probe to analyze olivine in suites of spinel peridotite xenoliths and thus avoided the limitations of electron probe analysis at low concentrations, but they found poor correlation between pressures calculated from Ca-in-olivine and empirical geotherms. O'REILLY et al. (1997) concluded that analytical problems and uncertainties in P propagated from those in T severely limit the usefulness of the technique as a barometer for spinel peridotites. FRANZ et al. (1996a, b) demonstrated the zonation of Ca in olivine provided information on late-stage thermal events that affected garnet peridotite.

The empirical Ni-in-garnet thermometer of GRIFFIN et al. (1989A) has been applied to determine temperatures of equilibration of garnet and olivine. Ni levels in peridotite garnets are too low for sufficiently accurate electron probe analysis with normal procedures, but proton probe analysis works well, and laser ablation ICP-MS has great promise (NORMAN et al., 1996). CANIL (1994) determined Ni contents of olivine-garnet pairs experimentally and presented a

calculation. DOROSHEV et al. (1997) have determined compositions of coexisting spinel and garnet in the system $MgO-Al_2O_3-SiO_2-Cr_2O_3$ at pressures to 6 GPa, and they have made P-T estimates for entrapment of inclusions in diamonds from these results.

The P-T dependence of the Cr content of orthopyroxene in equilibrium with garnet is directly analogous to the dependence of Al. NICKEL (1989) formulated a Cr-geobarometer to fit experimental data in a model system, and he suggested that the barometer is effective for garnet peridotites equilibrated at 850°–1400°C and 2 to 5 GPa. Applications to peridotite xenoliths have been limited, partly because the better known Al-barometer can be applied to the same rocks. Also, Cr zonation of mantle garnets and py-

calibration that has been discussed by CANIL (1996) and GRIFFIN and RYAN (1996). RYAN et al. (1996) proposed a revised formulation calibrated from the olivine-garnet thermometer of O'NEILL and WOOD (1979). The thermometer is sufficiently sensitive to temperature to be of great value, particularly for garnets included in diamonds, and for garnet xenocrysts (GRIFFIN and RYAN, 1995; GRIFFIN et al., 1996b; SOBOLEV et al., 1997). Zonation of Ni in garnets has been used to infer temperature histories for peridotites (SMITH et al., 1991; GRIFFIN et al., 1996a). Other trace elements distributions, such as that of Zn between chromite and olivine (RYAN et al., 1996), also have great promise for thermobarometry.

TEXTURES, MINERAL HETEROGENEITIES, AND KINETIC CONSTRAINTS

The probability that assemblages in mantle xenoliths represent equilibrium is higher than in exhumed rocks, because eruption is fast, and because many xenoliths were erupted from regions hot enough to equilibrate intergrown minerals on short geologic time scales. Nonetheless, departures from equilibrium have been recognized in many xenoliths. These departures complicate comparisons of thermobarometers, but they also provide insights into mantle histories. Departures from equilibrium are discussed below with contexts provided by rates of diffusion and observations of recrystallization.

Mineralogic changes that may be related to transport and interactions with the erupting medium are typically expressed by sharp rims and bimodal compositions and by gradients adjacent to altered margins. Decompression melts may form within xenoliths, particularly in those that contained hydrous minerals, and these melts may react with the xenoliths and crystallize compositionally distinct pyroxene, olivine, and spinel, as discussed by YAXLEY et al. (1997). Spinel grains have reacted with such late-stage melts in many xenoliths (WITT-EICKSCHEN and SECK, 1991; SMITH and RITER, 1997). Overgrowths of olivine and diopside have been identified in Siberian garnet peridotites by BOYD et al. (1997). Clinopyroxene grains in some xenoliths have marginal zones formed by late-stage alteration (CARSWELL, 1975). Garnet rims commonly are destroyed by kelyphitic reactions, prohibiting analysis of rim compositions. Some orthopyroxene grains have gradients at garnet contacts, and the nature of these gradients depends upon the presence or absence of kelyphitic rims (CARVALHO and LEONARDOS, 1997). IONOV et al. (1993) reported orthopyroxene rims up to about 200 μm thick and enriched in Ca and Al. Judicious selection of textural context of analyses

minimizes problems of interpretation associated with such changes that appear associated with the eruption event.

Mantle-melt interactions not directly associated with the eruptive process but related to precursory magmatic events may make it difficult to determine if calculated P and T represent ambient conditions in large mantle volumes. Xenoliths in many cases may be samples of mantle perturbed by such precursory processes (IRVING, 1976; GURNEY and HARTE, 1980). Effects of these interactions have been recognized clearly in high-T xenoliths. Garnets in many such xenoliths have rims enriched in incompatible elements such as Ti and Zr, and the preservation of gradients of such elements indicates that the inferred melt-mineral interactions took place not long before eruption (SMITH, 1988; SMITH and BOYD, 1989; GRIFFIN et al., 1989b; GRIFFIN et al. 1996a; SHIMIZU et al., 1997). The compositional changes recorded by zoning of incompatible elements likely were accompanied by temperature changes, although such temperature changes are less well-documented. Application of the Ni-in-garnet thermometer of GRIFFIN et al. (1989A) to Ni-zoned garnets indicates that xenoliths recorded temperature increases of up to 260°C within geologically short intervals before eruption (SMITH et al., 1991). Pyroxene in the high-T peridotites typically is more homogeneous than garnets (SMITH and EHRENBERG, 1984), but examples of heterogeneities are not uncommon. For instance, BOYD et al. (1997) described orthopyroxene zoned to rims enriched in Ca, Al, Cr, Na, and Ti. BODINIER et al. (1987) described Cr-zoned pyroxenes. HOPS et al. (1989) described chemically distinct orthopyroxene neoblast populations in single xenoliths.

Although diffusion rates for many cations in peridotite minerals are poorly defined, enough is known to provide a context for interpretation of P-T calculations and rock histories. GRIFFIN et al. (1996a) and BRENKER and BREY (1997) reviewed cation diffusion rates in olivine, garnet, and pyroxene. Rates may depend upon oxygen fugacity, composition, crystallographic direction, pressure, and perhaps on water fugacity, as well as on temperature (e.g., Ganguly et al., 1998). Hence the values of diffusion coefficients at ~1200°C cited below provide only qualitative guides to relative rates in mantle minerals. The self diffusion coefficient for Fe in Fe-Mg garnet is near 10^{-18} m^2/s at 1 GPa and 1200°C (GANGULY et al., 1998). Diffusion of divalent cations in olivine has been considered relatively well-known, but CHAKRABORTY (1997) found Fe-Mg interdiffusion in olivine to be about two orders of magnitude slower than reported in several previous studies, with a coefficient near $5*10^{-17}$ m^2/s in magnesian olivine at

1200°C, still faster than in garnet. JUREWICZ and WATSON (1988) reported a diffusion coefficient near 10^{-16} m²/s for Ca in olivine at 1 atmosphere and 1220°C, much greater than the self diffusion coefficient near 10^{-20} m²/s for Ca in diopside at 1200°C reported by DIMANOV et al. (1996). Relatively little is known about diffusion of other cations in pyroxene, particularly for trivalent cations; limited data for diffusion of Al in clinopyroxene suggest a coefficient as low as about 10^{-21} m²/s at 1180°C (JAOUL et al., 1990), but faster diffusion was reported by GROVE and WAGNER (1993). Relative diffusion coefficients of cations in pyroxenes may be better defined by relative lengths of diffusion gradients in xenolith minerals than by experiments now available. Comparisons of diffusion gradients in zoned mantle pyroxenes by WITT-EICKSCHEN et al. (1993), SMITH and BARRON (1991), OZAWA and TAKAHASHI (1995), and SMITH and RITER (1997) indicate substantially slower diffusion for Al and Cr than for Fe, Mg, and Ca, with differences increasing at lower temperatures. Because diffusion rates of important cations appear to differ by at least four orders of magnitude at a single temperature, core compositions can be changed by diffusion for some cations but not others, and such changed core compositions do not record equilibrium at any time. Cores of some mineral grains may equilibrate completely during changing conditions while cores of other minerals may not equilibrate at all. Examples have been discussed by BRENKER and BREY (1997) and SMITH and RITER (1997). Mineral rims are more likely than cores to represent equilibrium assemblages, and hence where appropriate rim compositions are available, they have been used in the comparisons of thermobarometers.

Possible effects of recrystallization complicate interpretations based on observations of zonation and knowledge of diffusion rates. Recrystallization, not diffusion, may be the dominant process for reequilibration of pyroxenes in cool spinel peridotite (SMITH and RITER, 1997). In hot garnet peridotite affected by melt percolation, recrystallization also may produce nearly equilibrated pyroxenes, although diffusion gradients have been preserved in garnets (SMITH et al., 1991; SHIMIZU et al., 1997). In rocks with some minerals zoned by diffusion, and others homogenized by recrystallization, rim compositions also are most appropriate for thermobarometry.

ACCURACIES OF CALCULATED PRESSURES AND TEMPERATURES

Accuracies of calculated pressures and temperatures have been difficult to determine because of the paucity of calibrations with natural compositions and the uncertainties of extrapolations to different compositions. BREY et al. (1990) and BREY and KOHLER (1990) made important contributions to solving both these problems, and their TBKN clinopyroxene-based thermometer and PBKN Al-in-orthopyroxene barometer now are the best-established for application to typical garnet lherzolite. PEARSON et al. (1994) have shown that the TBKN-PBKN combination approximately satisfies the constraint imposed by the occurrence of either graphite or diamond in xenoliths; this necessary constraint is of most value at 900°–1100°C and 4–5 GPa, near the intersection of typical cratonic geotherms and the graphite-diamond curve. IONOV et al. (1993) found that the TBKN-PBKN combination also approximately satisfies the constraint imposed by the garnet-spinel peridotite transition, at about 2 GPa and 1000°C. Accuracy of PBKN pressures is also supported by the approximate concurrence at pressures from about 2.5 to 5 GPa with those based on Cr-in-orthopyroxene (SMITH and BOYD, 1992; FRANZ et al., 1996b) and on Ca-in-olivine (KOHLER and BREY, 1990). Accuracy of TBKN temperatures for African xenoliths is supported by the approximate agreement with garnet-clinopyroxene temperatures (KROGH, 1988) (Fig. 2A) and garnet-olivine temperatures (O'NEILL and WOOD, 1979) (Fig. 2B), as discussed by BREY (1989) and BREY and KOHLER (1990). When compared to experiments on fertile Ti-rich mantle compositions in the range 1100°C to 1250°C, however, TAYLOR (1998) found that TBKN overestimated experimental conditions by 50° to 100°C; the comparison may document the sensitivity of thermobarometry to bulk composition. Furthermore, because P and T are coupled in calculations for garnet peridotites, errors cannot be evaluated independently, and it is not yet possible to assign quantitative uncertainties to calculated values.

Comparisons with other thermobarometers indicate possible deficiencies in the TBKN-PBKN combination near the high end of the 900°–1400°C range of the experiments of BREY et al. (1990). At temperatures from 1100°C to 1200°C, TBKN yields values typically at least 50–100°C hotter than all thermometers compared in Figs. 1 through 4, except those of KROGH (1988), O'NEILL and WOOD (1979), and GANGULY et al. (1996). A possible problem at yet higher temperatures is suggested by the scatter of PBKN pressures for Siberian xenoliths (Figs. 1D, F). The scatter may be due to disequilibrium, or it may faithfully record P-T conditions present in the dynamic environment from which these peridotites were erupted; each possibility is consistent with the heterogeneities and zonations of minerals in these xenoliths discussed by BOYD et al. (1997). It is also possible, however, that the scatter is due to calibra-

tion defects. CARSWELL and GIBB (1987b) discussed chemical differences between orthopyroxene from Siberia and from southern Africa that might lead to systematic errors for inaccurate calibrations. Differences between PBKN and PMC74 pressures are pronounced only for rocks in which the orthopyroxene contains less than 1 wt% Al_2O_3 (Fig. 1F). For the high P-T samples plotted in Fig. 1D, Siberian orthopyroxenes contain 0.47 to 0.74 wt% Al_2O_3, whereas the corresponding African samples contain 0.81 to 1.46 wt%. In the experiments cited by BREY (1989) and BREY et al. (1990) in this same P-T range, product orthopyroxenes contain 0.91 to 1.97 wt% Al_2O_3, all more than the Siberian samples. BREY et al. (1990) did not determine Na in many of the orthopyroxene products of their experiments, although Na-Al-Cr coupling may be important in formulating the orthopyroxene barometer, as may be ferric iron abundance (CARSWELL and GIBB, 1987b; CARSWELL, 1991; CANIL and O'NEILL, 1996). Accuracies for mineral chemistries different from those in calibration experiments are difficult to establish without secure thermodynamic models, and models may be inadequate for Al-poor orthopyroxene.

Possible deficiencies in the TBKN-PBKN combination below 900°C, the lowest temperature in the experiments of BREY et al. (1990), are also suggested by the comparisons of thermobarometer results. There are systematic differences between TBKN and thermometers that have been independently calibrated, other than those of KROGH (1988) and O'NEILL and WOOD (1979). BREY and KOHLER (1990) noted that the TBKopx thermometer based on Ca in orthopyroxene was systematically different than TBKN for African xenoliths, although it yielded appropriate results for the experiments of BREY et al. (1990). They suggested that minor elements adversely affected TBKopx values. Similar temperatures relative to TBKN are recorded by TBKopx for both spinel and garnet peridotite suites (Figs. 3A, B), however, although the contents of Al and Cr of orthopyroxene are significantly higher in spinel peridotite than in garnet peridotite. Moreover, trends of THar and TGang96 (orthopyroxene-garnet), TBallhaus (olivine-spinel), and TWells and TA97 (clinopyroxene-based two-pyroxene) are qualitatively similar to the TBKopx trend (Figs. 2-4), although these trends differ one from another quantitatively. All these thermometers roughly agree at temperatures near 900°–1000°C, but the comparisons indicate that TBKN may yield temperatures too low by 50° or more at 800°C. Such a discrepancy is not unexpected, as temperatures cooler than 900°C are below the experimental range of BREY et al. (1990), and also

low temperatures are unfavorable for clinopyroxene-based two-pyroxene thermometry.

Potentially the most accurate thermometers for spinel peridotites at temperatures below 1000°C are TBKopx, based on Ca-in-orthopyroxene (KOHLER and BREY, 1990), and TWES, based on Al-Cr-in-orthopyroxene (WITT-EICKSCHEN and SECK, 1991). The calibration of TBKopx may not account correctly for Na and other minor elements (BREY and KOHLER, 1990), however, and the calibration of TWES is based upon TBKopx. Moreover, the relative calibration may not be correct for many common bulk compositions, as TBKopx values are typically slightly hotter than TWES for the data sets plotted in Fig. 3D. Comparisons of TWES and TBKopx, in conjunction with characterization of zoned minerals, have great potential for elucidating temperature histories of spinel peridotites (WITT-EICKSCHEN and SECK, 1991; WITT-EICHSCHEN et al., 1993; SMITH and RITER, 1997). Fe-Mg exchange thermometers, such as TBallhaus (Fig. 3E), also are potentially accurate below 1000°C, and the olivine-spinel pair is likely to equilibrate during cooling to low mantle temperatures, but applications are complicated by uncertainties in calculated ferrous/ferric ratios in spinel.

APPLICATIONS TO MANTLE CONDITIONS AND EVOLUTION

One of the more contentious issues in thermobarometry of mantle xenolith populations has been the interpretation of P-T arrays that extend to temperatures hotter than about 1200°C. One such array is that for the Udachnaya xenoliths (Figs. 1A-D) described by BOYD et al. (1997). Depending upon the methods used and the xenolith population, the arrays make smooth trends, or form two segments with contrasting slopes, or form segments at different temperatures but overlapping pressures (BOYD, 1973; BREY, 1989, 1991; CARSWELL and GIBB, 1987b; FINNERTY and BOYD, 1987; FINNERTY, 1989). When a geotherm such as the 40 mW/m² curve of POLLACK and CHAPMAN (1977) is fit to the lower-temperature part of an array, the higher-temperature points may define a line segment "inflected" to temperatures hotter or cooler than the curved geotherm. Interpretations of the inflections in part have been guided by expectations of geotherm curvature rather than by clear departures from linear trends. Departures from linear or gently-curving trends do exist in such arrays for various methods of P-T calculation, however, as shown for Siberian xenoliths by both TBKN-PBKN (BREY, 1989, 1991) and TFB86-PMC74 (FINNERTY and BOYD, 1987) (Figs. 1A, B). The best-established combination, TBKN-PBKN of BREY and KOHLER

(1990), yields temperatures consistently higher than those of several independently calibrated thermometers at 1100–1200°C (Figs. 1-4), and as discussed above, at higher temperatures there may be errors related to inadequate corrections for compositional variations, particularly for low-Al pyroxenes. In light of the uncertainties in coupled thermobarometer solutions at high T, quantitative analysis of such trends is premature.

Disequilibrium documented by zonation in garnet, intergrain heterogeneities, and trace-element partitioning is common in these high-T rocks (*e.g.,* SMITH and BOYD, 1987, 1989; HOPS *et al.,* 1989; GRIFFIN *et al.,* 1996a; SHIMIZU *et al.,* 1997; BOYD *et al.,* 1997). The range of diffusivities discussed above can be used to constrain how long before eruption grains could have been zoned at about 1200°C. For diffusivity values from 10^{-21} to 10^{-16} m²/s, corresponding times for nearly complete homogenization of grains 1 mm in diameter are 2 million to 20 years. The observed zonations must have formed in less time than required for homogenization. Moreover, many xenoliths with zoned garnets record higher temperatures and would homogenize faster than the times calculated with 1200°C diffusivities. Because perturbations by deformation, metasomatism, and advective heat transport appear to have affected many high-temperature xenoliths in geologically short intervals before eruption, as discussed by BOYD (1973), IRVING (1976), GURNEY and HARTE (1980), and others, it would be surprising if most high-T arrays record conductive gradients.

The xenolith P-T arrays in the 900–1100°C interval provide accurate constraints on mantle conditions at the time of eruption and important constraints upon mantle evolution, if the mineral assemblages had equilibrated to ambient conditions in large mantle volumes. It has been suggested that even if the calculations are accurate for the mineral assemblages within xenoliths, however, these assemblages were not equilibrated to ambient geotherms, but perhaps represent perturbed or "fossil" geotherms (FRASER and LAWLESS, 1978; IRVING, 1976). Observations of compositional zonation within minerals of peridotite xenoliths and comparisons of methods of thermometry strongly support the hypothesis that many P-T arrays in the 900°–1100°C range do represent ambient steady-state geotherms at the time of eruption. Garnet is zoned in Cr-Al in some of these xenoliths (SMITH and BOYD, 1992), but all minerals appear nearly homogeneous in others. Homogeneous minerals and rims of zoned minerals yield approximately concurrent temperatures in this temperature range by various methods of thermometry, including those in Figs. 1-4 and others (BREY *et al.,* 1990; KOHLER and BREY, 1990). Concurrent methods depend upon partitioning of Ca, Fe, Mg, Al, and Cr between various mineral pairs. The relative consistency of these methods is a strong argument for equilibrium because the cations equilibrate by diffusion at contrasting rates. Moreover, observations of gradients within grains in some xenoliths confirm that diffusion was rapid enough to induce zonation in this temperature range during mantle events (*e.g.,* WITT-EICKSCHEN *et al.,* 1993; OZAWA and TAKAHASHI, 1995; FRANZ *et al.,* 1996a; SMITH and RITER, 1997). The near homogeneity of all minerals in some xenoliths sampled from this P-T range is evidence that these minerals had equilibrated and that their chemistries do not record perturbations shortly before eruption. Hence, many xenolith arrays in the 900–1100°C range appear to record ambient geotherms accurately.

Because many P-T arrays do appear both to be accurate in the range 900–1100°C and to record ambient geotherms appropriate for large mantle volumes, they constrain hypotheses of mantle evolution. Though geotherms calculated by POLLACK and CHAPMAN (1977) have been widely used as a basis for interpretation of the P-T arrays, they represent only one set of solutions that satisfy observed cratonic heat flows. RUDNICK *et al.* (1998) have emphasized that families of geotherms satisfy heat flow constraints, and that calculated geotherms depend upon poorly known distributions of heat sources. RUDNICK *et al.* (1998) further noted that if the xenolith P-T arrays are accurate, they constrain heat source distributions and the lithospheric thickness. O'REILLY and GRIFFIN (1996) have discussed use of the P-T arrays to elucidate changes of mantle geotherms in space and time.

Interpretation of calculated temperatures below 800–900°C is more difficult. HARTE and FREER (1982) emphasized that diffusion would limit equilibration of mantle rocks below about 900°C, so that the uppermost mantle may contain "frozen" mineral compositions. Many xenoliths of both garnet and of spinel peridotite record temperatures below 900°C by a variety of thermometers (Figs. 1-4), and there is also strong evidence for disequilibrium in some of these rocks. For instance, PEARSON *et al.* (1995) and GUNTHER and JAGOUTZ (1997) found that garnet and clinopyroxene separates from some low-temperature garnet peridotites from the Udachnaya pipe, the source of the Siberian population in the data base used here, were in isotopic disequilibrium at the time of eruption. Analyses of phases near grain contacts nonetheless may represent equilibrated compositions,

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even if bulk compositions of mineral separates document disequilibrium.

Comparisons of thermobarometry calculations can be used to test the assumption of equilibrium, if calibrations are consistent. In view of the disequilibrium expected during cooling, it is surprising that arrays calculated by various thermometers are similar below 900°C (Figs. 3, 4). Comparisons of TWES temperatures, based on Al and Cr in orthopyroxene, and TBKopx values, based on Ca in orthopyroxene, provide an unusually good test for equilibrium of spinel peridotites, because WITT-EICKSCHEN and SECK (1991) calibrated TWES from TBKopx. All but one of the Siberian spinel peridotites of BOYD et al. (1997) plot in a cluster with TWES high compared to TBKopx (Fig. 3D), as expected if divalent elements equilibrated to lower temperatures than trivalent elements during cooling. Similar diffusion-related disequilibria have been documented in crustal granulites by FITZSIMONS and HARLEY (1994) and PATTISON and BEGIN (1994), who found rocks in which Fe-Mg exchange thermometers indicate temperatures at least 100°C cooler than those based on Al solubility in orthopyroxene. In contrast, TWES-TBKopx relationships of low-T Colorado Plateau spinel peridotite xenoliths in Fig. 3D are like those of higher-T samples, and so the Colorado Plateau rocks appear equilibrated. These rocks recrystallized during prograde metamorphism (SMITH and RITER, 1997). One Siberian sample plots with the low-T Plateau spinel peridotites, and so recrystallization may have equilibrated rim compositions in that xenolith. The importance of recrystallization in cool mantle rocks is not well-established, although it provides a mechanism for equilibration despite slow diffusion rates.

Characterization of compositional gradients can establish scales at which minerals re-equilibrate and can indicate if diffusion was the dominant mechanism. SMITH and BARRON (1991) analyzed gradients to document that Al and Cr diffused in mantle pyroxenes to distances of hundreds of micrometers only at calculated temperatures above about 800°C, but that Fe and Mg diffusion was more effective during further cooling. They found diffusion gradients in pyroxene and garnet within 200 μm of mutual contacts in rocks with calculated temperatures below 800°C. Such gradients preserve evidence of the limited scale of equilibration. In these rocks, analyses of volumes in grain interiors will not yield P-T conditions at the time of eruption and may not yield P-T values that are accurate for any part of the rock history. Additional searches for compositional gradients near grain contacts will help to resolve the relative importance of diffusion and recrystallization in cool mantle and to assess the validity of calculated temperatures below 900°C.

CONCLUSIONS

The accuracy of thermobarometric calculations for garnet peridotite xenoliths is best established for the two-pyroxene thermometer (TBKN) plus Al-in-orthopyroxene barometer (PBKN) of BREY and KOHLER (1990) and for P-T conditions in the range 2–5 GPa and 900–1100°C. Even within this limited P-T range, there are significant differences between conditions calculated with independently calibrated thermobarometers. These differences are due to calibration problems, not to disequilibria, as they are present in calculations using compositions of homogeneous minerals and rims of zoned grains. Diffusion rates of important cations in peridotite minerals cover a wide range, and so rim compositions of minerals are more likely to represent equilibrium assemblages than core compositions. The characterizations of mineral homogeneity support the hypothesis that P-T arrays in the 900°–1100°C range represent geotherms at the time of eruption.

At temperatures above 1100–1200°C, accuracies of calculated conditions are less certain, although constraints from experiments and the general concurrence of two different methods of two-pyroxene thermobarometry (Fig. 1) establish that the P-T arrays are approximately correct. Detailed features of high-temperature geotherms, such as the presence of inflections (kinks), are not well established. Calculated results are particularly uncertain for rocks that contain orthopyroxene with less Al than that in any of the calibration experiments, as do some of the samples in the Siberian suite of BOYD et al. (1997). It is unclear if the scatter of points in high-temperature P-T arrays is due to calibration problems, or to disequilibrium, or if the points accurately record mantle processes. The common preservation of compositional zonation in minerals of high-temperature xenoliths testifies to dynamic conditions in sources immediately preceding eruption, and hence departures from smooth P-T arrays are expectable.

At temperatures below 900°C, relatively slow diffusion rates may cause disequilibrium, as emphasized by HARTE and FREER (1982). Although clinopyroxene-based two-pyroxene thermometry may yield more accurate temperatures above 900–1000°C, orthopyroxene-based thermometry potentially is more accurate in cooler mantle. In spinel peridotite, one test of equilibrium is relative consistency between the Al-Cr-in-orthopyroxene thermometer of WITT-EICKSCHEN and SECK (1991) and the Ca-

in-orthopyroxene thermometer of Brey and Kohler (1990). Observations of diffusion gradients at pyroxene-garnet boundaries confirm that equilibration by intergranular diffusion is limited below about 800°C even in slowly cooled mantle. Assemblages in cool uppermost mantle may still equilibrate during recrystallization. Characterization of compositional gradients in minerals of low-T xenoliths will help to clarify interpretations of calculated temperatures below 900°C.

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