The Canadian Mineralogist
Vol. 34, pp. 1179-1193 (1996)

TRACE-ELEMENT ZONING IN MANTLE MINERALS: METASOMATISM AND THERMAL EVENTS IN THE UPPER MANTLE

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ABSTRACT

Studies of trace-element zoning in mantle-derived minerals can provide important constraints on the nature and time scales of metasomatic processes and thermal events in the upper mantle, and on diffusion rates. Zoning data on garnet in peridotite xenoliths restrict some metasomatic processes to geologically short time-spans (10–10^4 years) prior to the eruption of the host magmas, and suggest that the metasomatism is genetically connected to the magmatic events or their immediate precursors. Such metasomatism effects major changes in both the major-element and trace-element composition of the rocks, and these xenoliths should not be used to represent large volumes in the mantle. Modeling of heating and cooling rates, based on Ni zoning in garnet, suggests that the heating observed in high-T xenoliths is a transient phenomenon associated with local intrusion of magma bodies. The relative lengths of zoning profiles for various elements in single crystals of garnet suggest that diffusion coefficients, over the temperature range 1200–1400°C, decrease in the order Ni $\geq$ Fe, Mn > Ti, Zr $\geq$ Y (and heavy *REE*) $\approx$ Ca > Cr, Ga, V. Analyses of zoning profiles in garnet cooled from a high temperature suggest that rates of Ni diffusion are equivalent to those of Fe–Mg down to temperatures near 600°C. Pyroxene equilibration during thermal and metasomatic events probably involves volume diffusion over very short distances only, between high-mobility paths such as cleavage planes.

Keywords: zoning, mantle, diffusion, metasomatism, pyrope-rich garnet.

SOMMAIRE

L'étude de la zonation en éléments traces des minéraux du manteau peut permettre de mieux cerner la nature des processus et des événements métasomatiques du manteau supérieur, l'échelle de temps nécessaire pour leur développement, et les taux de diffusion. Les données sur le grenat des xénolithes péridotitiques indiqueraient que certains processus métasomatiques se sont deroulés sur une echelle de temps relativement courte (10–10^4 années) précédant l'éruption des magmas hôtes. Ainsi, la

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métasomatose serait-elle génétiquement donc liée aux événements magmatiques ou bien à leurs précurseurs immédiats. De telles transformations métasomatiques peuvent effectuer des changements importants à la fois dans la distribution des éléments majeurs et des éléments traces des roches; les xénolithes ainsi affectés ne devraient pas être considérés représentatifs de volumes importants du manteau. Un modèle des taux de réchauffement et de refroidissement, fondé sur la répartition du Ni dans le grenat, nous fait penser que le réchauffement indiqué dans les xénolithes équilibrés à température élevée est un phénomène éphémère, associé à la mise en place de venues de magma. La longueur relative des profils de zonation pour divers éléments dans des cristaux de grenat semble indiquer que les coefficients de diffusion, à une température comprise entre 1200 et 1400°C, diminuent dans l'ordre Ni ≥ Fe, Mn > Ti, Zr ≥ Y (et les terres rares lourdes) ≈ Ca > Cr, Ga, V. D'après nos analyses des profils de zonation des cristaux de grenat refroidis d'une température élevée, les taux de diffusion du Ni seraient équivalents à ceux du Fe et du Mg jusqu'à une température proche de 600°C. Le ré-équilibrage des grains de pyroxène au cours des événements thermiques et métasomatiques impliquerait probablement une diffusion volumique sur une très courte distance seulement, entre deux zones à mobilité accrue, des plans de clivage par exemple.

(Traduit par la Rédaction)

Mots-clés: zonation, manteau, diffusion, métasomatose, pyrope.

INTRODUCTION

Trace-element data on mantle minerals have greatly expanded our understanding of processes in the deeper parts of the lithosphere. Trace elements are especially useful for several reasons. The most obvious is that they expand the number of variables that can be used to characterize and analyze mantle processes. More importantly, they typically show a wider range of crystal–fluid (including melt) partition coefficients than do major elements, so that they are inherently more sensitive tracers of a process. This effect produces larger ranges in concentration, which leads in turn to more pronounced zoning profiles, and thus potentially to more precise modeling.

The potential of studies of trace-element zonation in the analysis of mantle processes has increased markedly in the last decade with the wider availability of ion microprobes, the more routine use of the proton microprobe (Ryan & Griffin 1993), and the recent introduction of accurate laser-ablation ICP–MS microprobes (*e.g.*, Jackson *et al.* 1992, Norman *et al.* 1996) and synchrotron X-ray-fluorescence microprobes (Lanzirotti 1995). These techniques, by providing precision at the 5–10% level for many trace elements, make it possible to use the inherently greater content of information in trace-element zoning profiles to study mantle processes. The analytical uncertainties on the data discussed here have been presented in the original papers; in particular, the uncertainties for individual points in some typical zoning profiles have been shown by Smith *et al.* (1993).

In this paper, we concentrate on data gathered by proton microprobe at CSIRO Exploration and Mining over a period of several years, and we review the implications of these data for mantle processes. This review emphasizes the broad conclusions drawn from these studies; these conclusions are robust, although simplifying assumptions have been made to model the data. Spherical geometries were assumed for

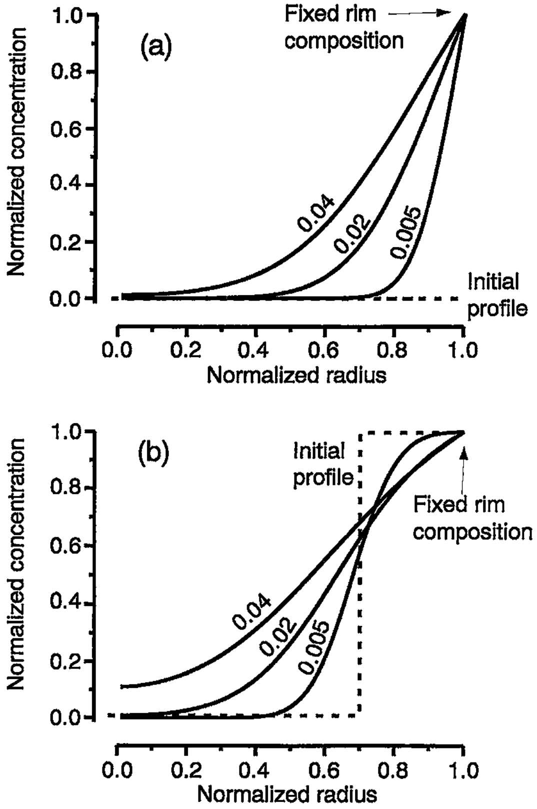


FIG. 1. Simple end-member diffusion models discussed in text. (a) Simple inward diffusion, with rim composition fixed; (b) diffusion between a homogeneous core and an instantaneously added overgrowth rim. Curves are labeled with values of Dt/a^2, where D is an effective diffusion-coefficient, t is time, and a is sphere radius, as used by Crank (1975).

the calculation of diffusion profiles, consistent with the shape of garnet grains in many samples of peridotite. Profile shapes are used to discriminate between two end-member models of zonation. In the simplest model (Fig. 1a), zonation is formed by radial diffusion in initially homogeneous garnet, induced by an instantaneous change in composition at the garnet rim (metasomatism), or by a change in temperature, or by both; the rim's composition is held constant after that change. The assumption of initial homogeneity is supported by the observation that grains of garnet in most peridotite xenoliths are nearly homogeneous, in accord with the fact that these xenoliths typically equilibrated at temperatures in the range from slightly below 900° to over 1400°C (*e.g.*, Nixon & Boyd 1973). In a more complex model (Fig. 1b), zonation is formed by radial diffusion between a core and a shell overgrowth; the composition of the outer rim of the shell is held constant. The inflected gradients produced by diffusion in these core–shell pairs are called "S-shaped" in the following discussions. Simple binary diffusion is assumed, as little is known about diffusion coefficients for elements like Ti, Zr and Cr in garnet, and less is known about interactions between diffusing elements. More accurate quantitative modeling of time scales for mantle processes will require more experimental data on diffusion coefficients. Here, we explore the constraints that zonation studies can provide on the relative diffusion-coefficients of several useful trace elements, until experimental measurements are available.

METASOMATIC PROCESSES

We have studied the zoning produced in pyrope-rich garnet by metasomatic processes affecting two general types of garnet peridotite xenoliths from kimberlites and other volcanic rocks: high-temperature (typically >1200°C), usually sheared peridotites, and low-temperature (typically 900–1100°C), granular peridotites. Most of the garnet grains analyzed for this purpose have subcircular cross-sections, have few cracks, and are free of alteration except near their rim, where thin zones of kelyphite may be present.

High-temperature processes

The pyrope-rich garnet of many high-T sheared peridotite xenoliths shows relatively weak zoning in Cr, Fe and Mg, and pronounced zoning in a range of minor and trace elements, including Ti, Zr, Y, and Ga (Smith & Boyd 1987, Griffin *et al.* 1989b, Smith *et al.* 1991, 1993). A typical example is shown in Figure 2; the Cr zoning profile defines a broad homogeneous core, with an outer zone progressively depleted in Cr toward the rim; the total relative variation in the major elements ranges from 4% for Fe to 20% for Cr. In contrast, TiO_2 increases by a factor of two from core to rim, whereas Zr increases by a factor of 12. The concentration of Y and Ga also rises from core to rim, whereas Zn and Ni show little zoning. The Zr and Ti profiles show pronounced inflections, giving S-shaped profiles that are not obvious in the Fe data because the range in the data (4% relative) is close to the precision of the electron microprobe (EMP) technique (*ca.* 2%).

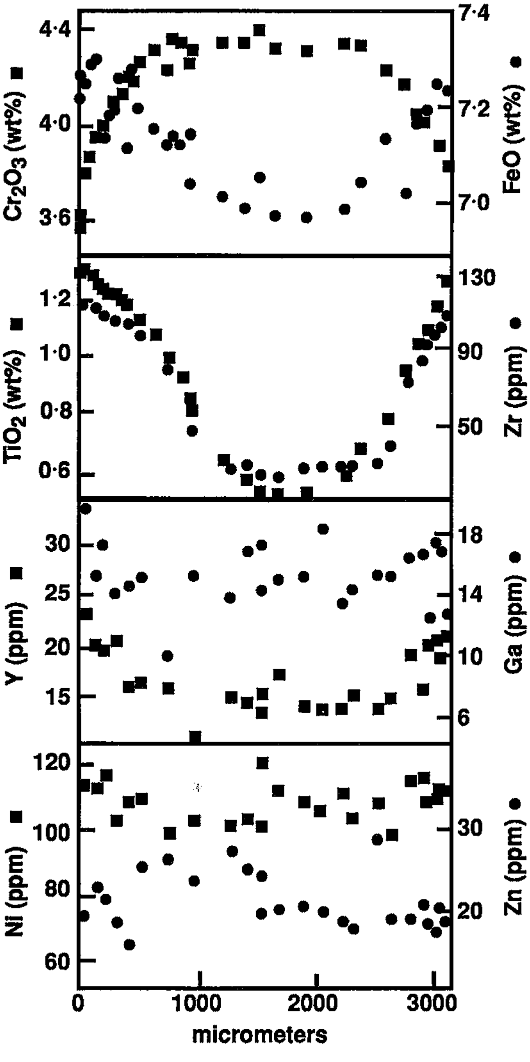


FIG. 2. Compositional profiles across FRB76E, a 3-mm grain of garnet from a high-T (1350–1400°C) sheared peridotite xenolith. Concentration of major elements determined by electron-microprobe (EMP) analysis, that of trace elements, by proton-microprobe (PMP) analysis. Typical precision for the individual trace elements (in ppm) is: Zr, ±3; Y, ±1.5; Ga, ±1; Zn, ±2; Ni, ±5. After Griffin *et al.* (1989b).

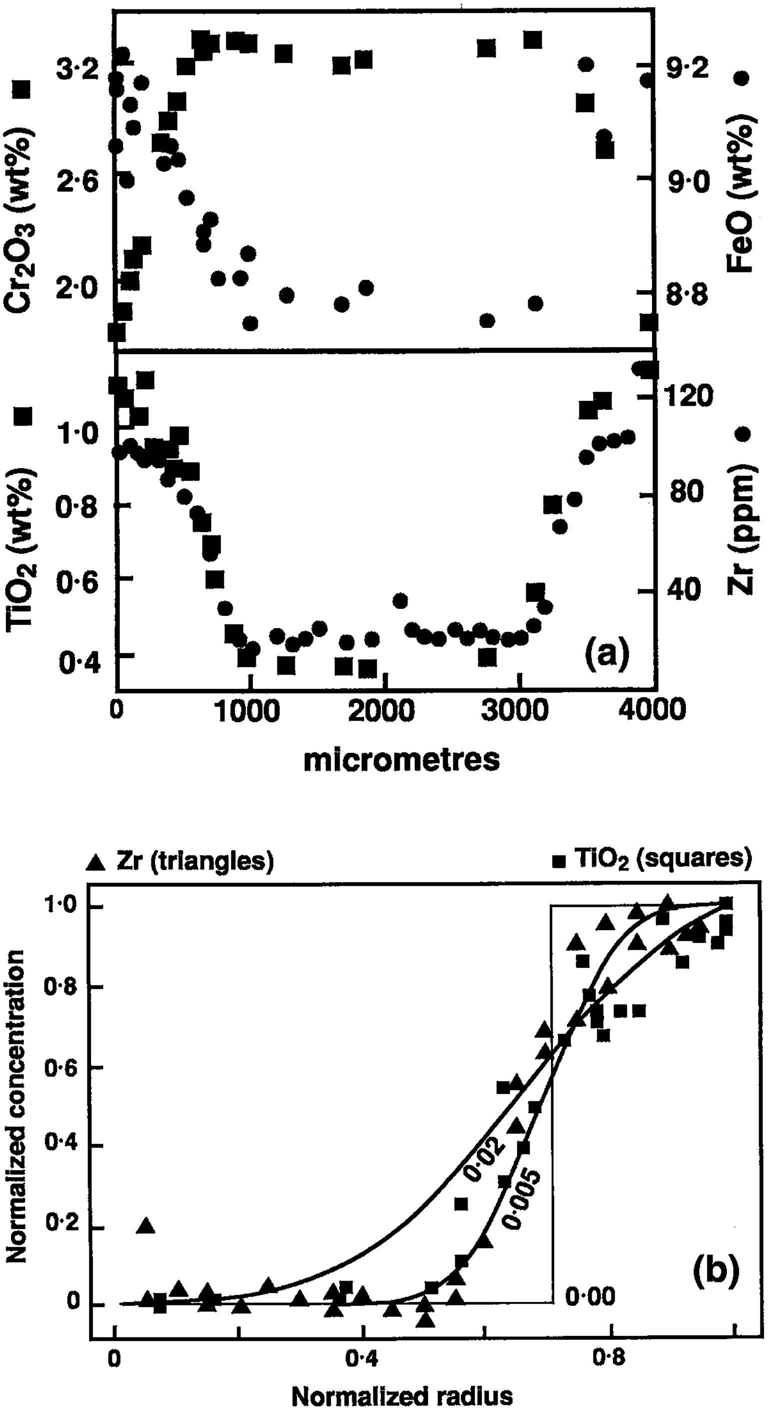


FIG. 3. Compositional profiles across a 4-mm grain of garnet from FRB 450, a sample of high-T sheared peridotite (Griffin *et al.* 1989b). (a) Analyses for Zr (proton probe), and FeO, Cr_2O_3, and TiO_2 (electron probe) along the same diameter. Note the well-defined S-shaped profile of Zr. (b) Zr and TiO_2 data compared to calculated diffusion-profiles between a core–overgrowth pair like that illustrated in Figure 1b. Curves were calculated numerically and are labeled with values of Dt/a^2, where D is a diffusivity, t is time, and a is the sphere radius, as discussed by Griffin *et al.* (1989b).

The origin of this type of zoning can be analyzed on the basis of the two simple models discussed above: inward diffusion of material from the rim of a pre-existing grain (Fig. 1a), and an overgrowth of new material, followed by diffusion during annealing (Fig. 1b). These models were applied to the data shown in Figure 2; Ti and Zr have pronounced S-shaped profiles, extending from the rim to *ca.* 1000 μm, whereas the Cr profile defines a homogeneous core extending out to *ca.* 750 μm from the rim. The inward-diffusion model produces simple bowl-shaped zonation profiles, which are not consistent with the Zr and Ti data. A more successful model (Fig. 3) treats the garnet as consisting of a homogeneous core with a 250-μm rim containing high levels of Ti and Zr. For purposes of modeling, the formation of the overgrowth was assumed to be instantaneous, with a sharp inner edge corresponding to the break-point in the Cr profile. A diffusion model with a value of $Dt/a^2 = 0.005$ [where D is an effective diffusion-coefficient, t is time, and a is sphere radius, as used by Crank (1975)] is contained in the envelope defined by almost all of the Zr data points, and approximates that for Ti (Griffin *et al.* 1989b).

Griffin *et al.* (1989b) adopted a diffusion coefficient of 10^{-17} m²/s for Zr and Ti, which gives a time span of *ca.* 60 years between the formation of the overgrowth and the quenching of the garnet by eruption of the host kimberlite to the surface of the earth. This diffusion coefficient was adopted to be in the range of estimates

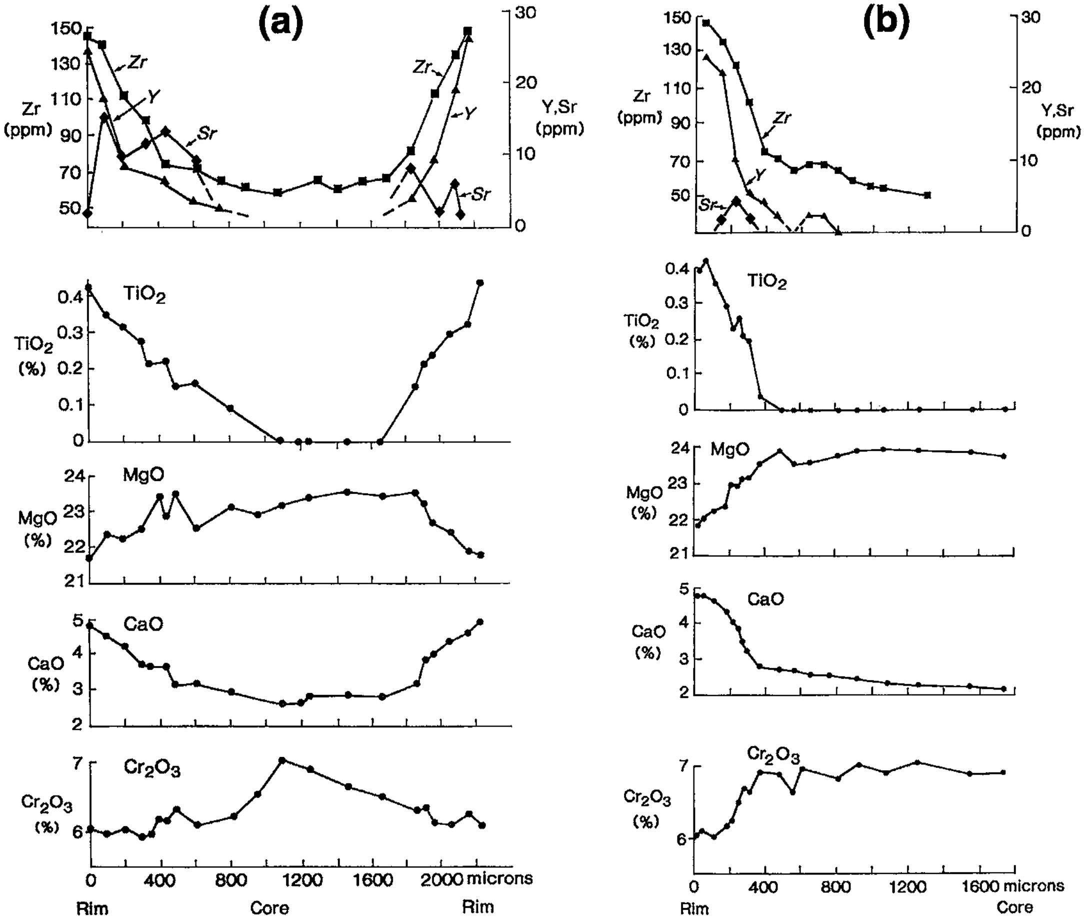
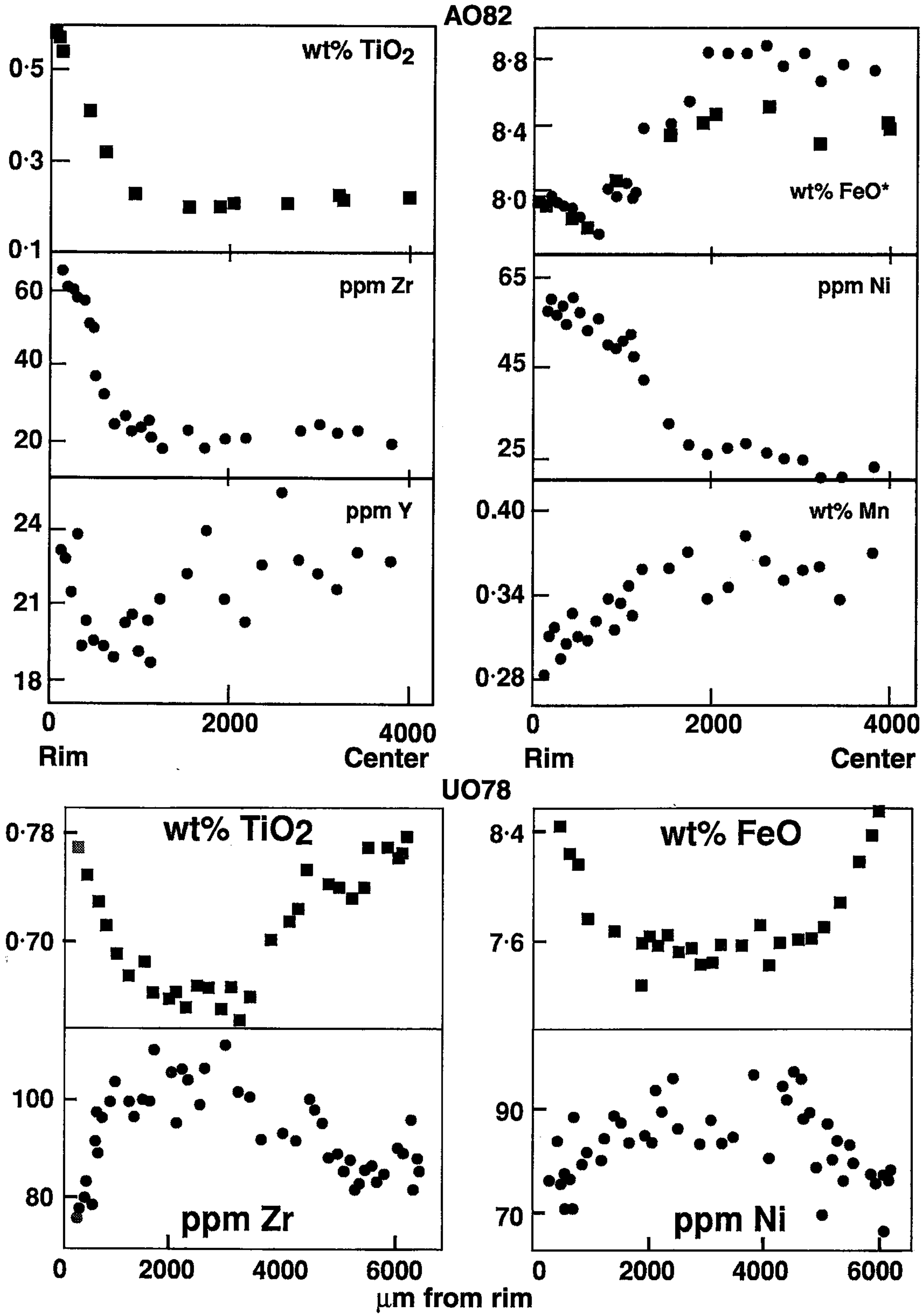


FIG. 4. Compositional profiles for two grains of garnet in harzburgite xenoliths (a: 945, b: 951/1) from the Wesselton kimberlite pipe (Shee *et al.* 1993, Griffin *et al.* 1996). Analytical uncertainties are comparable to those for Figure 2. The profiles for 945 suggest that the zoning formed by continuous inward diffusion of Zr, Y, Ti and Ca (*cf.* Fig. 1a); the S-shaped profiles for 951/1 indicate the formation of a thin overgrowth, superimposed on a weakly zoned core (*cf.* Fig. 1b).


AO82
wt% TiO2
0·5
0·3
0·1
wt% FeO*
8·8
8·4
8·0
ppm Zr
60
40
20
ppm Ni
65
45
25
ppm Y
24
21
18
wt% Mn
0.40
0·34
0·28
0
2000
4000
Rim
Center
UO78
wt% TiO2
0·78
0·70
wt% FeO
8·4
7·6
ppm Zr
100
80
ppm Ni
90
70
0
2000
4000
6000
µm from rim

of coefficients for other elements at 1200–1300°C, and it may be wrong by as much as three to four orders of magnitude. Even with this uncertainty, however, the short time-span calculated for the annealing process indicates that the metasomatism responsible for the garnet overgrowth was a geologically short-lived event, making a genetic connection with the kimberlite magmatism very probable.

The recognition of the zoning as the result of garnet growth carries other important implications as well. With an overgrowth width equal to 25% of the radius, over half of the garnet in the sample is contained in the overgrowth and thus probably was added to the rock late in its history. Similar results have been obtained for several other high-T sheared peridotite xenoliths (Griffin *et al.* 1989b, Smith *et al.* 1991, 1993). We conclude that the major-element compositions, as well as the trace-element patterns, of these rocks have been modified by metasomatic processes shortly before their eruption, and that they cannot be taken as representative of any long-lived mantle reservoir.

Low-temperature processes

Shee *et al.* (1993), Shimizu *et al.* (1993), Schulze (1995) and Griffin *et al.* (1996) have described major-element and trace-element zoning in the pyrope-rich garnet of granular harzburgite xenoliths from the kimberlites of the Kimberley area in South Africa. These xenoliths yield equilibration temperatures, by several methods, in the range 950–1050°C, and many contain Ti-rich phlogopite, interpreted as metasomatically introduced. The garnet typically shows a marked increase in Ca, and a decrease in Mg and Cr, toward the rim of the grains. Trace-element zoning also is pronounced, with Zr, Y and Ti all increasing toward the rim. However, the range of patterns is greater than in the high-temperature peridotites, and many compositional profiles show irregularities that are beyond the analytical uncertainty. Many samples show simple bowl-shaped profiles of zoning (Fig. 4); others show S-shaped profiles in an outer zone, superimposed on a broader bowl-shaped zoning, whereas still others show very broad S-shaped profiles extending nearly to the core of grains. We suggest that several metasomatic processes, commonly superimposed on the same grain, have produced the observed range in zoning profiles. Some grains of garnet have been subjected only to continuous inward diffusion of elements including Ca, Ti, Zr and Y (and outward diffusion of Mg and Cr); an overgrowth rim has formed both on this type of garnet and on some grains that show little prior zoning.

Shee *et al.* (1993) and Griffin *et al.* (1996), citing the relatively low temperatures, adopted values for D of 10^{-19} m^2/s, and derived time scales (prior to eruption of the kimberlite) of less than about 20,000 years for the formation of the bowl-shaped zoning profiles, and of less than 10,000 years for the modification of the overgrowths by diffusion; these are likely to be maximum estimates. The granular microstructures of the Kimberley xenoliths, the prevalence of bowl-shaped zoning profiles in the garnet, and the differences in the behavior of Zr, Y and Ti, all suggest that the mechanism of infiltration, and the composition of the fluids involved, were different from those that influenced the composition of the high-T sheared peridotites. This may be reflected in the longer apparent time-scales. However, even these times are geologically short, and they suggest that the composition of relatively shallow parts of the upper mantle (100–130 km) also has been modified significantly during episodes of kimberlite magmatism.

THERMAL EVENTS

Zoning profiles of Ni in garnet provide a means of analyzing the thermal history of garnet in some mantle-derived rocks. Griffin *et al.* (1989a) demonstrated that the partitioning of Ni between pyrope-rich garnet and olivine is strongly temperature-dependent; this "Nickel Thermometer" was refined and recalibrated by Ryan *et al.* (1996). The range of Ni content in olivine from mantle peridotites is small: 2940 ± 340 ppm [1σ; Ryan *et al.* 1996)], especially compared to the observed range in garnet (10–120 ppm Ni) over the T range 600–1400°C. The Ni content thus can be used to estimate the T of a grain of chromian pyrope, without knowledge of the exact composition of the coexisting olivine. This is especially useful in studying zoning profiles, since in principle we cannot be certain of the composition of the minerals that coexisted with the core of a zoned grain. Smith *et al.* (1991) calibrated the Mn content of garnet as a geothermometer, and showed that the T ranges derived from the use of Mn, Ni and Fe–Mg zonation in a single grain are comparable.

In nearly all examples of high-T garnet studied by us, Ni shows little or no zonal distribution (Fig. 2), and Ni levels indicate equilibration at high temperatures

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FIG. 5. Compositional profiles for two grains of garnet from The Thumb (Smith *et al.* 1991). In AO82, Ni, Fe and Mn profiles reflect heating during growth; in UO78, Fe and Ni indicate cooling, with profiles that do not reflect the overgrowth indicated by Zr and Ti profiles.

(Ryan *et al.* 1996). We interpret these findings as reflecting rapid equilibration of Ni contents by diffusion at high T, and the rapid quenching of the xenoliths by eruption of the kimberlite, usually near the peak of the thermal event.

However, several peridotite xenoliths from a minette at The Thumb show Ni zoning profiles reflecting both heating and cooling (Smith *et al.* 1991; Fig. 5). In sample UO78, Fe and Ni profiles are broad, bowl-shaped and complementary, and they cut across the more complex zoning shown by Ti and Zr (interpreted as the result of two grains growing together). The rimward increase in Fe and decrease in Ni are consistent with inward diffusion of Fe and outward diffusion of Ni, as would be predicted for equilibration with the surrounding olivine during cooling over *ca.* 70°C, near 1100°C. In sample AO82, S-shaped Zr and Ti profiles suggest a narrow overgrowth with a low Fe content. Mn, Fe and Ni show broader profiles, consistent with heating and the formation of the overgrowth rim at high T. Smith *et al.* (1991) successfully modeled the Ni profile in terms of a heating from 900° to 1160°C over a period of *ca.* 13,000 years, followed by the formation of an overgrowth and annealing at *ca.* 1160°C for 800 years (Fig. 6).

This model is not unique, and the time frame depends on correct values for diffusion coefficients. However, errors of several orders of magnitude would be required to change the important inferences that can be drawn regarding the processes involved. To produce the observed zoning, heat must be transported to the site of garnet growth. On a typical conductive "cratonic" geotherm, a temperature difference of 250°C corresponds to *ca.* 80–100 km of depth. The heating rate derived from garnet AO82 (0.02°/yr) is too high to allow the heat to be supplied by processes of thermal conduction over significant distances. Convective processes (upwelling of hot mantle) would move the thermal anomaly by distances of hundreds of meters/10^4 years, whereas magma percolation might move the heat source tens of km/10^4 years; these processes probably are too slow.

However, intrusion of magma, controlled by crack formation, can move heat at rates of km/min. This suggests that the intrusion of a nearby body of magma is the most likely heat source. The formation of the overgrowths, with their enrichment in incompatible elements, is taken as evidence for the introduction of a melt or a melt-related fluid. The broad zoning in Ni, relative to the sharp zoning of Ti and Zr, suggests that garnet AO82 was heated over a relatively long period before the arrival of the metasomatizing fluid. Both processes might be related to local and periodic hydrofracturing in the thermal aureole around a body of magma.

Both samples AO82 and UO78 give two-pyroxene and olivine–garnet temperatures in agreement with the Ni temperatures of their garnet rim, and P–T estimates for both rocks lie along an elevated geotherm (Smith *et al.* 1991). This agreement strongly suggests that equilibration of these geothermometers occurs on time scales of 10^3–10^4 years, at temperatures on the order of 1000–1100°C, and argues against the view (*e.g.*, Fraser & Lawless 1978) that geothermobarometry of mantle xenoliths as inherently flawed owing to lack of

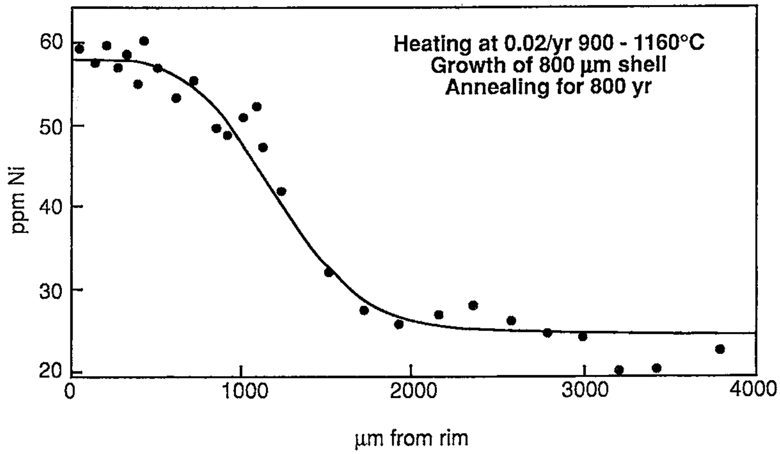

FIG. 6. Model for the formation of Ni zoning in garnet AO82 (Smith *et al.* 1991), assuming equilibration with the surrounding olivine during slow heating and the formation of an overgrowth, the width of which is defined by Zr and Ti profiles (Fig. 5).

equilibration over periods of millenia. The evidence for rapid equilibration of different geothermometers and geobarometers also emphasizes the transient nature of the elevated and "kinked" geotherms reflected by many high-T xenoliths. These geotherms probably are related to the magmatic episodes that bring the xenoliths to the surface, rather than being long-term features of the lithosphere.

DIFFUSION COEFFICIENTS

The review above demonstrates that trace-element zoning in mantle minerals can provide important constraints on the nature of mantle processes, and that an important part of these constraints lies in understanding the time scales of the different processes. The examples given above have depended on estimates of diffusion coefficients derived by analogy with available experimental data, which are few. Whereas the conclusions drawn above are robust, in the sense that the times involved are geologically short even if the diffusion coefficients are increased by several orders of magnitude (and even more so if they are decreased), there is clearly much room for improvement.

Quantitative modeling of zoning profiles to derive time scales requires a firm knowledge of the diffusion coefficients of individual trace elements in specific minerals, at P and T relevant to the upper mantle. These data are not currently available. Figure 7 shows a compilation of data for olivine, on which most work has been done. In terms of modeling, it is encouraging to note the small range in *D* displayed by a range of elements. At 1400°C, the diffusion coefficients for all of the displayed divalent elements are similar within an order of magnitude; at 900°C, the spread is still

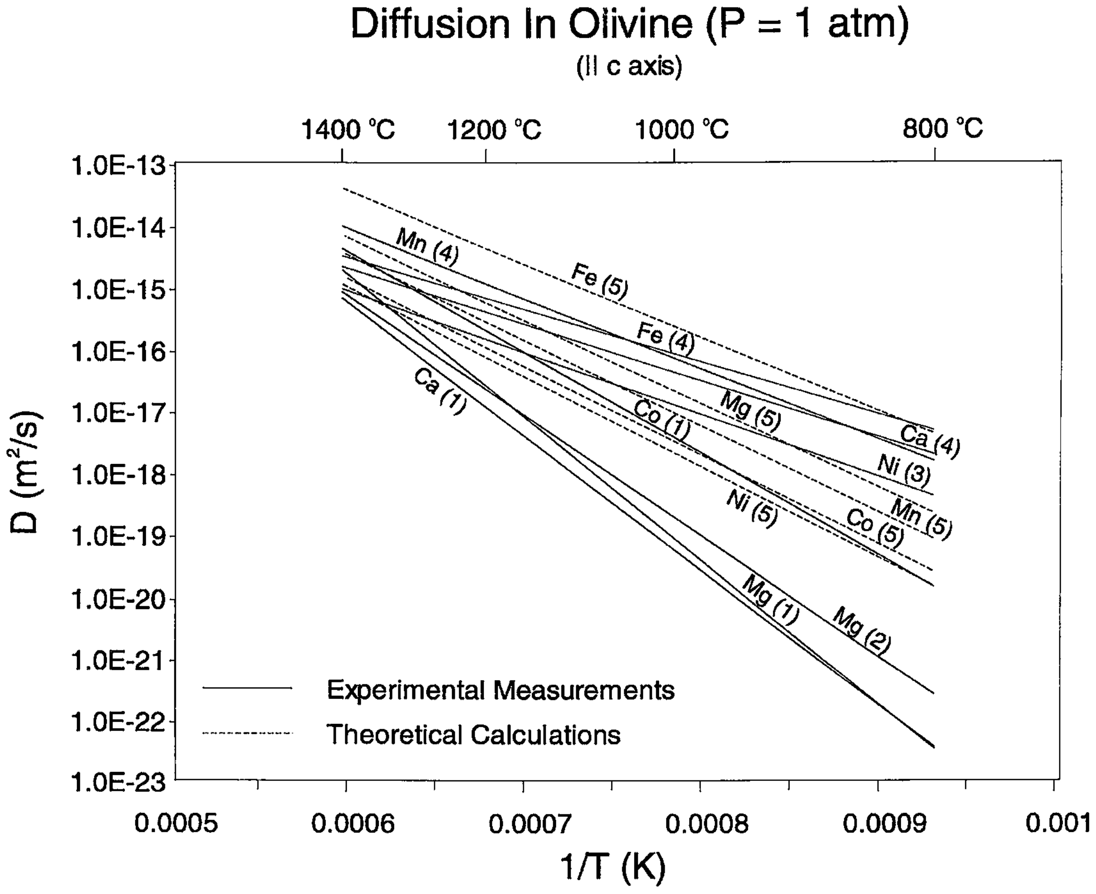

FIG. 7. Experimental and theoretical data for *D* as a function of T for various divalent elements in olivine. Numbers in brackets indicate sources of the data, as follows: (1) Morioka (1981), (2) Hallwig *et al.* (1981), (3) Clark & Long (1971), (4) Jurewicz & Watson (1988), and (5) Miyamoto & Takeda (1983).

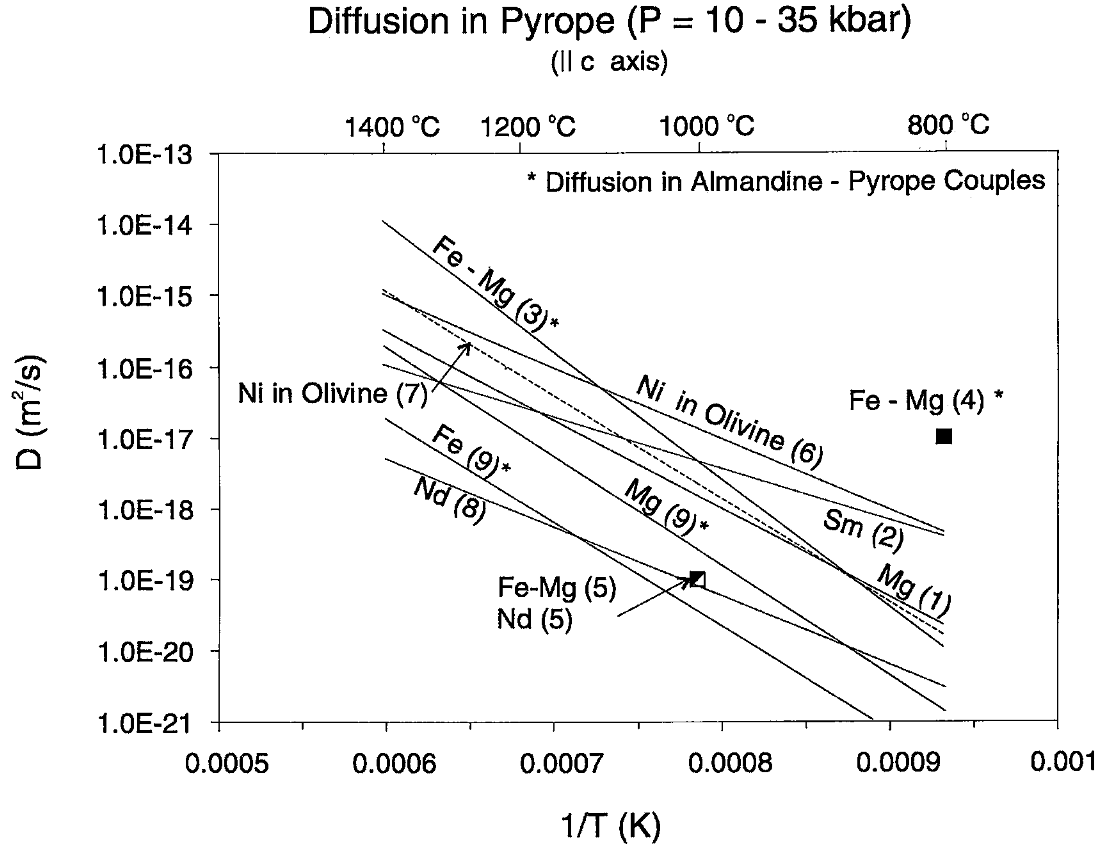

FIG. 8. Experimental data on *D* as a function of T for pyrope-rich garnet. Two curves for Ni in olivine are given for comparison with Figure 6. Numbers in brackets indicate sources of the data, as follows: (1) Cygan & Lasaga (1985), (2) Harrison & Wood (1980), (3) Duckworth & Freer (1981), (4) Loomis (1975), (5) Cohen *et al.* (1988), (6) Clark & Long (1971), (7) Miyamoto & Takeda (1983), (8) Burton *et al.* (1995), and (9) Ganguly *et al.* (1995).

less than two orders of magnitude, although there are discrepancies in the slope of the curves between different determinations for both Mg and Ca.

The situation for pyrope-rich garnet is less encouraging (Fig. 8), with few measurements (although some have been carried out at elevated pressures), large disagreements among the various estimates, and no data on high-field-strength elements such as Zr and Ti. Some measurements of Fe–Mg and Mg diffusion yield curves essentially identical to those measured in olivine, but the estimates of Loomis (1975) and Cohen *et al.* (1988), the latter based on geological arguments, differ significantly. The experimental data of Harrison & Wood (1980) for Sm suggest more rapid diffusion of the rare-earth elements (*REE*) (and, by inference, Y) than the geologically based estimates of Cohen *et al.* (1988) and Lanzirotti (1995); the higher rates would imply that Y should diffuse more rapidly than Fe–Mg, which appears to be inconsistent with the observational data presented above.

Some inferences about relative diffusivities of individual elements can be drawn by comparing zoning profiles for these elements in single grains of garnet. The most suitable examples are those where S-shaped concentration profiles suggest the presence of an originally sharp boundary that has been modified by diffusion during annealing. Figure 9 shows zoning profiles, generalized to smooth lines (*cf.* Fig. 2), for two grains of garnet in a sheared high-T lherzolite xenolith; both have a homogeneous core and an overgrowth defined by Cr zoning, but the sense of Cr zoning in the two grains is different, suggesting that the sample consists of two domains, juxtaposed by shearing (Griffin *et al.* 1989b).

Breaks in the Cr profiles are taken as marking the

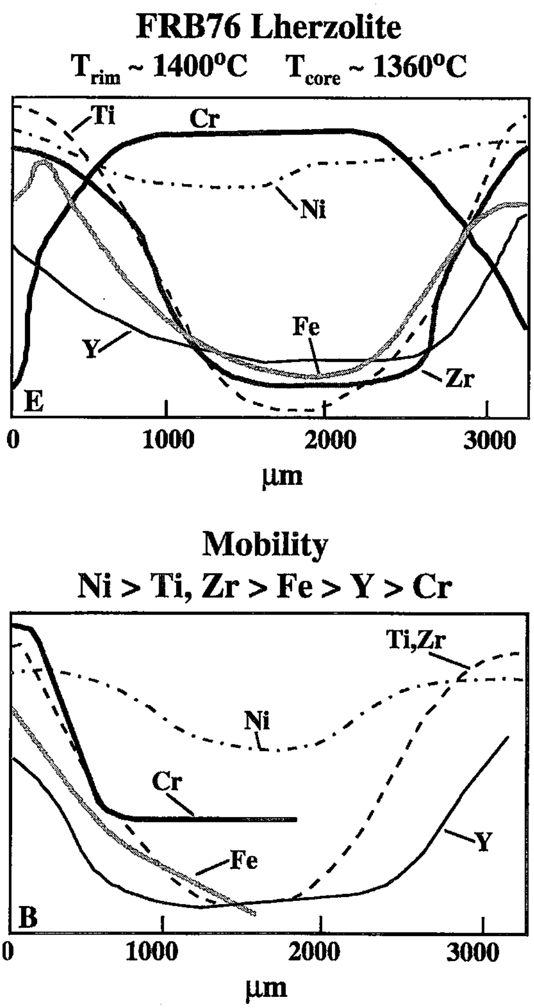

FIG. 9. Generalized zoning profiles (*cf.* Fig. 2) for a range of elements in two grains of garnet (E and B) from sheared high-T lherzolite FRB76 (after Griffin *et al.* 1991; *cf.* Fig. 2).

inner edge of the overgrowth rim; the relative immobility of Cr in mantle garnet is apparent in many other studies of peridotite (*e.g.*, Smith & Boyd 1987, 1992). The well-defined profiles of Ti and Zr preserve inflections near the Cr breaks, whereas the Fe profile is smooth. Hence, the diffusion coefficients of the tetravalent high-field-strength elements seem to be substantially less than that of Fe, but greater than that of Cr. In FRB76B, the profile for Y (a suitable proxy for the heavy *REE*) is shorter than those of Ti and Zr, but in garnet FRB450 (Griffin *et al.* 1989b), Y gradients are defined for distances similar to those for Ti and Zr, suggesting that Y has similar mobility. Ga data, although less definitive, suggest that its mobility is low and similar to that of Cr. Cr may diffuse so slowly because in garnet from lherzolite, at least, its movement must be coupled with that of Ca, as evidenced by the Cr–Ca correlation characteristic of such garnet (Sobolev 1977, Wood & Nicholls 1978).

Although geothermobarometry of such xenoliths suggests that the high-T sheared xenoliths from kimberlites have been subjected to heating during metasomatism, the Ni profiles of the garnet are relatively flat. This feature suggests that Ni diffused faster than any of the other elements listed here, although this conclusion is tentative, because we do not know the detailed thermal histories of most samples. Hickmott (1989, and pers. comm.) has studied garnet FRB76B by ion microprobe. His data indicate that diffusion lengths for Fe and Mn are similar; those for Y and Ca are similar to one another, but shorter than those of Ti and Zr. V, like Cr, apparently has been relatively immobile. At the high temperatures recorded by these grains of pyrope, mobilities of many major elements appear to be roughly similar (Smith & Boyd 1992). However, relative mobilities of cations over the temperature range 1200–1400°C, inferred from these data, appear to be as follows, from faster to slower: Ni > Fe ≈ Mn > Ti ≈ Zr ≥ Y (and heavy *REE* by proxy) ≈ Ca > Cr ≈ Ga ≈ V.

Canil (1994) has explained discrepancies between natural and experimental data on Ni partitioning between olivine and garnet by suggesting that Ni may diffuse through pyrope-rich garnet faster than (Fe, Mg) at low T (<1000°C), but more slowly at high T. However, this suggestion is not borne out by the zoning data [see discussion by Griffin & Ryan (1996)]. As noted above, the general lack of significant zoning of Ni in garnet from high-T peridotite xenoliths suggests that Ni diffuses more rapidly than other elements that do show zoning, at temperatures on the order of 1300–1400°C. The similarity in the length of Fe, Ni and Mn profiles in samples such as UO78 (Fig. 4) suggests that these elements diffuse at similar rates during cooling at *ca.* 1100°C.

Medaris *et al.* (1990) used the zoning of Fe and Mg toward olivine inclusions in garnet from the Mohelno peridotite massif to model cooling histories from *ca.* 1150° to *ca.* 600°C. Figure 10 shows the zoning profiles for both (Fe, Mg) and Ni; a smooth curve shows the Fe–Mg profile expected for a simple cooling model, and the more sharply broken profile observed is interpreted by Medaris *et al.* (1990) as indication of a two-stage cooling history related to uplift. A similar break is shown by the Ni data. The Nickel Temperature corresponds closely to the T measured by olivine–garnet Fe–Mg thermometry (O'Neill & Wood 1979) down to a distance of 40 µm from the contact, where the proton beam began to excite Ni in the olivine. Projection of the Ni zoning trend to the olivine contact

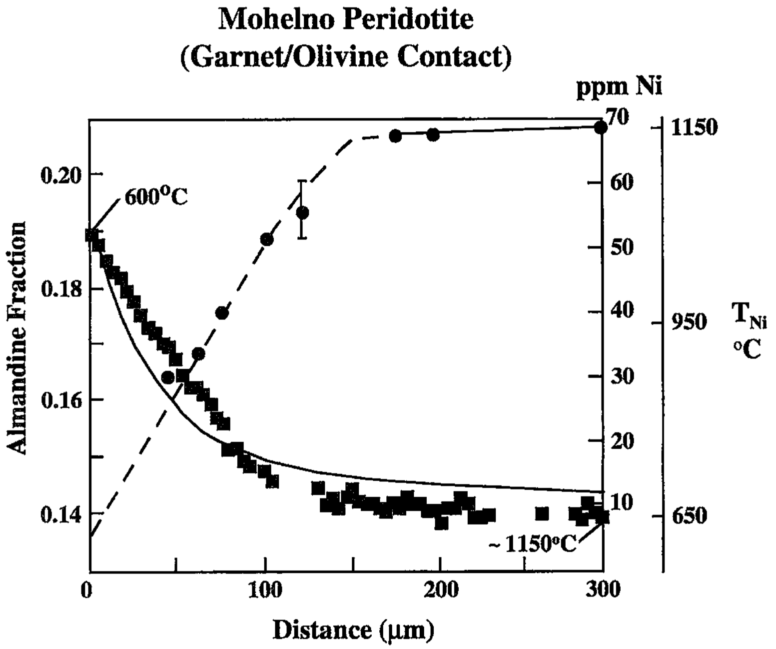

FIG. 10. Compositional profiles of Ni (circles) and Fe–Mg (squares) in garnet, approaching contact with an olivine inclusion (on left). Scale of Nickel Temperature (T_{Ni}) is given on right, and temperatures determined by Fe–Mg partitioning between olivine and garnet are shown at the two ends of the Fe–Mg traverse (from Medaris *et al.* 1990). Typical uncertainty of PMP Ni measurements is shown by the error bar on the 125 µm point. Smooth curve around Fe–Mg data illustrates the profile expected from a single-stage cooling history.

yields a temperature within error of the olivine–garnet Fe–Mg temperature determined for the contact. This finding suggests that the diffusion rates of Ni and Fe–Mg in garnet are similar between *ca.* 1150° and *ca.* 600°C, and that the equilibration of Ni between olivine and garnet remains rapid down to quite low temperatures.

Garnet is isotropic and lacks cleavage, so models involving volume diffusion probably are appropriate, except where material is introduced along a network of cracks (Matthews *et al.* 1992). Comparisons of gradients in coexisting grains of pyroxene and garnet provide insights into the relative mobilities of cations in these minerals, although volume diffusion may less commonly be the limiting process in pyroxene equilibration. Just as in garnet, zonation of pyroxene is commonly defined better for Cr than for any other element (*e.g.*, Bodinier *et al.* 1987). Opper & Seck (1989) noted that diffusivities for Cr and V in orthopyroxene were distinctly lower than for Ca, concordant with our observations for garnet. Comparative *D* values between clinopyroxene and garnet, however, are not well established.

The limited data on rates of volume diffusion in clinopyroxene suggest that *D* values for Ca, Mg and Sm at 1000°C are lower by three orders of magnitude than those for pyrope (Fig. 11). If these rates are relevant to metasomatic situations such as those seen in the xenoliths of high-T sheared peridotite, we would expect clinopyroxene in these xenoliths to display even more marked zoning than the garnet. Instead, we typically find that the clinopyroxene contains high levels of Sr and Zr, consistent with metasomatic enrichment, but that zoned grains are relatively rare (Smith *et al.* 1993). Assuming that the experimental determinations of *D* in pyroxene are correct, this general lack of pronounced zoning suggests that volume diffusion across whole grains is not the controlling factor in metasomatic enrichment of pyroxene grains, as it appears to be in garnet. Instead, rapid diffusion along kink bands and cleavages may allow widespread penetration of each pyroxene grain, limiting lattice diffusion to volumes between these high-mobility paths, perhaps to distances on the order of micrometers. Such rapid-diffusion paths have been documented by X-ray mapping of orthopyroxene in

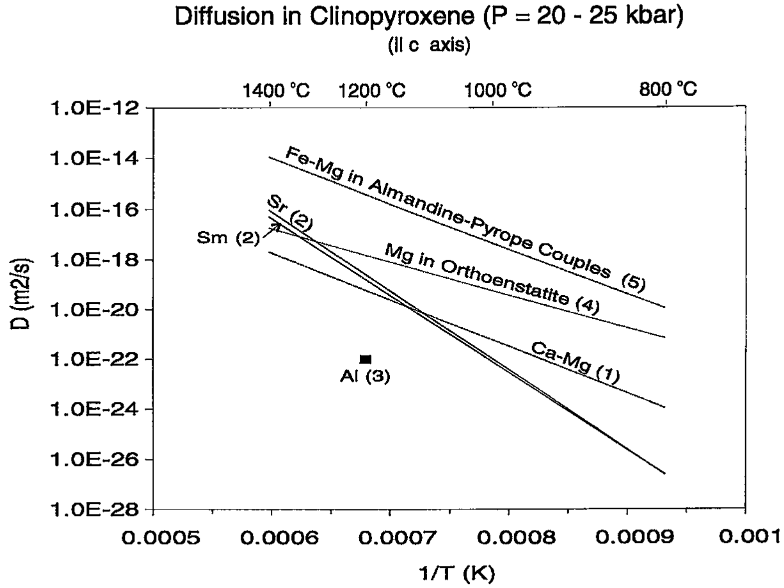

FIG. 11. Experimental data on D as a function of T for pyrope (from Fig. 8) and pyroxene. Numbers in brackets indicate sources of the data, as follows: (1) Brady & McCallister (1983), (2) Sneeringer *et al.* (1984), (3) Sautter & Harte (1990), (4) Schwandt *et al.* (1994), and (5) Duckworth & Freer (1981).

spinel peridotite (Ozawa & Takahashi 1995).

This review emphasizes the scattered and inadequate body of quantitative data on diffusion coefficients for trace elements in mantle minerals, at T and P conditions relevant to mantle processes. Given the potentially large amount of information on these processes contained in trace-element zoning profiles in mantle-derived garnet and other phases, an effort should be made to acquire high-quality measurements of diffusion coefficients, and thus to promote quantitative modeling. The information on relative diffusivities summarized here may serve as a guide to the selection of the most productive targets for such experimental work. In addition, these relative diffusivities may provide insights into the mobilities of other trace elements, such as the *REE*, Pb and U, that are critical for the geochronology of metamorphic garnet in crustal rocks, but for which diffusivities only can be estimated from geochronological arguments (*e.g.*, Cohen *et al.* 1988, Burton *et al.* 1995).

CONCLUSIONS

Studies of trace-element zoning in mantle-derived minerals provide important constraints on the nature and time scales of metasomatic processes and thermal events in the upper mantle. Zoning data on pyrope-rich garnet in peridotite xenoliths restrict some metasomatic processes to geologically short time-spans prior to the eruption of the host magmas, and suggest that the metasomatism is somehow genetically connected to the magmatic events or their precursors. Modeling of heating and cooling rates using Ni-in-garnet thermometry suggests that the heating observed in high-T xenoliths is a transient phenomenon associated with local intrusion of magma bodies. The relative length of zoning profiles for different elements in single grains of garnet indicates that diffusion coefficients, at temperatures over the range 1200–1400°C, decrease in the order Ni > Fe ≈ Mn > Ti ≈ Zr ≥ Y (and heavy *REE* by proxy) ≈ Ca > Cr ≈ Ga ≈ V. Analyses of zoning profiles in samples cooled from a high temperature suggest that diffusion rates of Ni are equivalent to those of (Fe, Mg) down to temperatures near 600°C.

ACKNOWLEDGEMENTS

We thank F.R. Boyd and L.G. Medaris, Jr. for providing important samples, Don Hickmott for access to his ion-probe data, Roger Mason for providing the impetus to write this paper, and Roger Mason and Bruce Watson for helpful and perceptive reviews. This is contribution no. 75 from the Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC).

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Received November 15, 1995; revised manuscript accepted September 28, 1996.