

Young geochemical features in cratonic peridotites from Southern Africa and Siberia

NOBUMICHI SHIMIZU

Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, U.S.A.

Abstract—Some geochemical features such as chemical zoning and mineral phase disequilibria are commonly observed in cratonic peridotite xenoliths and cannot be ancient, based on kinetics of diffusion and inter-phase chemical exchange under mantle conditions. These features can occur during interaction between infiltrating melt and lithospheric peridotites immediately prior to eruption. In cases where mineral zoning is found to be associated with grain growth from melt, bulk major and trace element compositions of peridotites can be modified substantially. It is suggested that estimation of the chemical composition of cratonic lithosphere without detailed considerations of mineralogy, isotopic compositions and trace element petrography can be misleading.

INTRODUCTION

Although antiquity of cratonic lithosphere is beyond any doubt, it is still unclear which geochemical features observable today are indeed ancient, and whether whole-rock major and trace element compositions of peridotite xenoliths are representative of pristine continental lithosphere.

The purpose of this paper is to examine geochemical features commonly observed in cratonic lithospheric peridotites which cannot be ancient, and discuss mechanisms for creating them and their potential significance in estimating lithospheric compositions.

ISOTOPIC EVIDENCE FOR ANTIQUITY OF CRATONIC LITHOSPHERE

The most convincing evidence for antiquity of cratonic lithosphere comes from the Re-Os systematics of lithospheric peridotite xenoliths (e.g., WALKER *et al.*, 1989; PEARSON *et al.*, 1995a; 1995b). Their typically unradiogenic Os isotopic compositions clearly indicate long-term Re-depleted systems. It is noticeable that ancient Re-depletion model ages (>2 Ga) occur widely, independent of: (1) host kimberlite eruption ages, (2) "stratigraphic" locations of peridotites, and (3) "fertility" of peridotites. It follows then that fertile high-temperature garnet peridotites sampled at the deepest level and depleted spinel peridotites at the shallowest level were both originated as residual peridotites left after ancient melt extraction processes. Therefore, their present-day differences in bulk chemical compositions (for examples, abundances of basaltic components) could have resulted from later (i.e. younger) processes.

A closer look at the data reveals, however, that there are peridotites that possess young Re-depletion model ages (for example, 0.5 Ga for PHN 1611 from Thaba Putsoa; 0.9 Ga for BD 2125 from Mothae; PEARSON *et al.*, 1995a), suggesting that the lithosphere has been an open system with respect to the Re-Os system. Os is a compatible element in mantle-melt systems and is enriched in residual peridotites. It is why Os isotopic composition is generally insensitive to later metasomatic processes and preserves major melt extraction events. The fact that the lithosphere has been open

to the Re-Os system has important implications for potential changes in major element compositions resulted from younger events.

For incompatible elements such as Sr and Nd, the open system character of lithospheric systems makes isotopic systematics difficult to interpret.

Clinopyroxenes separated from low-temperature peridotites often display unradiogenic Nd isotopic compositions ($\epsilon_{Nd} < 0$ at the time of host kimberlite eruption), indicating isotopic growth in LREE-enriched reservoirs (e.g., MENZIES and MURTHY, 1980; HAWKESWORTH *et al.*, 1983; among many others). RICHARDSON's discovery that peridotitic diamond inclusion garnets and subcalcic concentrate garnets possess extremely unradiogenic Nd with ancient model ages also made significant contributions to the consolidation of the notion that cratonic lithosphere is LREE-enriched (RICHARDSON *et al.*, 1984; 1985).

However, as discussed by numerous investigators, it is difficult to constrain timing of the enrichment process based on the Sm-Nd systematics. WALKER *et al.* (1989) calculated T_{DM} (a model age for an enrichment event by which Sm/Nd ratios observed in rock or mineral samples were acquired in an initially depleted mantle) for peridotites from the Kaapvaal lithosphere and concluded that LREE enrichment occurred in the mid-Proterozoic between 1.0 and 1.7 Ga. As shown by RICHARDSON *et al.* (1985), some low-temperature garnet peridotites show gross isotopic disequilibrium between clinopyroxene and garnet, two major repositories of Sm and Nd, and true meaning of the Sm-Nd model ages is uncertain. The reader is referred to detailed accounts of the isotopic systematics by PEARSON (1999, this volume).

The complexity of the situation is very well illustrated by the following example of a low-temperature garnet peridotite from the Premier kimberlite, which involves observations on the Re-Os system, the Sm-Nd mineral isochron work (both by PEARSON *et al.*, 1995a), and trace element petrography using an ion microprobe. Peridotite FRB1350 has $T_{DM} = 2.2$ Ga, and clinopyroxene, orthopyroxene and garnet mineral separates form a well-constrained Sm-Nd isochron with an age (1.15 ± 0.04 Ga) that agrees within uncertainties with that of host kimberlite eruption. The initial $^{143}\text{Nd}/^{144}\text{Nd}$ has $\epsilon_{Nd}(T) = +0.7$. The mineral isochron was interpreted as a result of continued isotopic exchange equilibria among minerals until quenching and closure of the system by eruption. The initial isotope ratio suggests isotopic growth in a system with nearly chondritic

but slightly depleted Sm/Nd since T_{DM} (PEARSON *et al.*, 1995a).

This seemingly straightforward situation becomes complicated by a close inspection of the rock. Figure 1 is a photomicrograph, showing that garnet occurs in cluster with clinopyroxene and displays "radial fingering" into olivine. This "replacement" texture is not expected for a rock in which long-term isotopic exchange equilibrium appears to have occurred. Ion probe analysis of garnet and clinopyroxene (Table 1) reveals that both clinopyroxene and garnet are zoned, that clinopyroxene also displays grain-by-grain heterogeneity for Sr by a factor of 2, and that partitioning of elements including Ti, Zr and REE between clinopyroxene and garnet is significantly deviated from equilibrium values obtained for high-temperature garnet peridotites as shown by SHIMIZU *et al.* (1997a). Figure 2 illustrates chondrite-normalized REE patterns for garnet and clinopyroxene, showing that "the finger-tip" and center of garnet have LREE-depleted typical garnet patterns that are parallel to each other but displaced by a factor of about 4. Clinopyroxene is highly LREE-enriched. The figure also shows that the ion probe data agree well with isotope dilution data on mineral separates (PEARSON *et al.*, 1995a). Mineral zoning and mineral phase disequilibria are completely inconsistent

with a simple interpretation of continued equilibrium based on the Sm-Nd mineral isochron.

One might invoke "metasomatism" immediately before eruption. However, it would be extremely fortuitous that metasomatism modified elemental abundances and distribution in minerals without changing the isotopic characteristics. If pre-existing minerals reacted with metasomatic agent and chemical heterogeneities resulted, isotopic characteristics would also be partly modified. Unless the metasomatic agent had identical Nd isotopic composition with the rock, the partial modification would result in isotopic zoning of minerals, and most likely fail to generate an isochron. In addition, incomplete melt/mantle reaction often produces "chromatographically fractionated" REE patterns in these minerals as described frequently in literature (*e.g.*, NAVON and STOLPER, 1987; BODINIER *et al.*, 1990; TAKAZAWA *et al.*, 1992; SHIMIZU *et al.*, 1997a). Alternatively, clinopyroxene and garnet, major repositories for REE, are entirely new phases grown as products of a young process that occurred immediately before eruption. The trace element data in connection with the petrographic evidence strongly suggest that clinopyroxene and garnet represent fresh precipitates from infiltrating melt and crystallized under disequilibrium conditions. Thus, mineral zoning and non-equilibrium ele-

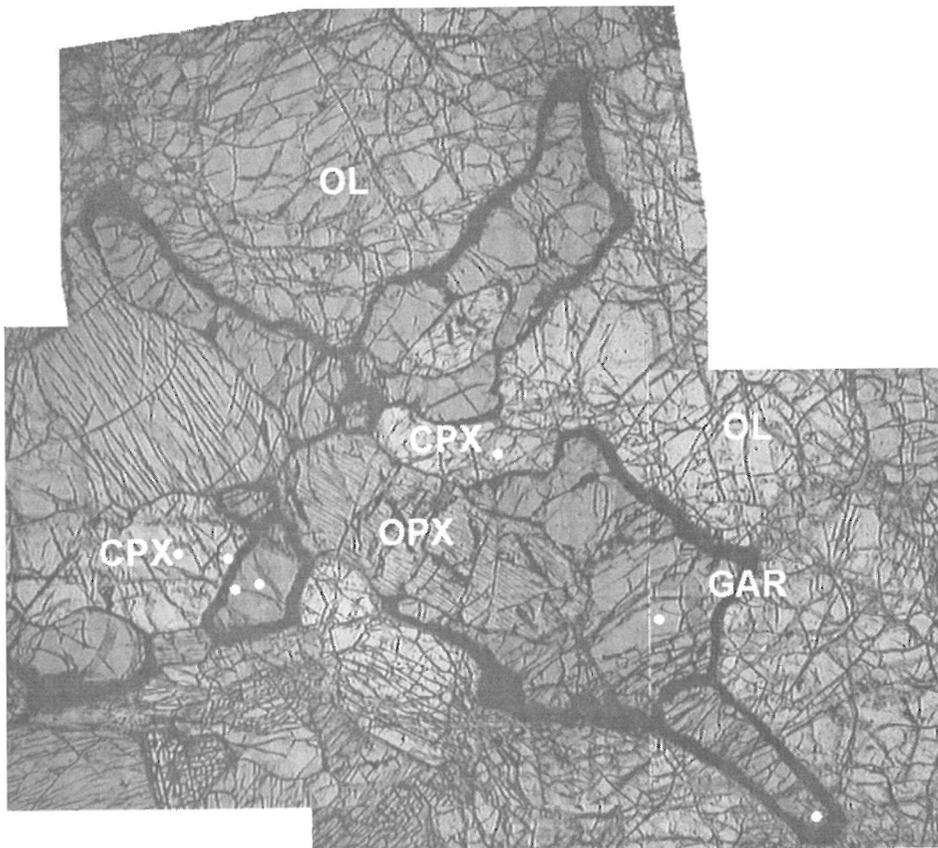


FIG. 1. Photomicrograph of FRB 1350. Garnet grains are surrounded by dark kelyphitic rims and show radial fingering into olivines. Clinopyroxene and orthopyroxene grains accompany garnet grains. The field of view is approximately 1 cm \times 1 cm. Positions analyzed for trace elements are indicated.

Table 1. Trace element abundances (ppm) in garnet and clinopyroxene in FRB1350

Sample ID	Garnet1 (Finger)	Garnet1 (Center)	Garnet2 (Edge)	Garnet2 (Center)	Cpx 1	Cpx 2
La	0.0072	0.0596	0.011	0.0113	18.3	16.0
Ce	0.0596	0.331	0.0622	0.0917	30.0	29.2
Nd	0.159	0.513	0.163	0.297	8.75	8.81
Sm	0.106	0.481	0.0936	0.177	1.42	1.31
Eu	0.033	0.183	0.0488	0.0548	0.241	0.318
Dy	0.282	0.756	0.312	0.511	0.251	0.169
Er	0.252	0.964	0.418	0.539	0.117	0.0778
Yb	0.399	1.72	0.622	0.792	0.0897	0.0652
Ti	113	70.1	77.8	—	117	122
V	237	197	186	—	293	292
Cr	18980	16409	17645	—	8627	8687
Sr	0.2	0.3	0.2	—	198	104
Y	2.0	7.0	3.3	—	0.4	0.4
Zr	1.9	3.0	1.9	—	4.8	4.4

The edge of Cpx 2 has Sr concentration of 135 ppm; concentrations of other elements are same as center.

ment distributions reflect dynamic nature of the process, which is also manifested in texture.

The Nd isotopic equilibrium among minerals at the time of crystallization is a direct consequence of precipitation from a melt. Parallel REE patterns observed for garnet cores and rims show that growth occurred under non-Rayleigh conditions, because closed system surface equilibrium crystallization would have resulted in decrease in compatible HREE with progress of the process. A hypothetical melt in equilibrium with garnet rim (*e.g.*, Grain 1, finger) would have ~ 0.08 ppm Yb [with $D_{Yb}(\text{garnet-melt}) = 4$], unrealistically low concentrations for any kimberlitic/carbonatitic/basaltic melts. Garnet cores (*e.g.*, Grain 1 center), on the other hand, yield concentrations within ranges (albeit near

the low end of the spectrum) for kimberlites. It may then be suggested that melt infiltration resulted in precipitation of garnet finger, and crystal growth continued inward as the system evolved toward equilibrium. Similar arguments based on the trace element partitioning suggest clinopyroxene growth under disequilibrium conditions.

This rock contains 32.8 modal % orthopyroxene, typical for Kaapvaal low-temperature garnet peridotites (BOYD, 1995). Although the evidence suggests the juvenile character of clinopyroxene and garnet in FRB1350, it is not possible to decide when the formation of extra-orthopyroxene occurred. Systematic relationships between trace element abundance patterns and orthopyroxene texture and mode should provide an important insight into this question, but no effort was made here in this direction.

It is important to note here that for FRB1350, LREE-enriched whole-rock pattern is generated by new minerals, and for both isotopically (Nd) and trace element patterns there is no evidence for a previous LREE-enriched environment.

The significance of the observation on FRB1350 is that important mineral phases such as clinopyroxene and garnet can be entirely new and the Sm-Nd system of a rock is completely dominated by a new material. Furthermore, if the present interpretation is correct, the major element composition of peridotites was also significantly modified, *i.e.*, most of CaO and Al₂O₃ in the rock are newly introduced by precipitation of clinopyroxene and garnet.

The observation can be extended for the majority of peridotites whose mineral phases possess non-ancient Nd model ages, due either to young "resetting events" or to young formation ages for REE repository minerals. For them, evidence for antiquity of the cratonic lithosphere is not easily detectable with respect to the Sr-Nd systematics.

How about subcalcic diamond inclusion garnets (*e.g.* RICHARDSON *et al.*, 1984), and subcalcic garnets in garnet dunites (PEARSON *et al.*, 1995)? Whether or not these are indeed ancient is a topic of debate (*e.g.* SHIMIZU and SOBOLEV, 1995; RICHARDSON and HARRIS, 1997; JACOB *et al.*, 1998; PEARSON *et al.*, 1995b; among others), and beyond the scope of this paper.

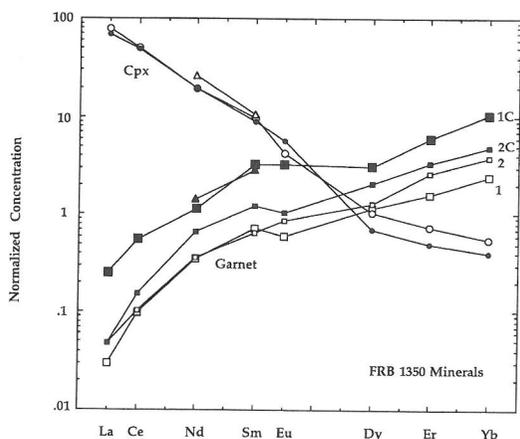


FIG. 2. Chondrite-normalized REE patterns for garnet and clinopyroxene grains in FRB 1350. Patterns marked 1, 1c, 2 and 2c are, respectively, garnet 1 (finger), garnet 1 (center), garnet 2 (edge) and garnet 2 (center). Also shown are Sm and Nd concentrations in clinopyroxene and garnet separates determined by isotope dilution (PEARSON *et al.*, 1995a).

It is important to note here that similar young geochemical and mineralogical changes have been observed in spinel peridotite xenoliths derived from oceanic lithosphere (e.g., HAURI *et al.*, 1993; HAURI and HART, 1994), which these authors have attributed to interaction between erupted magma and lithospheric wall-rocks.

GEOCHEMICAL FEATURES THAT CANNOT BE ANCIENT AND THEIR ORIGINS

Chemical zoning in garnet

Chemical zoning has been commonly observed in garnet in high-temperature garnet peridotites from both Archean and Proterozoic lithospheres. Smith and co-workers reported detailed trace element studies on numerous garnets (e.g., SMITH and EHRENBERG, 1984; SMITH and BOYD, 1987; 1989; GRIFFIN *et al.*, 1989; SMITH *et al.*, 1991). In most cases, core-to-rim zoning profiles for many elements share characteristic "S-shape" patterns in which a homogeneous core and a homogeneous but chemically distinct mantle are connected by a transition zone where concentrations vary smoothly (for example, see Fig. 12 of SMITH *et al.*, 1991). GRIFFIN *et al.* (1989) argued that the S-shaped concentration profiles are best explained by a mechanism in which a homogeneous overgrowth with distinct chemistry was attached to a pre-existing homogeneous core and subsequent diffusion produced smooth profiles. Zoned garnets from the Thumb, the Colorado Plateau, showed apprecia-

ble rimward increase in Ni associated with S-shaped zoning for other trace elements. SMITH *et al.* (1991) argued that the Ni zoning was produced during heating of lithosphere prior to melt infiltration by which garnet overgrowth was produced.

It is important to note that overgrowths are often enriched in Fe relative to cores and suggest that infiltrating melt may also have exchanged Mg/Fe with pre-existing garnet cores.

Diffusion profiles provide time-scales in which diffusional "relaxation" took place. Using diffusion coefficients for Ti and Zr estimated on the basis of similarity in profile lengths of these elements with that of Fe ($D = 10^{-17} \text{ m}^2/\text{sec}$), GRIFFIN *et al.* (1989) estimated relaxation time-scales for temperatures (1200 ~ 1300°C) to be as short as 60 ~ 240 years. It is highly significant to note that important geochemical and mineralogical modifications of at least some lithospheric peridotites occurred immediately before eruption.

Garnet zoning can also be produced without overgrowth as discussed by GRIFFIN *et al.* (1989), when a rim of initially homogeneous crystal was exposed to melt and elements were exchanged at the surface and subsequently "penetrated" into the interior by diffusion. An example can be seen in a high-temperature garnet peridotite, Uv246/89, from Udachnaya (SHIMIZU *et al.*, 1997a). Figure 3a illustrates that Ti and Zr concentrations increase approximately by a factor of 10 toward

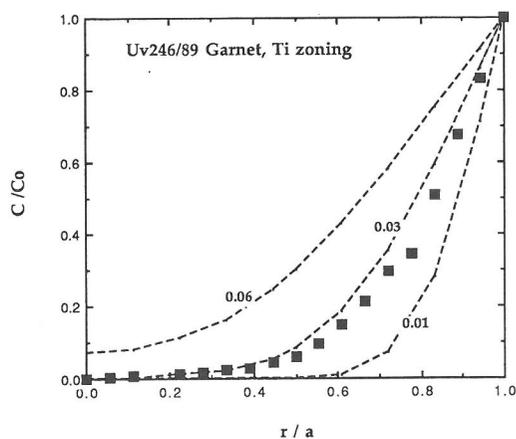
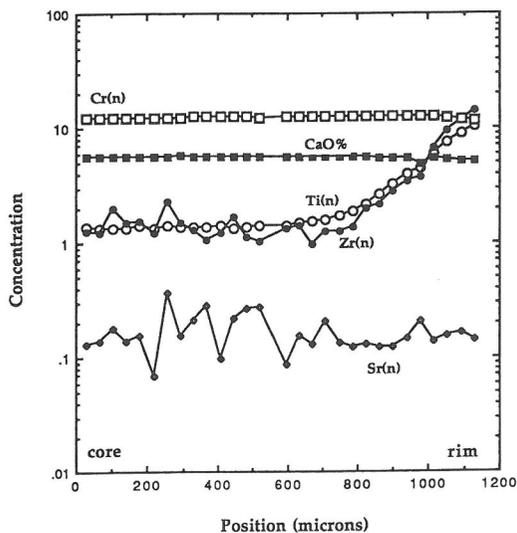


FIG. 3a. Left. Core-to-rim zoning of Cr, CaO, Ti, Zr, and Sr in garnet in Uv 246/89 from Udachnaya [data from SHIMIZU *et al.* (1997a)]. CaO is in wt%, other elements are expressed as chondrite-normalized values.

FIG. 3b. Right. Ti zoning expressed in terms of non-dimensional concentration vs non-dimensional position (r/a) in a sphere. $C/C_0 = (C - C_{\text{minimum}})/(C_{\text{maximum}} - C_{\text{minimum}})$. Dashed curves are for model diffusion gradients for different Dt/a^2 values. Note that Ti zoning (solid squares) can be approximated by a curve with $Dt/a^2 = 0.03$.

the rim over a distance of $600\mu\text{m}$. Figure 3b shows that the Ti zoning can be adequately fit with a model for diffusional penetration into a sphere with constant surface composition with $Dt/a^2 = 0.03$, where D is diffusion coefficient, a grain radius and t time. Using $D = 10^{-17} \text{ m}^2/\text{sec}$ and $a = 600 \mu\text{m}$, the diffusion profile was produced within 35 years, a time-scale comparable to those of GRIFFIN *et al.* (1989). Recent experimental results by GANGULY *et al.* (1998) show that Fe diffusion coefficients in pyrope-almandine garnets under mantle conditions ($P > 3.0 \text{ GPa}$, $T > 1200^\circ\text{C}$) range from $3.3 \times 10^{-19} \text{ m}^2/\text{sec}$ to $2.7 \times 10^{-18} \text{ m}^2/\text{sec}$. Even with these values, time scales for diffusional relaxation for the Uv246/89 garnet are within 10^3 years.

More complex chemical zoning was observed for garnets with subcalcic core and calcic rim (*e.g.*, SHIMIZU *et al.*, 1994; SHIMIZU *et al.*, 1997b). Figure 4 shows a rim-to-rim transect of a garnet in dunite (PHN5600) from Jagersfontein, South Africa (SHIMIZU *et al.*, 1994). Note that CaO, Zr and Ti show S-shaped patterns mentioned above. M~HREE (not shown) also show similar zoning patterns. With these

elements alone, an interpretation similar to that of GRIFFIN *et al.* (1989) would apply. Zoning patterns of other elements shown here (Sr and Ce) require an alternative interpretation, however. Rimward increase in CaO, Zr and Ti coincides with initial decrease followed by increase in Sr, Ce and Nd (not shown for clarity). These temporal variations cannot be explained by diffusional relaxation, but indicate that chemical zoning was formed during crystal growth. Whether or not the surface of the crystal was in equilibrium with crystallizing medium (melt ?) during growth can be assessed by trace element abundances and abundance patterns. For instance, the low-Ca core of PHN5600 (see Fig. 4) is uniform for Zr ($\sim 30 \text{ ppm}$) and Ti ($\sim 40 \text{ ppm}$). Using D_{Ti} (garnet-melt) = 0.7 and D_{Zr} (garnet-melt) = 2, an "equilibrium" melt should have 57 ppm Ti and 15 ppm Zr with $\text{Ti}/\text{Zr} = 3.8$. These values are clearly far too low to resemble any realistic kimberlitic/carbonatitic/basaltic melts, suggesting that distribution of these elements during growth of the core was not in equilibrium. Strongly sinusoidal REE patterns in the core

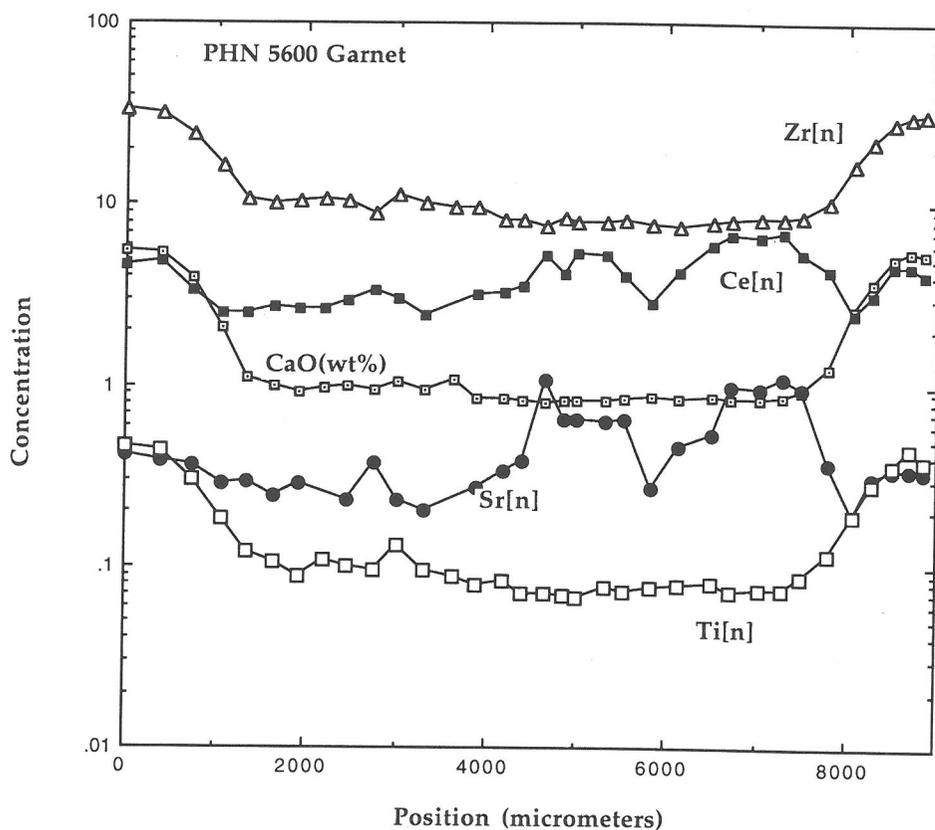


FIG. 4. Rim-to-rim zoning patterns for Zr, Ce, CaO, Sr, and Ti in garnet from dunite PHN 5600 from Jagersfontein, South Africa. Data from SHIMIZU *et al.* (1994). CaO is in wt%, other elements are in chondrite-normalized values.

are also indicative of non-equilibrium conditions. SHIMIZU *et al.* (1997b) attempted to explain continuous variations of REE patterns in a zoned garnet from dunite (Uv4/76) from the Udachnaya kimberlite pipe with a kinetic model.

Although it is difficult to determine whether there was a hiatus between core and rim growth, judging from large variations in trace elements in the low-Ca core (for example, the Sr concentration varies approximately by a factor of 8 in Uv4/76 and a factor of 5 in PHN5600 over a distance of 500 μm), diffusion kinetics suggests that core formation age must be young. These observations also reinforce the fact that significant addition of "garnet component" happened as a result of a young process.

Mineral phase disequilibria

Minerals in direct contact under mantle conditions would maintain elemental exchange equilibrium. General success of geothermo/barometry demonstrates that peridotite minerals are generally in equilibrium with respect to major elements involved.

BREY (1989) pointed out, however, that low-temperature garnet peridotites from Kaapvaal and Udachnaya possess characteristic mineral chemical features which cannot be explained by equilibrium. Based on experimental mineral chemistry data obtained for primitive mantle compositions, he concluded that garnets in low-temperature peridotites from Kaapvaal and Udachnaya have too low CaO for a given Cr_2O_3 to be in equilibrium with clinopyroxene, and attributed it as a "remnant of an exsolution history from orthopyroxene in earlier higher temperature harzburgites."

RICHARDSON *et al.* (1985), GUNTHER and JAGOUTZ (1994; 1997), among others, have found that many low-temperature garnet peridotites show isotopic disequilibrium between clinopyroxene and garnet, two major repositories of elements in the Sm-Nd and Rb-Sr systems. This phenomenon is generally attributed to metasomatism shortly before eruption. It is unclear, however, whether one of the phases formed during metasomatism without equilibrating with the other or to what extent isotopic and elemental exchange occurred between the metasomatic agent and pre-existing mineral phases.

SHIMIZU *et al.* (1997a) reported large variations of trace element abundance patterns in clinopyroxene and garnet in low-temperature peridotites from Udachnaya. Their results can be summarized as follows: 1) distribution of REE between clinopyroxene and garnet is not consistent with equilibrium partitioning between these minerals; 2) variations of REE patterns in garnet are much greater than those of

clinopyroxene, and appear to be the cause for the mineral phase disequilibria; and 3) temporal variations of REE patterns follow systematic progressive changes, in which garnet appears to lag behind clinopyroxene.

Figure 5 shows schematically how garnet REE patterns change during reaction between garnet and infiltrating melt in much the same way as the clinopyroxene-melt relationship discussed previously (*e.g.*, BODINIER *et al.*, 1990; TAKAZAWA *et al.*, 1992). As melt is not in equilibrium with "initial" garnet, reaction begins and REE patterns in garnet are modified progressively from 1 to 5 (and to eventual "equilibrium" pattern). Initially, LREE respond faster than other REE due to their low partition coefficients. As their concentrations approach equilibrium values, reaction rates decrease to the level below the rate for MREE. Continuous reaction would thus produce a spectrum of REE patterns with a continuous "wave" sweeping from LREE toward HREE. During this process of chromatographic changes, sinusoidal REE patterns are produced. Clinopyroxene in the same rock reacts with melt much faster and is almost completely equilibrated when garnets are still sinusoidal. Figure 6 illustrates REE patterns for garnets from Udachnaya peridotites which qualitatively represent various stages of modification. For example, Uv 25/91 corresponds to the stage 1, followed by a

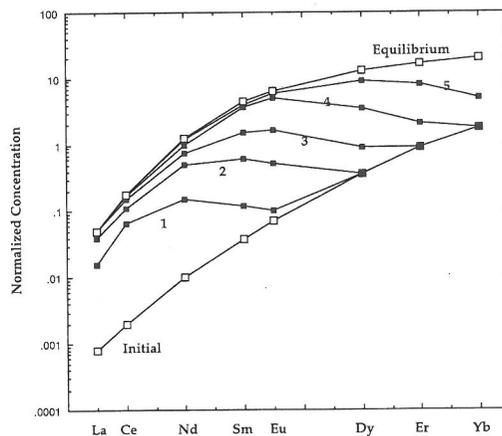


FIG. 5. Diagram showing schematic variations of REE patterns in garnets at various stages of melt/rock reaction process. Concentrations for initial and equilibrium garnets were selected to clarify evolution of patterns from an early stage of reaction (shown as stage 1) to an advanced stage (stage 5) of the reaction process. For simplicity of the discussion, a series of progressive change is shown in the figure. Starting with different initial and equilibrium patterns, varieties of patterns can be produced by this process. Natural examples shown in Fig. 6 reflect variabilities in initial and melt chemistry.

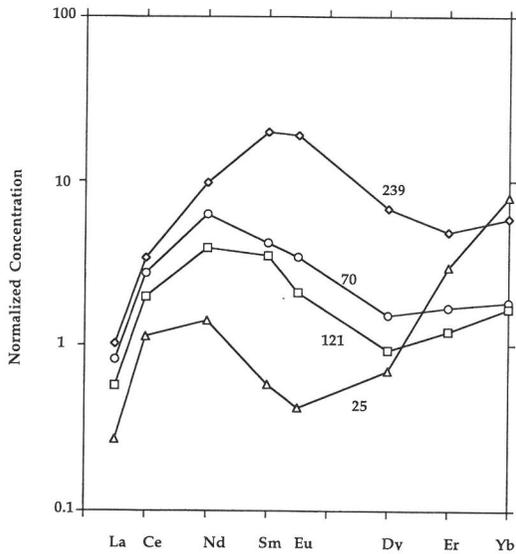


FIG. 6. Chondrite-normalized REE patterns for garnets in Udachnaya peridotites (data from SHIMIZU *et al.*, 1997a), qualitatively representing various stages of garnet-melt interaction as shown in Fig. 5.

series of patterns for Uv 121/91, 70/92 and 239/89. Because of the difference in their kinetic behavior, clinopyroxene-garnet phase disequilibria emerge, and indeed they occur typically with garnets with sinusoidal REE patterns.

Although the rate of elemental exchange at mineral phase interface is not well understood, disequilibria of the magnitude observed in Udachnaya peridotites would not survive for a long geological time scale under mantle conditions, and therefore the melt/rock reaction process which is responsible for the REE variations and disequilibria can also be considered young. Because the sinusoidal REE patterns are interpreted to be of "reactive" origin, pre-metasomatic rocks were garnet-bearing. It is difficult to determine whether growth of garnet accompanied the reaction, however.

HOW SIGNIFICANT CAN THESE FEATURES BE IN ESTIMATING GEOCHEMICAL/PETROLOGICAL CHARACTERISTICS OF SUBCRATONIC LITHOSPHERE?

The discussion presented above demonstrates that melt/rock reaction process (mantle metasomatism) could precipitate new cpx and/or garnet and thus abundances of CaO and Al₂O₃ in bulk-rock peridotites could be a predominantly young feature. When overgrowth occurs on pre-existing garnet, an increase in garnet mass can be estimated by the width of the

overgrowth zone relative to the radius of the original core. Assuming that garnet is approximated by a spherical geometry, if an overgrowth zone has a width 1/4 of the radius of the core, *i.e.*, the overgrowth is about 20% of the given radius, the mass of garnet in the rock is roughly doubled by the overgrowth. This suggests that amounts of "garnet component" added to a rock in which measurable garnet overgrowth occurred can be substantial. For instance, zoning patterns of Uv4/76 garnet (see Fig. 10 of SHIMIZU *et al.*, 1997b) suggest that the high-Ca rim has a comparable width with the diameter of the low-Ca core. This amounts to a 20-fold increase in garnet mass in the rock. Not only Al₂O₃, but also Cr₂O₃, CaO and FeO in the rock are thus significantly increased during the process. In order to assess pre-metasomatic chemical composition, it is therefore crucial to determine whether garnet was added to the rock via a young process and if so, how much.

Another important consideration is pervasiveness of melt/rock reaction process. Is metasomatism lithosphere-wide or is it restricted to the immediate vicinity of melt pathways?

As shown by NAVON and STOLPER (1987), BODINIER *et al.* (1990), FREY *et al.* (1991), TAKAZAWA *et al.* (1992), among others, lithospheric melt/rock reaction typically produces a spectrum of chromatographically fractionated REE patterns in cpx (and spinel peridotite whole-rocks). Magnitude of metasomatic changes is determined by mass balance between melt and rock in the system, and are thus a function of space and time. The farther away from melt pathway, the smaller the melt/rock ratio and so is degree of metasomatic changes.

If metasomatism is caused by lithosphere-wide melt infiltration from below, a positive correlation might be expected between depth and degree of metasomatism. Shallow spinel peridotites would be much less metasomatized than deep garnet peridotites. It would also result in depth-wise homogenized isotopic compositions of Nd and Sr; garnet peridotites would be isotopically more homogenous than spinel peridotites. It might also be expected that individual kimberlite pipes might yield xenolith suites that are similar to each other with respect to mineralogy and geochemical characteristics.

None of the above is true for any cratonic lithosphere studied thus far. Large isotopic variations in peridotite minerals, particularly those in low-temperature peridotites, have been well documented (*e.g.*, RICHARDSON *et al.*, 1985; MENZIES and MURTHY, 1980; HAWKESWORTH *et al.*, 1983; WALKER *et al.*, 1989; PEARSON *et al.*, 1995a; 1995b; among many others). On the other hand, high-temperature garnet peridotites contain minerals that are typically in iso-

topic equilibrium and their $\epsilon_{Nd}(T)$'s cluster in a small range from +3.5 to +4.5, independent of host kimberlite eruption age (Premier, 1.15 Ga; Udachnaya, 0.35 Ga; other Kaapvaal kimberlites, 0.090 Ga; references cited above).

Trace element abundance patterns vary widely in clinopyroxene and garnet (e.g., SHIMIZU *et al.* 1997a). For both Udachnaya (SHIMIZU *et al.*, 1997a) and Premier (HASSLER *et al.*, 1996) clinopyroxenes in shallow spinel peridotites display a spectrum of REE patterns ranging from "spoon"-shaped and sharply inflected (at Nd) ones indicating relatively low grades of metasomatism to LREE-enriched completely re-equilibrated ones. Clinopyroxene and garnet in low-temperature garnet peridotites from these (and other) localities are equally variable. Trace-element variations observed in garnets in the Udachnaya suite (SHIMIZU *et al.*, 1997a) are particularly large, ranging from very depleted patterns with little indication of metasomatism (those in garnet harzburgites which resemble orthopyroxene in REE patterns) to variously sinusoidal ones to completely re-equilibrated patterns.

These observations strongly indicate that melt/rock reaction might be spatially confined to the immediate vicinity of melt pathways in which various degrees of metasomatism were established mainly as a function of distance from melt pathways. The fact that a large spectrum of metasomatism is sampled by kimberlite pipes with ≤ 1 km diameter is a good indication for scale lengths of the process.

The occurrence of phlogopite, a typical mineral phase for "modal metasomatism," in peridotites presents additional evidence for localization of metasomatism. A statistical work by SCHULZE (1995) on the Kaapvaal peridotites and unpublished data by N. Pokhilenko on the Premier xenolith suite suggest that phlogopite occurs in about 30% of both spinel and garnet peridotites.

It is therefore suggested that young geochemical features derived from melt/rock reaction can alter not only incompatible trace element abundances but also major element compositions of rocks especially with respect to elements such as CaO and Al_2O_3 . As discussed above, increase in garnet mass as a result of the melt/rock reaction process could be substantial. Trace element evidence suggests that melt/rock reaction appears to be restricted to the immediate vicinity of melt pathways. Large isotopic variations in peridotite minerals lend support for this contention. This makes one wonder whether the lithospheric mantle 10 km away from any kimberlite pipe might be geochemically and mineralogically different, and whether sampling by kimberlites and basalts might seriously bias our views of the lithosphere. The ob-

servations and geochemical evidence presented here certainly suggest that estimation of the chemical composition of cratonic lithosphere without detailed considerations of mineralogy, isotopic compositions and trace element petrography can be grossly misleading.

Acknowledgments—More than 25 years ago at Geophysical Laboratory, I met Joe and my career in geochemistry of peridotites began. He introduced me to sheared and granular nodules, pyroxene geotherms, and garnet dunites. He has been a leader, a great critique, and a good listener to many of us. I sincerely hope our relationship continues for many years to come. I thank Yingwei Fei for organizing the Boyd Symposium and for giving me an opportunity to celebrate Joe's contributions to science. I also thank Ken Burrhus and Graham Layne for continued support for the IMS 3f ion probe at Woods Hole Oceanographic Institution. Nick Sobolev and Nick Pokhilenko contributed greatly in providing samples from Udachnaya and other parts of the Siberian cratonic root. Constructive reviews by E. Hauri and G. Pearson are gratefully acknowledged.

REFERENCES

- BODINIER J. L., VASSEUR G., VERNIERS J., DUPUY C., AND FABRIES J. (1990) Mechanisms of mantle metasomatism: geochemical evidence from the Lherz orogenic peridotite. *J. Petrol.* **31**, 597–628.
- BOYD F. R. (1995) Origins of peridotite xenoliths: Major element considerations. In *High Pressure and High Temperature Research on Lithosphere and Mantle Materials* (eds. G. RANALLI, F. RICCI LUCCHI, C. A. RICCI, AND T. TROMSUNDORFF), University of Siena, Italy.
- BREY G. P. (1989) Geothermobarometry for lherzolites: Experiments from 10 to 60 kb, new thermobarometers and application to natural rocks. *Habil. Thesis*, Tech Hochsch. Darmstadt, Germany, Chapter VIII, pp. 166–217.
- FREY F. A., SHIMIZU N., LEINBACH A., OBATA M., AND TAKAZAWA E. (1991) Compositional variations within the lower layered zone of the Horoman Peridotite, Hokkaido, Japan: Constraints on models for melt-solid segregation. *J. Petrol. Special Lherzolite Issue*, 211–227.
- GANGULY J., CHENG W., AND CHAKRABORTY S. (1998) Cation diffusion in aluminosilicate garnets: experimental determination in pyrope-almandine diffusion couples. *Contrib. Mineral. Petrol.* **131**, 171–180.
- GRIFFIN W. L., SMITH D., BOYD F. R., COUSENS D. R., RYAN C. G., SIE S. H., AND SUTER G. F. (1989) Trace-element zoning in garnets from sheared mantle xenoliths. *Geochim. Cosmochim. Acta* **53**, 561–567.
- GUNTHER M. AND JAGOUTZ E. (1994) Isotopic disequilibria (Sm/Nd, Rb/Sr) between minerals of coarse grained, low temperature peridotites from Kimberley floors, southern Africa. *Proc. 5th Intern. Kimberlite Conf.*
- GUNTHER M. AND JAGOUTZ E. (1997) The meaning of Sm/Nd apparent ages from kimberlite-derived, coarse grained low temperature garnet peridotite from Yakutia. *Russ. Geol. Geophys.* **38**, 229–239.
- HASSLER D. R., SHIMIZU N., AND BOYD F. R. (1996) The trace element geochemistry of peridotites from the Premier kimberlites, South Africa, *EOS* **77**, F816.
- Hauri E. H., SHIMIZU N., DIEU J. J., AND HART S. R. (1993)

- Evidence for hotspot-related carbonatite metasomatism in the oceanic upper mantle. *Nature* **365**, 221–227.
- HAURI E. H. AND HART S. R. (1994) Constraints on melt migration from mantle plumes: A trace element study of peridotite xenoliths from Savai'i, Western Samoa. *J. Geophys. Res.* **99**, 24301–24321.
- HAWKESWORTH C. J., ERLANK A. J., MARSH J. S., MENZIES M. A., AND VAN CALSTEREN P. (1983) Evolution of the continental lithosphere: evidence from volcanics and xenoliths in southern Africa. In *Continental Basalts and Mantle Xenoliths* (eds. C. J. HAWKESWORTH AND M. J. NORRY), pp. 111–138, Shiva Publ. Ltd.
- JACOB D. E., JAGOUTZ E., AND SOBOLEV N. V. (1998) Neodymium and strontium isotopic measurements on single subcalcic garnet grains from Yakutian kimberlites. *Neues Jahrb. Min.*, in press.
- MENZIES M. A. AND MURTHY V. R. (1980) Enriched mantle: Nd and Sr isotopes in diopsides from kimberlite nodules. *Nature* **283**, 634–636.
- NAVON O. AND STOLPER E. (1987) Geochemical consequences of melt percolation: the upper mantle as a chromatographic column. *J. Geol.* **95**, 285–307.
- PEARSON D. G. (1999) Evolution of cratonic lithospheric mantle: an isotopic perspective. This volume.
- PEARSON D. G., CARLSON R. W., SHIREY S. B., BOYD F. R., AND NIXON P. H. (1995a) Stabilisation of Archaean lithospheric mantle: A Re-Os isotope study of peridotite xenoliths from the Kaapvaal craton. *Earth Planet. Sci. Lett.* **134**, 341–357.
- PEARSON D. G., SHIREY S. B., CARLSON R. W., BOYD F. R., POKHILENKO N. P., AND SHIMIZU N. (1995b) Re-Os, Sm-Nd, and Rb-Sr isotope evidence for thick Archaean lithospheric mantle beneath the Siberian craton modified by multistage metasomatism. *Geochim. Cosmochim. Acta* **59**, 959–977.
- RICHARDSON S. H., GURNEY J. J., ERLANK A. J., AND HARRIS J. W. (1984) Origin of diamonds in old enriched mantle. *Nature* **310**, 198–202.
- RICHARDSON S. H., ERLANK A. J., AND HART S. R. (1985) Kimberlite-borne garnet peridotite xenoliths from old enriched subcontinental lithosphere. *Earth Planet. Sci. Lett.* **75**, 116–128.
- RICHARDSON S. H. AND HARRIS J. W. (1997) Antiquity of peridotitic diamonds from the Siberian craton. *Earth Planet. Sci. Lett.* **151**, 271–277.
- SCHULZE D. J. (1995) Low-Ca garnet harzburgites from Kimberley, South Africa: Abundance and bearing on the structure and evolution of the lithosphere. *J. Geophys. Res.* **100**, 12513–12526.
- SMITH D. AND EHRENBERG S. N. (1984) Zoned minerals in garnet peridotite nodules from the Colorado Plateau: Implications for mantle metasomatism and kinetics. *Contrib. Mineral. Petrol.* **86**, 274–285.
- SMITH D. AND BOYD F. R. (1987) Compositional heterogeneities in a high-temperature lherzolite nodule and implications for mantle processes. In *Mantle Xenoliths* (ed. P. H. NIXON), pp. 551–561, Wiley and Sons, New York.
- SMITH D. AND BOYD F. R. (1989) Compositional heterogeneities in minerals of sheared lherzolite inclusions from African kimberlites. *Geol. Soc. Aust. Spec. Publ.* **14**, 709–724.
- SMITH D., GRIFFIN W. L., RYAN C. G., AND SIE S. H. (1991) Trace element zonation in garnets from The Thumb: Heating and melt infiltration below the Colorado Plateau. *Contrib. Mineral. Petrol.* **107**, 60–79.
- SHIMIZU N., BOYD F. R., SOBOLEV N. V., AND POKHILENKO N. P. (1994) Chemical zoning of garnets in peridotites and diamonds. *Mineral Mag.* **58A**, 831–832.
- SHIMIZU N. AND SOBOLEV N. V. (1995) Young peridotitic diamonds from the Mir kimberlite pipe. *Nature* **375**, 394–397.
- SHIMIZU N., POKHILENKO N. P., BOYD F. R., AND PEARSON D. G. (1997a) Geochemical characteristics of mantle xenoliths from the Udachnaya kimberlite pipe. *Russ. Geol. Geophys.* **38**, 205–217.
- SHIMIZU N., SOBOLEV N. V., AND YEFIMOVA E. S. (1997b) Chemical heterogeneities of inclusion garnets and juvenile character of peridotitic diamonds from Siberia. *Russ. Geol. Geophys.* **38**, 356–372.
- TAKAZAWA E., FREY F. A., SHIMIZU N., OBATA M., AND BODINIER J. L. (1992) Geochemical evidence for melt migration and reaction in the upper mantle. *Nature* **359**, 55–58.
- WALKER R. J., CARLSON R. W., SHIREY S. B., AND BOYD F. R. (1989) O, Sr, Nd and Pb isotope systematics of southern African peridotite xenoliths: Implications for the chemical evolution of subcontinental mantle. *Geochim. Cosmochim. Acta* **563**, 1583–1595.

