

The amount of pyroxene components dissolved in the garnet solid solution becomes greater as pressure increases (about 2 mol % at 50 kbar, 9 mol % at 75 kbar and 20 mol % at 100 kbar). The ratio of grossular to pyrope molecules in the garnet solid solution decreases as temperature increases. The net amount of pyroxene components dissolved in the garnet solid solution, however, seems to be relatively insensitive to temperature at a given pressure. The composition of garnet obtained at 75 kbar and 1200°C in the CMAS system is slightly enriched in grossular component than that of a natural garnet lherzolite run at the same P/T condition by Akaogi & Akimoto (1979).

Alumina contents of ortho- and clinopyroxenes coexisting with garnet are shown in Fig.3 and Fig.4, respectively. Alumina isoplethal lines for the pyroxenes were drawn in accordance with the reversed experimental results of Parkins & Newton (1981) at 20 to 40 kbar and 900° to 1100°C. The dT/dP slope and the

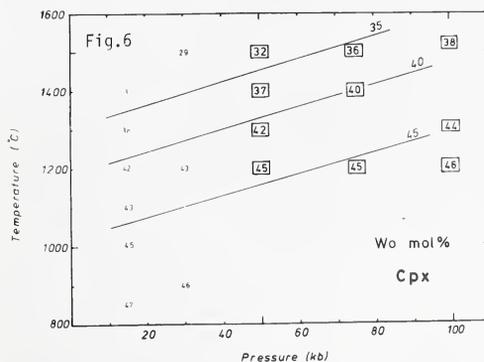
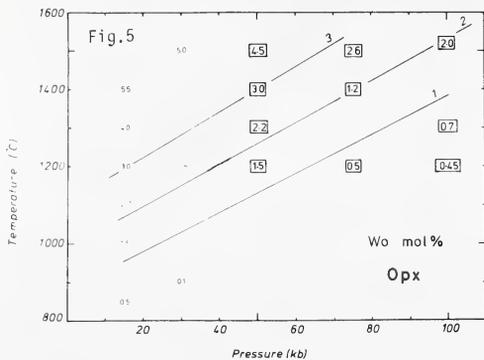
location of the isoplethal lines for orthopyroxene are in harmony with the estimation by Parkins & Newton but are not consistent with those of Akella (1976). The dT/dP slope of the isoplethal lines for clinopyroxene estimated by Parkins & Newton (broken lines in Fig.4), however, are appeared to be overestimated. In consequence of the gentle dT/dP slope of the isoplethal lines for clinopyroxene, the alumina content of clinopyroxene coexisting with orthopyroxene and garnet in the CMAS system is greater than that of orthopyroxene at pressures above about 50 kbar, whereas it is less aluminous than the latter at 30 kbar (Boyd,1970).

The pressure/temperature dependence of the Wo mol% (defined as  $100Ca/(Ca+Mg+0.5Al)$  in the CMAS system) of the coexisting ortho- and clinopyroxenes are shown in Fig.5 and Fig.6, respectively. Because pyroxenes in the present study contains very small amount of  $Al_2O_3$  (Fig.2), the Wo mol % of the pyroxenes in the CMAS system should not be different appreciably from those in the Al-free system. The present results, therefore, are compared with the reversed experimental data in the diopside-enstatite system by Mori & Green(1975) and Lindsley & Dixon (1976) in the pressure range 15 to 30 kbar. The pressure effect on the pyroxene solvus (Mori & Green,1975) is confirmed to be present at least up to 100 kbar in the light of the present results (Fig.5, Fig.6), and it follows that the equilibrium temperature estimation from the pyroxene solvus cannot be made without knowing the pressure of equilibration.

Given above observations, sheared garnet lherzolite xenoliths from Lesotho kimberlites (Nixon & Boyd,1973) are considered to have derived from the pressure range 50 to 70 kbar, whereas the granular garnet lherzolites from the same area may have originated at pressures below 50 kbar. The inferred pressures for the sheared lherzolite xenoliths are higher than the estimations by the previous authors (e.g. Boyd,1973; Parkins & Newton,1980).

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## H12 CHEMICAL AND ISOTOPIC CHARACTERISATION OF UPPER MANTLE METASOMATISM IN PERIDOTITE NODULES FROM THE BULTFOONTEIN KIMBERLITE

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Further major, trace element and Sr-isotope measurements, together with new REE and Nd-isotope measurements, have been made on samples from a much larger peridotite suite than that studied previously [1,2]. For present purposes the suite has been divided into garnet peridotites (GP) which contain no texturally equilibrated or "primary" phlogopite, garnet phlogopite peridotites (GPP), phlogopite peridotites (PP) and phlogopite K-richterite peridotites (PKP). The latter two groups contain no garnet, while diopside may or may not be present in all four groups. The above sequence was previously considered [1] to represent one of progressive mantle metasomatism, culminating in the devel-

opment of K-richterite. However, in view of the greatly increased number of PP rocks now obtained, which appear to have been essentially harzburgitic in original composition, it is questionable whether garnet removal was involved or is essential in the development of the PP and PKP groups. Most samples studied are coarse grained peridotites, with deformed textures being much more common in the GP and GPP groups. However three PKP samples have deformed textures in which both phlogopite and K-richterite have been involved in the deformation process, indicating that these minerals formed before kimberlite emplacement. Additional PKP samples include many more veined examples in which the

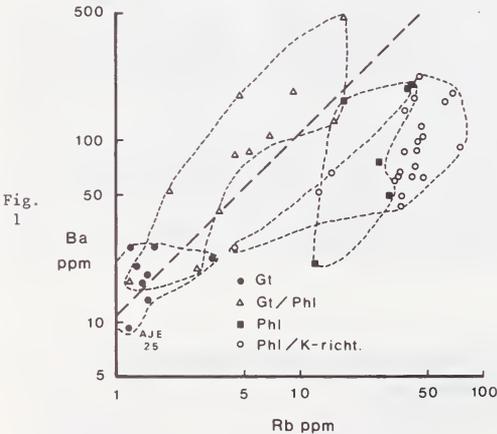
veins consist dominantly of K-richterite, usually enclosing corroded diopside, phlogopite and opaque oxides including Ba-K-Zr-Sr-rich titanate[1], attesting to the chemical nature of the infiltrative metasomatism. Some angular PKP samples have K-richterite-rich coatings on bounded surfaces, suggestive of vein infilling in cracks and fractures; although this may suggest that metasomatism has occurred on a localized scale, the K-richterite in the veined samples is not confined to the veins. Also, other larger samples which are not veined contain sparse texturally equilibrated K-richterite, indicative of subsolidus replacement. Microprobe major element analyses of metasomatic minerals from both veined and unveined samples provide no real evidence for chemical disequilibrium except for Cr, and thus the textural and mineralogical evidence indicates that the metasomatism has both occurred and attained local equilibrium on at least the scale of the samples studied.

Major and trace element data support previous conclusions about the depleted nature of all samples with respect to basaltic constituents such as Ca and Al, and their enrichment in incompatible elements, consistent with ideas that these samples represent mantle which has undergone basaltic removal prior to metasomatic enrichment [1,3]. Incompatible mantle enrichment generally increases in the sequence GP-GPP-PP-PKP, with the degree of enrichment varying as shown in Table 1.

Table 1 : Average enrichment factors for incompatible elements, normalized against nominal mantle concentrations. Number of samples in brackets.

	Rb	Ba	Nb	K	Sr	Zr
GP (9)	4.5	4.9	7.0	2.3	3.1	1.1
GPP (11)	19	23	16	15	7.7	2.4
PP (7)	73	30	12	49	5.8	2.8
PKP (22)	115	25	34	62	10	10

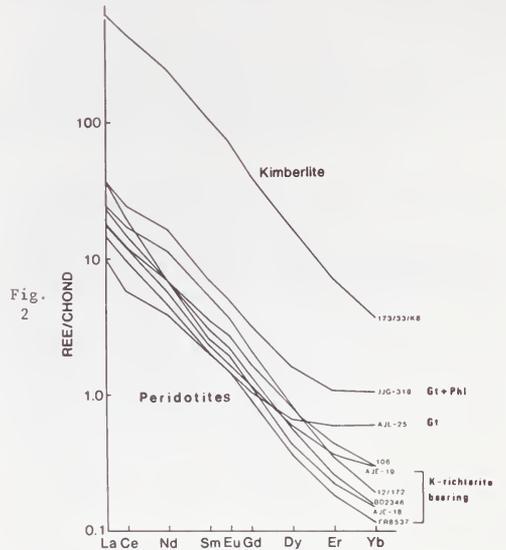
It is noteworthy that even the least metasomatised GP samples show incompatible element enrichment relative to the nominal mantle composition; however, the effects of possible kimberlite contamination are likely to be most apparent in these samples, since they lack primary mica or amphibole. While there is a general similarity in incompatible element enrichment in the other three groups, differences are apparent as shown most clearly by the Ba-Rb plot presented in Fig 1. (dashed line is Ba/Rb ratio for nominal mantle).



The distinction between the GP and GPP groups on the one hand, and the PP and PKP groups on the other cannot be due to original mineralogy and must reflect either two chemically distinctive metasomatic processes or a more complex situation (multi-stage) which must involve a systematic decrease in the Ba/Rb ratio of the metasomatising fluids with progressive metasomatism. The latter is demanded if the four peridotite groups are metasomatically related [1]. REE data presented in Fig. 2 show that all samples are enriched in LREE, but with the PKP group showing greater relative LREE enrichment, in view of their greater HREE depletion. (note that the PKP data suggest that alkali basalts and kimberlites could be produced from such a source without the necessity of involving garnet control).

Interpretation of the combined mineralogical, tex-

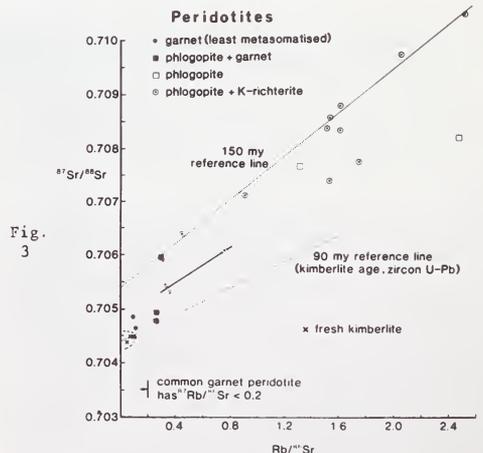
tural and chemical data follows conventional wisdom in assuming that amphibole-bearing samples are derived from shallower mantle depths. Our suggestion that garnet removal was not involved, or at least not



essential, in the development of the PP and PKP groups is substantiated by the REE data. We infer that the GP and GPP groups were metasomatised at greater depths than the PP and PKP groups, the original source rocks for the latter being more refractory (Al-poor harzburgite) in composition. The metasomatic fluids at the time of metasomatism were chemically distinctive but it is not yet possible to typify their source(s). The isotope evidence is now considered in order to further evaluate this question, the role of kimberlite activity, and the timing of metasomatism.

Previous Sr-isotope whole rock data [2] together with our new data, are shown in Fig. 3.

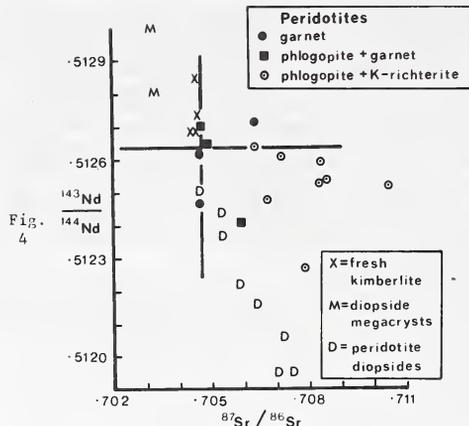
Although the new data show more scatter, they confirm the conclusion [2] that metasomatism is unrelated to kimberlite emplacement at 90 m.y., since all but two samples have distinctly higher initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios than the kimberlite at that time. The data allow an earlier association between some of the metasomatised samples and the(proto) kimberlite, or its source, in the upper mantle at 150 m.y., but further evaluation of the whole rock data is best assessed by reference to Sr-isotope data obtained on mineral separates, HCl leached whole rocks and minerals and associated leach solutions, and different portions of the same rock. General observations from three PKP rocks are : (i) K-richterite and/or diopside - phlogopite tie lines yield ages close to 90 m.y., indicating approximate isotopic equilibrium



at pipe emplacement (ii) progressively leached phlogopite fractions from the same separate show a dramatic increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Rb}/^{86}\text{Sr}$ , consistent with removal of calcite lamelli, but still define an age of 87 m.y., (iii) whole rock initial ratios are generally lower than for diopside or K-richterite, (iv) different portions of the same rock are not in isotopic equilibrium (see three circled points joined by a solid line in Fig. 3) and (v) leaching of one whole rock yielded a leached residue with a higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (.70546), and a leach solution with a lower initial ratio (.70503) than the original rock (.70525).

Summary of the above suggests that while the major Rb and Sr hosts, phlogopite, diopside and K-richterite are in approximate isotopic equilibrium, the rocks analysed also contain (exotic?) components with un-equilibrated strontium. These could be fluids of kimberlite origin (cf. "secondary" phlogopite selvages around garnets in GPP rocks) since mixing plots ( $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $1/\text{Sr}$ ) show that this is not due to the simple addition of the kimberlite itself. Rocks with lowest Rb and Sr would be most affected; least metasomatised GP rock AJE25 [2] has an initial ratio of .70473 while its diopside has an initial ratio of .70512, in support of the above contention. Thus, while some samples shown in Fig. 3 may have had their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios decreased slightly during kimberlite emplacement, the overall scatter is considered to be a consequence of mantle metasomatism which has affected all the peridotites analysed. This is emphasized by diopside analyses, which show high and variable  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Fig. 4) and Sr contents, 200-1000 ppm Sr [2]. The metasomatic fluids appear to have had variable  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr contents and while it is possible to infer a chemical distinction in terms of Rb/Sr between the garnet-bearing and garnet-free peridotites, no clear distinction can be made regarding the timing of metasomatic event(s). The significance of the 150 m.y. reference line in Fig. 3, considered [2] to be related to the cessation of Karoo igneous activity, remains an open question, and must be viewed in context with the Nd-isotope data presented in Fig. 4.

The  $^{143}\text{Nd}/^{144}\text{Nd}$  data confirm the enriched nature of the peridotites, consistent with previous data for peridotite diopsides [3], compared with present day Bulk Earth (intersecting lines in Fig. 4), kimberlites [4, this study] and diopside megacrysts [4]. The lower  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of peridotite diopsides, reported as being separates from the GPP group, with respect to the PKP rock data for a given  $^{87}\text{Sr}/^{86}\text{Sr}$  value (Fig. 4), might suggest that the former indicate an earlier metasomatic event than inferred for the PKP data, based on consideration of Nd model (CHUR) ages. However, the most "enriched" diopside has now been found to be



for a PKP, and not a GPP, rock.  $^{143}\text{Nd}/^{144}\text{Nd}$  data for this rock, two other GPP rocks and associated diopside and mica analyses [3] are as follows :

Sample	Type	Rock	Diopside	Phlogopite
CK26	GPP	.51265±2	.51223±2	.51185±7
CK27	GPP	.51270±2	.51250±3	.51224±10
CK32	PKP	.51227±1	.51195±4	-

The implied disequilibrium, together with the proximity of CK26 and CK27 to the kimberlite data (Fig. 4) suggest that, as with Sr, the whole rocks contain un-equilibrated Nd of kimberlite origin. Nevertheless, the relatively low  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in rock CK32, coupled with the even lower ratios in its diopside (and the phlogopites), suggest an earlier age of metasomatism than indicated by the Sr-isotope data, and it is possible that rock CK32 may contain two mantle metasomatic age components. More detailed isotopic work is clearly required before the timing of mantle metasomatism and the mantle differentiation events (melting, plume activity, subduction) possibly involved in the production of the metasomatic fluids, can be defined.

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VOLUME INSTABILITIES IN THE MANTLE AS A POSSIBLE CAUSE FOR KIMBERLITE FORM

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The occurrence of kimberlites and their mode of formation are evidence for punctual instabilities in the mantle which lead to the build-up of extremely high fluid pressures in an alkali-rich, mostly potassic environment. The geological setting points at the mantle underneath stable shields. The driving force is provided mainly by  $\text{CO}_2$  with additional  $\text{H}_2\text{O}$ , but the gases contained in fluid inclusions, for instance in diamonds, are varied. They comprise hydrocarbons, alcohols, oxygen, nitrogen, and others.

In order to understand kimberlites and kimberlite formation it is essential to gain an insight into the dynamic processes which occur under the confining pressure of the mantle. Obviously these processes are related to the presence and to the local accumulation of dissolved fluid phases. Hence, it is important to understand their dissolution mechanism, to know what solute species might form and what their role could be in the temporal evolution of a potential kimberlite source region.

The usual approach followed by petrologists is to analyze the phases present in a given

rock and to relate these findings to experimental data from high pressure laboratory studies. It is well known that carbonates and hydroxyl-bearing phases precipitate from  $\text{CO}_2$ - and  $\text{H}_2\text{O}$ -rich magmatic systems. It has therefore been concluded that carbonate ions,  $\text{CO}_3^{2-}$ , and hydroxyl ions,  $\text{OH}^-$ , are the prevalent solute species. This view has recently been challenged (FREUND 1981a and references cited therein) by the discovery of solute carbon in synthetic  $\text{MgO}$  and in natural, mantle-derived olivine which is not carbonate but a novel carbon species characterized by a valence state near zero and by a special nature of the chemical bond with the surrounding oxygens. The name "atomic carbon" has been coined for such dissolved carbon species which formally derive from the  $\text{CO}_2$  dissolution mechanism.

The "atomic carbon" dissolved in oxides and silicates has unusual properties, both chemical and physical unlike any carbonate carbon. The "atomic carbon" is capable of reacting with the lattice oxygen to give  $\text{CO}_2$  or  $\text{CO}$  depending on experimental parameters. With the hydrogen derived from lattice-bound  $\text{OH}^-$ , i. e. from the dissolution mechanism of  $\text{H}_2\text{O}$ , this carbon re-