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Introduction: An accompanying paper in this volume (Erlank and Rickard) concludes that a suite of potassic richterite bearing peridotites, mostly from the Bultfontein pipe, are the products of upper mantle metasomatism. It is suggested that the formation of K-richterite by metasomatic replacement marks the final stage of this process, with phlogopite <u>+</u> diopside forming in these nodules at an earlier stage. Many phlogopite bearing nodules which lack K-richterite are also interpreted as members of the same metasomatic suite, and since they are much more abundant than the K-richterite bearing varieties, a widespread upper mantle metasomatic event, specifically as indicated by nodules from the major pipes in the Kimberley area, is implied. The conclusions reached above are based on bulk rock, mineralogical and textural evidence and the purpose of this communication is to provide further evidence for the proposed mantle metasomatic process.

Sr-isotope relationships: Many of the peridotite nodules in kimberlite have such low concentrations of Rb and Sr (e.g. Barrett, 1975) that we would not advocate bulk rock isotopic analysis, in view of the potentially large contribution of Rb and Sr contamination from the enclosing kimberlite (e.g. Erlank, 1970). However, the metasomatic rocks chosen for study (freshest varieties from the Bultfontein pipe only have been used) contain much higher concentrations of Rb and Sr, with the bulk of these elements being contained in diopside, phlogopite and K-richterite. Thus we consider that the nett effect of potential kimberlite contamination is minimized in these nodules. Rb and Sr concentrations(in ppm), as measured by XRF ($2\delta \sim 0.5$ ppm for both elements) are: K-richterite bearing nodules, Rb = 34-75, Sr = 55-237; others, Rb = 17-31, Sr = 37-165. Mass spectrometric measurements were made on two Micromass 30 instruments (2 δ averaged 0.00007). The results are shown in the form of an isochron diagram in Fig. 1. Our interpretation is directed towards the questions of whether the isotopic data can provide evidence for the nature and timing of the metasomatic process, and to what extent the isotopic data are influenced by kimberlite emplacement. In passing, it is pertinent to note that most kimberlite nodules (i.e. the common peridotites lacking K-richterite and with minor phlogopite) have Rb/Sr ratios that are lower than the sample with the lowest Rb/Sr ratio in Fig. 1.

Reference to Fig. 1. shows that (a) all K-richterite bearing nodules but one define an apparent "age" of 148 ± 7 m.y. (1 δ) by York Model 1 regression, (b) the other K-richterite bearing nodule, together with two phlogopite-rich nodules have isotopic relationships which are roughly consistent with the age of pipe emplacement, i.e. 90 m.y., (c) the data for the garnet bearing sample plot near the intersection of the two age lines shown in Fig. 1 and (d) all nodules have Sr^{07}/Sr^{80} ratios markedly higher than that for fresh Bultfontein kimberlite (data from Barrett and Berg, 1975). Since the initial Sr^{87}/Sr^{80} ratios for all nodules at 90 m.y. are much higher than for the kimberlite it is clear that the metasomatic process is not related to kimberlite formation and intrusion. Thus we infer that the isotopic relationships observed in the nodules are of mantle origin.

The 148 m.y. event implied in Fig. 1 is considered to represent the last time the six K-richterite bearing nodules involved comprised a single closed isotopic system, and we suggest that it indicates the Rb-Sr closure age for the postulated metasomatic process. We consider that the agreement of this age with the apparent cessation of Karroo intrusive activity at about 155 m.y. (Fitch and Miller, 1971) is highly significant. Furthermore, unpublished $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ measurements of Karroo basalts and dolerites from the central Karroo basin by one of us (AJE) are generally in the range 0.705 - 0.707. The initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio of 0.7054 at 148 m.y. for the K-richterite bearing nodules is within this range. Thus there may be a genetic connection between the postulated mantle metasomatic and Karroo events, with representatives of both indicating derivation from an isotopically modified mantle region.

Mass spectrometric analysis (by J.F. Minster) of co-existing phlogopite and K-richterite (supplied by K. Aoki) for one of the K-richterite bearing nodules plotting on the 148 m.y. line in Fig. 1 yields a two point age of 85 m.y. with initial $Sr^{87}/Sr^{80} = 0.7078$. This indicates approximate mineral isotopic equilibration on the scale of a hand specimen, from 148 m.y. until pipe emplacement, and is in agreement with the work of Barrett (1975), who noted that co-existing phlogopite and diopside from kimberlite nodules (K-richterite free) were in approximate isotopic equilibrium at pipe emplacement.

Two interpretations may be offered for the nodules which are aligned along the 90 m.y. reference line in Fig. 1. Either these are representative of a system (presumably smaller than that pertaining to the other nodules discussed above) which continued to equilibrate (approximately) until pipe emplacement or they are products of a younger mantle metasomatism just prior to, and unrelated to, the Bultfontein kimberlite emplacement. If the latter is true, then the two metasomatic events are of the same nature, with K-richterite being the last forming mineral in both sequences. The prima facie evidence is for the second interpretation given above.

<u>Sr content of diopsides</u>: Combination of the data given by Barrett (1975) and Shimizu (1975) for diopsides shows that those from discrete and sheared (Lesotho) nodules have lower Sr contents than those from granular nodules. There is also a tendency for the former to have lower Sr^{87}/Sr^{80} ratios when compared to the latter. As noted by Shimizu (1975), the high Sr contents of the diopsides from the granular nodules are difficult to explain because experimentally determined solid/liquid partition coefficients (D=0.05-0.08, Shimizu, 1974) indicate a very high Sr content for any magma or fluid that may have equilibrated with these diopsides. The concentrations implied (which could be at the percentage level) rule out any known type of basaltic magma, and only carbonatites are known to possess the necessary high Sr concentrations. The suggestion arises that the high Sr diopsides could have equilibrated with CO_2 (and Sr) - rich fluids within the upper mantle during the previously postulated metasomatic process.

A secondary ion mass spectrometric (SIMS) technique (Shimizu and Allegre, this volume) has been used for measuring the Sr content of diopsides, in order to monitor possible variations in concentration due to alteration and inhomogeneity between and within grains. Replicate analysis of different spots (~30-50µm) on the same grain, and of different grains from the same nodule. showed Sr to be homogeneously distributed within counting statistics $(2\delta = 5-10\%)$ for diopsides from all but two nodules. The SIMS data and published isotopedilution data for Sr in diopsides are shown in Fig. 2. Nodules which are considered to be representative of the metasomatised suite (phlogopite + richterite + garnet bearing) have much higher Sr contents in their diopsides that the least metasomatised peridotite nodule, which contains no primary phlogopite. Thus we consider that the SIMS data provide supporting evidence that the diopsides from the metasomatised suite acquired their high Sr contents by equilibration with Sr-rich fluids during the postulated metasomatic process. References: Barrett, D.R. (1975) Phy. Chem. Earth 9, 637; Barrett, D.R. and Berg, G.W. (1975) Phy. Chem. Earth 9, 619; Erlank, A.J. (1970) Carnegie Instit. Wash. Year Book <u>68</u>, 433; Fitch, F.J. and Miller, J.A. (1971) Bull. Volcanologique 35, 64; Kramers, J.D. (1977) Earth Planet. Sci. Lett. <u>34</u>, 419; Shimizu, N. (1974) Geochim. Cosmochim. Acta 38, 1789; Shimizu, N. (1975) Phy. Chem. Earth 9.

