Contact relationships between MARID rock and metasomatised peridotite in a kimberlite xenolith

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A rare kimberlite mantle xenolith displaying a direct contact relationship between a MARID rock and metasomatised peridotite is described. There is an abrupt textural transition from a MARID (phlogopite-K-richterite-diopside) portion, to a 2 cm rind of peridotite (olivine pseudomorphs-phlogopite-K-richterite-diopside-chromite). Small, but significant differences in mineral composition exist across the boundary, the most important of which are lower Fe/Mg ratios in the peridotite rind. Our interpretation is that MARID magmas crystallised and expelled fluids which metasomatised surrounding peridotite wall-rock, and the xenolith has sampled a cumulate-wall-rock contact of this nature.

INTRODUCTION

Ever since the classic paper by Dawson and Smith (1977) on the MARID (Mica-Amphibole-Rutile-Ilmenite-Diopside) suite of mantle xenoliths found in southern African kimberlites, there has been debate about the nature of the relationship between MARID nodules and the metasomatised peridotite xenoliths also brought to the surface by these kimberlites. Dawson and Smith (1977), debated whether MARID rocks might represent the product of "ultrametasomatism" of peridotite, or whether they were igneous cumulates crystallised from "kimberlitic" magmas. We report here data relevant to this debate, on a nodule (LD99) from Newlands kimberlite. This sample is a MARID rock which has attached to it a narrow rind of altered, metasomatised peridotite.

The Newlands kimberlite pipes are located 25 km north-west of Barkly West in the Cape Province of South Africa. Petrographically and isotopically the Newlands kimberlite is classified

as a Group II (micaceous) kimberlite, with a preferred emplacement age of 114 Ma (Smith, 1983). The pipes contain a large variety of crustal and mantle xenoliths (Daniels, 1980). With relatively few exceptions, metasomatised peridotite and MARID xenoliths have been found only in Group I (basaltic) kimberlites, and in particular from the Kimberley group of pipes. However, the Newlands pipes have produced several MARID nodules in recent years, and with the discovery of sample LD99, a fragment of metasomatised peridotite can be added to the list. The purpose of this communication is to document for the first time, a direct contact relationship between MARID rock (mantle liquid), and metasomatised peridotite (mantle wall-rock), in the same kimberlitic xenolith.

SAMPLE DESCRIPTION

Sample LD99 is a MARID nodule $30 \times 20 \times 20 \text{ cm}^3$ in size, with a remnant of peridotite attached to one side in the form of a ~2 cm wide

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Fig. 1. Line drawing illustrating textural relationships within nodule LD99, and the nature of the MARID-PKP contact. The contact is emphasised by the bold line, and alteration is omitted for clarity. R=K-richterite; P=phlogopite; D=diopside; Ol=olivine pseudomorphs comprising carbonate grains within a serpentine mesh texture. Diopside is further indicated by use of a speckled ornament. The small inclusions within diopside and K-richterite in the MARID portion are phlogopite.

rind. Textural relationships within each portion, and the nature of the contact are illustrated in Fig. 1. The whole rock is slightly deformed; many phlogopite grains are kinked or strained.

The MARID portion of the rock is fine to medium-grained and is rather altered—phlogopite has been leached to talc along cracks, and secondary carbonate is abundant. It mostly comprises interlocking square laths of greenish tinged phlogopite around 1 mm in size and cloudy, rounded, irregular shaped diopside grains with a more variable grainsize of 0.5–2 mm. Sparse medium to coarse (1–5 mm) subhedral grains of K-richterite are present. No ilmenite or rutile are present, but this is true of many rocks which have been classified as MARID in terms of their chemical composition and general appearance (Dawson and Smith, 1977; Waters, 1987a). Other MARID nodules from Newlands do contain these oxide minerals.

Roughly visually estimated modal proportions in volume % in the MARID portion of sample LD99 are: phlogopite 70–80, diopside 15–20, and K-richterite 2–3. There is a coarse-grained zone between the MARID and peridotite parts of the rock made up of phlogopite (grains up to 5 mm in size), which is in places intergrown with equally coarse diopside. The significance of this zone is not clear, but we cannot be certain that it is not simply a variation in texture within the MARID rock which happens to be situated in this position.

The peridotite rind has a rather different texture and mineralogy, and the transition between MARID and rind portions is fairly sharp, in spite of heavy alteration. Clearly recognisable relict olivine grain outlines and characteristic mesh-structured serpentine alteration, indicate that approximately 90% of the rind must originally have been olivine, although it is now

Table 1. Selected electron-probe mineral analyses in nodule LD99

Phlogopite:	MARID				PKP rind		
SiO ₂	43.28	42.74	42.79	42.86	42.21	43.19	42.91
TiO ₂	1.32	1.25	1.20	1.40	1.33	1.37	1.45
Al ₂ O ₃	11.04	10.49	11.33	10.67	10.12	10.14	10.24
Cr ₂ O ₃	0.36	0.32	0.46	0.22	0.33	0.39	0.17
FeO	5.36	5.28	5.44	5.70	5.23	4.76	5.16
MgO	23.94	24.70	23.86	24.08	24.59	24.92	24.79
Na ₂ O	0.21	0.13	0.20	0.16	0.18	0.23	0.26
K ₂ O	10.22	9.84	10.20	9.91	10.16	10.63	10.39
Total	95.73	94.75	95.48	95.00	94.15	95.63	95.37
mg	88.8	89.3	88.7	88.3	89.3	90.3	89.5
	c.1	r.1	c.2	c.3	c.1	c.2	c.3

K-richterite:	MARID				PKP rind			
SiO ₂	54.20	53.84	53.32	52.96	52.42	52.69	52.78	52.75
TiO ₂	0.68	0.73	0.80	0.89	0.86	0.85	0.91	0.85
Al ₂ O ₃	1.60	1.76	1.53	1.59	1.61	1.54	1.52	1.51
Cr ₂ O ₃	0.26	0.25	0.35	0.37	0.38	0.29	0.29	0.34
FeO	3.53	3.60	3.31	3.33	3.32	3.48	3.25	3.18
MgO	21.54	21.61	21.26	21.57	21.73	21.95	22.47	22.04
CaO	6.95	7.12	7.16	7.12	7.28	7.20	7.39	7.18
Na ₂ O	2.91	3.00	2.92	2.76	2.62	2.66	2.80	2.80
K ₂ O	5.55	5.48	5.64	5.71	5.80	5.80	5.83	5.75
Total	97.25	97.39	96.29	96.30	96.02	96.46	97.24	96.40
mg	91.6	91.4	92.0	92.0	92.1	91.8	92.5	92.5
	c.1	r.1	c.2	c.3	r.3	c.1	r.1	c.2

Diopside:	MARID				PKP rind			
SiO ₂	54.71	54.95	54.67	54.80	54.75	54.33	54.31	54.03
TiO ₂	0.22	0.22	0.22	0.23	0.21	0.23	0.24	0.25
Al ₂ O ₃	0.72	0.85	0.68	0.71	0.51	0.36	0.30	0.33
Cr ₂ O ₃	0.78	0.76	0.66	0.67	0.66	1.08	1.11	1.30
FeO	4.62	4.60	4.56	4.70	5.33	4.23	3.89	3.88
MnO	0.12	0.16	0.18	0.14	0.20	0.10	0.13	0.12
MgO	17.79	18.03	17.65	17.67	17.57	17.42	17.22	17.33
CaO	19.55	19.23	20.02	19.81	19.4	20.48	20.65	20.60
Na ₂ O	1.30	1.37	1.22	1.21	1.21	1.10	1.03	1.11
K ₂ O	0.04	0.06	0.05	0.06	0.09	0.04	0.04	0.04
Total	99.85	100.23	99.91	100.00	99.96	99.37	98.92	98.99
mg	87.3	87.5	87.3	87.0	85.4	88.0	88.8	88.8
	c.1	r.1	c.2	r.2	c.3	c.1	c.2	c.3

Miscellaneous:	talc ^a	phl ^b	chrom ^b
SiO ₂	54.75	39.58	0.00
TiO ₂	0.14	1.68	6.88
Al ₂ O ₃	0.60	10.99	1.20
Cr ₂ O ₃	0.34	1.03	46.94
FeO	5.34	6.44	31.78
MnO	0.03	n.d	0.48
MgO	26.38	26.04	11.58
CaO	0.49	n.d	n.d
Na ₂ O	0.18	0.05	n.d
K ₂ O	0.37	8.77	n.d
Total	88.62	94.58	98.86
mg	89.8	87.8	39.4

^atalc alteration of MARID portion; ^bphlogopite (phl) and chromite (chrom) in melt pool in PKP rind. Core and rim of grains indicated by c and r respectively; e.g. c.1 is core of grain 1. mg = $100 \times \text{Mg} / (\text{Mg} + \text{Fe}_{\text{total}})$; n.d = not detected.

Table 2. Comparison of mineral compositions in LD99 with those in other southern African MARID and PKP xenoliths

Phlogopite:	MARID			LD99M ave	LD99P ave	PKP		
	min	max	ave			min	max	ave
SiO ₂	40.70	43.52	42.00	42.92	42.77	40.01	44.30	42.72
TiO ₂	0.20	4.86	1.29	1.29	1.38	0.41	1.84	0.69
Al ₂ O ₃	8.22	11.68	10.33	10.88	10.17	9.55	11.98	10.82
Cr ₂ O ₃	0.01	0.46	0.14	0.34	0.30	n.d	0.54	0.34
FeO	4.86	12.27	7.14	5.44	5.05	2.12	5.39	3.87
MnO	0.01	0.11	0.03	n.d	n.d	n.d	0.08	0.02
MgO	21.24	26.68	23.79	24.14	24.77	24.50	29.10	26.24
CaO	n.d	0.22	0.02	n.d	n.d	n.d	0.39	n.d
Na ₂ O	0.03	0.44	0.16	0.18	0.22	n.d.	0.49	0.17
K ₂ O	6.63	10.83	9.81	10.04	10.39	8.77	11.07	10.01
Total	92.97	95.93	94.71	95.23	95.05	92.02	96.91	94.93
mg	77.7	91.0	85.6	88.8	89.7	89.3	95.7	92.4
N			80(27)	4	3			82(22)

K-richertite:	MARID			LD99M ave	LD99P ave	PKP		
	min	max	ave			min	max	ave
SiO ₂	52.32	56.83	54.48	53.35	52.74	53.55	56.60	55.37
TiO ₂	0.16	1.42	0.56	0.79	0.87	0.27	1.84	0.47
Al ₂ O ₃	0.22	1.97	1.14	1.62	1.52	0.13	1.79	0.98
Cr ₂ O ₃	n.d	0.49	0.18	0.32	0.31	0.12	1.18	0.49
FeO	2.73	6.17	4.18	3.42	3.30	1.33	3.45	2.33
MnO	n.d	0.13	0.05	n.d	0.03	n.d	0.22	0.04
MgO	19.66	23.21	21.32	21.54	22.15	22.00	23.90	22.75
CaO	5.58	7.49	6.76	7.13	7.26	5.09	7.65	6.69
Na ₂ O	1.63	4.48	3.40	2.84	2.75	3.25	4.72	3.88
K ₂ O	3.38	5.54	4.80	5.64	5.79	3.18	5.18	4.59
Total	95.56	97.96	96.87	96.65	96.70	95.58	98.60	97.62
mg	85.0	93.7	90.1	91.8	92.3	92.1	96.8	94.6
N			66(22)	5	3			72(26)

Diopside:	MARID			LD99M ave	LD99P ave	PKP		
	min	max	ave			min	max	ave
SiO ₂	53.86	55.06	54.39	54.74	54.22	54.07	55.65	54.87
TiO ₂	n.d	0.43	0.16	0.22	0.24	0.09	0.71	0.20
Al ₂ O ₃	0.04	1.59	0.59	0.70	0.33	0.16	0.59	0.36
Cr ₂ O ₃	0.08	1.78	0.50	0.71	1.16	0.82	3.60	2.53
FeO	2.89	7.05	5.07	4.72	4.00	1.93	3.78	2.66
MnO	n.d	0.24	0.13	0.15	0.12	n.d	0.11	0.05
MgO	13.68	17.74	16.04	17.74	17.32	15.79	18.16	16.82
CaO	19.21	23.81	21.41	19.64	20.58	19.20	22.02	20.60
Na ₂ O	0.51	2.83	1.47	1.25	1.08	1.15	2.20	1.72
Total	98.88	100.93	99.76	99.93	99.09	98.73	101.10	99.81
mg	77.6	91.3	84.9	87.0	88.5	89.3	94.2	91.6
N			38(13)	6	3			27(9)

Data ranges, where min=minimum, max=maximum, and ave=average, are given for primary-textured minerals from MARID and PKP xenoliths in southern African kimberlite pipes (largely Kimberley Group), and are taken from Erlank *et al.*, (1987), and Waters (1987). N=number of analyses, with number of samples analysed given in parentheses; mg=100×Mg/(Mg+Fe_{total}); n.d=not detected; Averaged data are given for LD99M (MARID portion of LD99), and LD99P (PKP portion of LD99).

totally replaced by secondary carbonate. Corroded, but uncarbonated grains of K-richterite, diopside and phlogopite ranging between 1 to 3 mm in size are present between the olivine pseudomorphs. Modal proportions in the rind are difficult to estimate because of the alteration, but are around 90 volume % olivine, and 1–4 volume % each of K-richterite, diopside and phlogopite. The peridotite would be classified as a PKP rock (Phlogopite K-richterite Peridotite), in the terminology of Erlank *et al.*, (1987), and will be referred to as such here. A small melt pool (0.03 mm) containing serpentine, tiny red-dish subhedral grains of phlogopite, small euhedral diopsides and blocky Cr-spinel is present in the peridotite rind. Such pools are a common feature of metasomatised peridotites.

MINERAL CHEMISTRY

Selected mineral analyses for nodule LD99 are given in Table 1. To appreciate the mineral compositions in the MARID (LD99M) and PKP rind (LD99P) portions of the nodule, it is instructive to discuss them in the context of mineral data from other MARID and PKP xenoliths from southern African kimberlites (Table 2).

Firstly, some observations concerning MARID and PKP rocks in general can be noted. Minerals in MARID rocks are characterised by relatively low abundances of Al_2O_3 and Cr_2O_3 , but moderate to high concentrations of TiO_2 and FeO compared to those in the majority of mantle peridotites, particularly unmetasomatised varieties (Dawson and Smith, 1977; Boyd and Nixon, 1978). As a rule, metasomatised peridotites, and in particular the PKP group, are intermediate in composition between MARID and unmetasomatised peridotites (Jones *et al.*, 1982; Erlank *et al.*, 1987). Indeed, ranges of mineral compositions in MARID and PKP rocks tend to overlap to limited degree, and often define continuous trends from one group to the other (Table 2 and Fig. 2). The most notable distinction between MARID and PKP minerals is the higher average FeO contents (and hence lower mg numbers), and lower Cr_2O_3 concentra-

Fig. 2. FeO vs MgO in weight % in a) phlogopite, b) K-richterite, and c) diopside, in nodule LD99. Triangles=MARID portion; circles=PKP rind of nodule. Fields are shown for mineral data in MARID and PKP rocks from southern African kimberlites. The line joining two MARID datapoints indicates core and rim analyses of the same grain. Data are from Table 1, Erlank *et al.* (1987), and Waters (1987b).

tions in MARID phases (Dawson and Smith, 1977; Erlank *et al.*, 1987).

Returning to sample LD99, it can be seen from Table 2 and Fig. 2, that minerals in the MARID portion fall within the compositional range displayed by minerals in MARID rocks. The PKP rind data plot at the limit of the PKP range in the region of overlap with MARID minerals. In fact mineral compositions throughout the nodule are broadly similar, although Fe/Mg ratios (expressed as mg number in Tables 1 and 2) in minerals in LD99M are slightly, but significantly higher than in LD99P (Fig. 2). Phlogopite and K-richterite in the two regions show few other compositional differences, but diopside in the PKP rind is richer in Cr_2O_3 and CaO, and is poorer in FeO and Al_2O_3 than in LD99M. The diopside Al/Cr ratio varies from an average of 0.22 in LD99P, to 0.76 in LD99M.

Although small, the differences in mineral chemistry between the two portions of the nodule mostly appear to be consistent with differences generally present between MARID and PKP groups. One discrepancy is that minerals in the PKP rind are slightly richer on average in TiO_2 than in the MARID portion, whereas MARID minerals, particularly phlogopites, tend to have higher TiO_2 contents than PKP minerals. However the actual TiO_2 concentration differences between minerals in the two portions of LD99 are small, especially when the spread in the data is considered (see Table 1), and hence this discrepancy may not be significant.

The compositional differences between the two portions of the nodules are more marked for diopside than the other minerals. This may be due to the fact that at least some, if not all of the diopside in the PKP rind pre-dated metasomatism, whereas all of the phlogopite and K-richterite was metasomatically introduced. As shown above, Al/Cr ratios in diopside from the two portions are distinctly different. Fe-Mg exchange by solid state diffusion is much faster than Al-Cr exchange by diffusion (Freer, 1981), which is consistent with the view that

some proportion of the diopside in the PKP rind was pre-metasomatic.

The coarse-grained zone between LD99M and LD99P is chemically indistinguishable from the MARID portion, suggesting that it may indeed simply be a coarser part of the MARID rock.

DISCUSSION

Chemical and textural evidence that MARID rocks are igneous crystallisation products has been presented by Dawson and Smith (1977), Jones *et al.* (1982), and Waters (1987a). They further suggest that PKP rocks resulted from metasomatism by fluids expelled by crystallising MARID magmas. This view is consistent with the textural, mineralogical and chemical data in the MARID and PKP rocks in contact in nodule LD99, and leads us to envisage the following scenario.

MARID magmas intrude subcontinental mantle lithosphere and crystallise, releasing fluids which infiltrate/diffuse through the host rocks. Intense metasomatism of surrounding peridotites leads to the development of K-richterite, phlogopite, $\pm$ diopside, ($\pm$ exotic titanates, Erlank *et al.*, 1987), in peridotites in close contact with the MARID intrusions. Nodule LD99 is interpreted as being a rare sample of the actual contact between MARID magmas and host mantle peridotite. Phlogopite and K-richterite crystallising in these contact rocks are very similar in composition to these minerals in the MARID body, due to their proximity to the source of the metasomatising fluids. Diopside in the metasomatised peridotites may be largely original (pre-metasomatic), but its composition is modified by reaction with the MARID fluids. As the fluids move further away from the intrusion, they evolve in composition by interaction with the surrounding mantle. The influence of pre-metasomatic peridotite composition becomes progressively more marked, and metasomatic mineral compositions shift away from those characteristic of MARID rocks, towards those seen in unmetasomatised

peridotites. Amphibole-free, but phlogopite-bearing peridotites are produced further away from the intrusion. At the limits of the infiltration diffusion activity, the effects of the fluids are seen in enhanced incompatible element abundances in peridotites which show no modal metasomatism.

In volume terms, these last two groups (i.e. those lacking K-richite), are more significant than the spectacularly metasomatised PKP rocks. Erlank *et al.* (1987) estimate from peridotite xenoliths sampled by the Kimberley pipes, that a maximum of 10% are PKP rocks, whereas 80% contain phlogopite only, with the remainder not modally metasomatised. Even so, it is puzzling as to why contact rocks like nodule LD99 have not been found before. However, our observations show that they are likely to be extremely friable in view of their hydrous nature, so that their chances of preservation are reduced. Their identification in the field may also have been a problem.

In conclusion, we observe small, but significant differences in mineral composition between the MARID core of the nodule LD99, and its PKP rind. Minerals in the rind have lower Fe/Mg ratios, and diopside has higher Cr_2O_3 and CaO but lower Al_2O_3 than in the MARID portion. There is an abrupt textural transition between the peridotite rind and the MARID portion of nodule. We believe that the PKP rocks, represented here by the peridotite rind, were metasomatised by fluids emanating from MARID magmas as they cooled and crystallised. At this stage there is little evidence to directly link MARID and kimberlite magmas (Erlank *et al.*, 1987; Waters, 1987a).

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REFERENCES

- Boyd, F. R. and Nixon, P. H. (1978) Ultramafic nodules from the Kimberley pipes, South Africa. *Geochim. Cosmochim. Acta* **42**, 1367–1382.
- Daniels, L. R. M. (1980) Some aspects of the xenolith suite from the Newlands Kimberlites, South Africa. Unpublished B. Sc. Hons thesis, University of Cape Town.
- Dawson, J. B. and Smith, J. V. (1977) The MARID (mica-amphibole-rutile-ilmenite-diopside) suite of xenoliths in kimberlite. *Geochim. Cosmochim. Acta* **41**, 309–323.
- Erlank, A. J., Waters, F. G., Hawkesworth, C. J., Haggerty, S. E., Allsopp, H. L., Rickard, R. S. and Menzies, M. (1987) Evidence for mantle metasomatism in peridotite nodules from the Kimberley pipes, South Africa. *Mantle Metasomatism*, eds. Menzies, M. A., and Hawkesworth, C. J. Academic Press, London, pp. 221–311.
- Freer, R. (1981) Diffusion in silicate minerals and glasses: a data digest and guide to the literature. *Contrib. Mineral. Petrol.* **76**, 440–454.
- Jones, A. R., Smith, J. V. and Dawson, J. B. (1982) Mantle metasomatism in 14 veined peridotites from Bultfontein mine, South Africa. *J. Geol.* **90**, 435–453.
- Smith, C. B. (1983) Pb, Sr and Nd isotopic evidence for sources of southern African Cratitic kimberlites. *Nature* **304**, 51–54.
- Waters, F. G. (1987a) A suggested origin of MARID xenoliths in kimberlites by high pressure crystallisation of an ultrapotassic rock such as lamproite. *Contrib. Mineral. Petrol.* **95**, 523–533.
- Waters, F. G. (1987b) A geochemical study of metasomatised peridotite and MARID nodules from the Kimberley pipes, South Africa. Unpublished Ph.D. thesis, University of Cape Town.