

## Geochemical Features of Some Archaean and Post-Archaean High-Magnesian-Low-Alkali Liquids [and Discussion]

R. W. Nesbitt, S.-S. Sun, E. G. Nisbet, M. J. O'Hara and J. V. Smith

*Phil. Trans. R. Soc. Lond. A* 1980 **297**, 365-381

doi: 10.1098/rsta.1980.0222

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## Geochemical features of some Archaean and post-Archaean high-magnesian–low-alkali liquids

BY R. W. NESBITT† AND S.-S. SUN‡

*Department of Geology, University of Adelaide, South Australia 5000*

High-magnesian–low-alkali liquids are found as mafic lavas ranging in age from Archaean to Cainozoic. The most magnesian lavas are represented by Archaean spinifex textured peridotitic komatiites, and in this study these liquids are used as a comparative base for younger, less magnesian liquids. The post-Archaean lavas fall into three categories: (1) the Cape Smith (Proterozoic)–Baffin Bay (Cainozoic) group, (2) the low-Ti ophiolitic basalts of Cyprus, which represent remelting of a sequentially depleted source, and (3) the boninite group, which are the products of (wet?) melting of a source that had previously experienced depletion and addition of incompatible element enriched phases.

With the use of parameters such as  $\text{Al}_2\text{O}_3/\text{TiO}_2$ ,  $\text{Sc}/\text{Zr}$ ,  $\text{Ti}/\text{V}$ , a comparison of Archaean komatiites with the younger high magnesian lavas indicates that the bulk of the variation seen in these rocks types can be interpreted in terms of the amount of partial melting and nature of residual phases. However, some of the variability that occurs within individual lava provinces (particularly among the light rare earth elements) is best explained by a heterogeneity superimposed on a previously homogeneous source. The abundance of high-magnesian liquids declines sharply after the Archaean as does the maximum MgO content achieved by the lavas.

### INTRODUCTION

The existence, in the geological record, of ultramafic rocks that represent the crystallization products of crystal-free high-magnesian liquids has until recently been a matter of debate. The disagreement resulted from the fact that most ultramafic rocks are the products of either crystal settling (i.e. cumulates) or melt extraction (i.e. residuates). However, there is now a general consensus that high magnesian liquids were erupted at the surface of the Earth, and the term komatiite (Viljoen & Viljoen 1969) is generally used to describe the resultant suite of rocks. Within the komatiite suite there is a spectrum of cumulates and resultant differentiates (see, for example, Arndt *et al.* 1977) and those komatiites that represent crystal-free, high-magnesian liquids can generally be recognized either by the development of spinifex texture (Nesbitt 1971) or by their characteristic geochemistry (Nesbitt & Sun 1976).

An important feature of the geochemistry of spinifex textured komatiites is the low abundances of incompatible elements (including the alkali elements). This characteristic is generally interpreted to signify that the liquids represent large (more than 30%) amounts of mantle melting rather than small fraction melting at high pressures. Our study concerns these high-magnesian–low-alkali liquids and excludes rocks types such as lamprophyres and alkali picrites which characteristically have high MgO and high incompatible element contents (e.g. some of the Karroo lavas; Cox & Jamieson 1974).

In the decade since their recognition in the Archaean of South Africa (Viljoen & Viljoen

† On leave from the Institut de Géologie, University of Rennes, Rennes Cedex 35042, France.

‡ Present address: C.S.I.R.O. Division of Mineralogy, Delhi Road, North Ryde, N.S.W., Australia 2113.

1969), komatiites have been documented in many other Archaean terrains and there are now considerable petrological and geochemical data on these rock type (see, for example, Nesbitt & Sun 1976; Arndt *et al.* 1977; Nisbet *et al.* 1977; Blais *et al.* 1978). In this study we have used the geochemical data of Archaean komatiites as a comparative base for the evaluation of some younger high-magnesian-low-alkali lavas, which we have examined. Our principal interest in the study is the broad implications of whether post-Archaean komatiites exist and whether high magnesian liquids of different ages tell us something of the chemical evolution of the Earth's mantle.

TABLE 1. HIGH-MAGNESIAN-LOW-ALKALI LIQUIDS USED IN THE STUDY

Cainozoic	
(a) mid-ocean ridge basalts	7.6-10.4 % MgO
(b) high-magnesian andesites	
(i) Cape Vogel P.N.G.	19 % MgO
(ii) Mariana Trench	13.8 % MgO
(c) Baffin Island	
(i) Cape Dyer	9.8-28.9 % MgO
(ii) Padloping	9.8-27.70 % MgO
(d) Svartenhuk (W Greenland)	6.0-26.0 % MgO
Mesozoic	
Cyprus ophiolite	8-13 % MgO
Proterozoic	
Cape Smith (Quebec)	8-24 % MgO
Archaean	
(a) Yilgarn and Pilbara (W Australia)	11-32 % MgO?
(b) Belingwe (Rhodesia)	16-29 % MgO
(c) Barberton (S Africa)	11-32 % MgO
(d) Munro (Canada)	20-24 % MgO

#### SAMPLES USED

Table 1 lists the samples used in the study and the general MgO range of each group. The greatest number of samples used are of Archaean age and come from Western Australia, Canada, Rhodesia and South Africa. We have reported in detail on these samples elsewhere (Nesbitt *et al.* 1979). The samples were selected because of the presence of spinifex texture and relic primary mineralogy. In the Barberton samples, however, relic primary mineralogy was rare, but in view of the importance of the area to the general problem of komatiites they were included in the list of samples studied. Samples of Proterozoic age used in the study come from the western end of the Cape Smith-Wakeham Bay Belt of northern Quebec. High-magnesian rocks were initially reported from this area by Wilson *et al.* (1969), and subsequently Schwarz & Fujiwara (1977) suggested that these rocks had komatiitic affinities. We have analysed eleven high-magnesian rocks from this province and all show good quench textures, some with relic equant skeletal olivine and all with good plumose sprays of pyroxene. We estimate the parent liquid contained about 18 % MgO because those with higher MgO contents (maximum 24 % MgO) have also an abundance of equant olivine. We have not observed plate or random spinifex textured olivine (Nesbitt 1971) in these rocks, which is an indication that ultramagnesian (more than 20 %) compositions were not attained. Tectonically, the Cape Smith area is an important one because the structural setting indicates that the lavas were erupted through a well developed sialic crust (see, for example, Dimroth *et al.* 1970).

These lavas thus afford an opportunity to examine the possibility of crustal contamination on primitive lavas.

High-magnesian rocks younger than Precambrian have been examined from Cyprus (Mesozoic), Svartenhuk, Baffin Island, Cape Vogel and oceanic ridge systems (Cainozoic). The Cyprus rocks were originally reported as high-magnesian lavas by Gass (1958) and were subsequently examined in more detail by several workers (e.g. Smewing *et al.* 1975). This area

TABLE 2. TYPICAL ANALYSES OF SAMPLES USED

	(1)	(2)	(3)	(4)	(5)	(6)
SiO <sub>2</sub>	47.79	55.22	47.65	55.28	49.00	44.43
Al <sub>2</sub> O <sub>3</sub>	16.77	7.90	13.41	11.81	11.32	5.36
Fe <sub>2</sub> O <sub>3</sub>	10.33	11.49	11.35	8.81	11.94	12.53
MnO	0.21	0.20	0.19	0.15	0.19	0.22
MgO	10.60	19.01	14.18	13.04	14.51	31.72
CaO	10.98	4.75	10.69	9.15	10.06	4.87
Na <sub>2</sub> O	2.46	0.36	1.66	1.53	1.49	0.32
K <sub>2</sub> O	0.05	0.48	0.19	0.18	0.15	0.0
TiO <sub>2</sub>	0.87	0.24	1.01	0.31	0.74	0.28
P <sub>2</sub> O <sub>5</sub>	0.06	0.04	0.10	0.04	0.05	0.02
Loss	+ 0.50	—	—	2.95	—	6.5
Zr	50	40	57	16	40	16
Nb	1	2.5	7	1	4	0.5
Y	25	3.4	20	8	15	6
Sc	41	34	35	36	34	21
V	196	172	244	209	235	124
Ni	245	328	450	(380)	480	1655
Co	77	59	—	58	—	110
Cr	569	1462	1220	(976)	1620	3100
Rb	1	5	4	4	3	5
Sr	114	9	113	62	55	11
Ba	8	34	66	15	16	4

(1) Low-TiO<sub>2</sub>, high-MgO mid-ocean ridge basalt, Chain 21-17. Data from Sun *et al.* (1979).

(2) Boninite from Cape Vogel, Papua New Guinea. University of Adelaide sample number A331/540.

(3) Basalt from Padloping, Baffin Island. University of Adelaide, A331/467.

(4) Low-TiO<sub>2</sub> basalt from the Upper Pillow Lava sequence, Troodos Complex, Cyprus. Smewing, sample 6aXT.

(5) High-MgO lava from Cape Smith, Quebec. University of Adelaide, A331/445.

(6) Archaean spinifex textured peridotitic komatiite from Yakabindie, W Australia. University of Adelaide, A331/277.

has now become a classic example of an ophiolite complex although the exact structural setting (mid-ocean ridge, marginal basin or island arc complex) is a subject of debate (e.g. Myashiro 1973; Sun & Nesbitt 1978*a*). Gass & Simonian (1978) suggest that some of the more primitive lavas should be referred to as komatiites, a view based mainly on low TiO<sub>2</sub> and high Ni and Cr contents. Geochemically these lavas contrast with the younger lavas from Greenland and Baffin Bay, which we have examined. These Tertiary high-magnesian lavas were originally reported on by Clarke (1970) who examined samples from Svartenhuk (West Greenland) and Cape Dyer (Baffin Island). As well as re-analysing some of Clarke's powders we have also analysed samples from Padloping, which is close to the Cape Dyer locality. Texturally, the rocks are characterized by phenocrystal olivine (sometimes skeletal) in a matrix of quench pyroxene and plagioclase.

The high-magnesian-high-SiO<sub>2</sub> suite of clinostatite-bearing lavas from Cape Vogel (Dallwitz *et al.* 1966) have now been recognized in several other localities, e.g. Bonin Is (Kuroda & Shiraki 1975) and Mariana Trench (Anon. 1977). We have analysed material from Cape Vogel as well as a sample dredged from the Mariana Trench (Sun & Nesbitt 1978*a*) and despite the presence of microphenocrysts we suggest that these lavas crystallized from high (more than 13%) MgO liquids.

The final group of samples that we have examined consists of a suite of mid-ocean ridge basalts (m.o.r.b.) dredged from the Mid-Atlantic Ridge, the East Pacific Rise and Indian Ocean. They have been reported on in detail elsewhere (Sun *et al.* 1979). Although these samples do not contain the extremely high MgO concentrations found in the older basalts, they do represent the most magnesian modern lavas currently available to us.

In table 2, we give typical analyses of the various rock types used in the study.

#### GENERAL PHILOSOPHY

Our general philosophy in dealing with high-MgO lavas is based on the simple assumption that they are mantle melts and therefore relate in some way to their parent material. It is recognized that apart from source variations, other factors such as amount of melting, nature of the residue, *P-T* conditions at the point of separation of the liquid from its source, and crystal fractionation, all contribute to the final liquid composition. Furthermore, processes such as continuous melting with variable melt retention (Langmuir *et al.* 1977), and polybaric assimilation (Cox 1978), can produce variable chemistry in a related suite of lavas. Such diverse parameters all contribute to the complexity of evaluating a suite of lavas of varying age and tectonic setting. We therefore propose to outline the general characteristics that we observe in Archaean lavas and attempt a generalized comparison with those of younger age.

In our initial study of Archaean mafic lava geochemistry (Nesbitt & Sun 1976), a surprising consistency was observed among certain elemental ratios, which can be described under two basic patterns. The first pattern is one in which the ratio remains constant over wide ranges of MgO content. The best example of this type of pattern is the Ti/Zr ratio which approximates the chondritic value of 110. This value is found in the spinifex textured peridotitic komatiites (s.t.p.k.) over a 20–32% MgO range as well as being characteristic of many of the Archaean tholeiitic lavas. The second pattern is one of progressive change which in some cases flattens off to a constant value (often chondritic). This type of behaviour can be interpreted as the result of one element's being more incompatible than the other. For example, in the case of the Zr/Y ratio, it is evident that at lower degrees of melting or advanced degrees of crystallization, Y is held back from the melt (in the residue) or removed by pyroxene settling. However, when melting is extensive, the Zr/Y ratio is close to chondritic (about 2.5) suggesting that all of the Y is in the melt (see fig. 3*c*, Nesbitt & Sun 1976).

Our interpretation of the major element ratio Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (Sun *et al.* 1979) is similar to the interpretation of the Zr/Y ratio. The chondritic Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio is about 20 and in a melting model is controlled by the tendency of Al to remain in the source and of Ti to enter the melt. In s.t.p.k. the ratio is close to or just greater than chondritic, indicating that at this level of melting there are no significant amounts of aluminium left in the source. In m.o.r.b., however, the ratio shows a progressive increase (Sun *et al.* 1979) which can be correlated with increasing amounts of melting (i.e. increasing amounts of Ti). The ratio can also be interpreted in terms



of sequential melting and variable melt retention (Sun & Nesbitt 1978*a*, Nesbitt *et al.* 1978) and in this respect is a useful tool in the comparison of high-magnesian lavas.

There are some element pairs in which the ratio shows progressive change toward a chondritic value, but even when the MgO content is large (i.e. amount of melting is large), a chondritic value is not achieved. An example of this is the V/Zr ratio for which a chondritic value of about 11–13 seems probable. In s.t.p.k., the value for this ratio is about 9, i.e. consistently lower than the chondritic value. This can be interpreted in a variety of ways. If we assume a chondritic value for the source, then we must also assume that V is held back (perhaps by olivine) in the source. Alternatively although the bulk Earth may have a chondritic V/Zr value, the mantle may not have this value, implying that there is V in the core. If neither the bulk Earth nor the mantle have chondritic V/Zr values, then this fact must be included in any model of Earth accretion.

The TiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> elemental ratio, like the Ti/Zr ratio, remains constant (about 10) in s.t.p.k. and Archaean tholeiites, but unlike the Ti/Zr ratio it is not chondritic. The collinear variation of TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> abundances over a large range of partial melting suggests that this value is a mantle characteristic (Sun & Nesbitt 1977).

A TiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> ratio of 10 is also found in most m.o.r.b. with depleted light rare earth (l.r.e.e.) patterns and we interpret this to indicate that despite earlier removal of melts, the behavioural characteristics of the two elements under these conditions is very similar. Sun *et al.* (1979) comment on this ratio and show that in m.o.r.b., small variations in the value can be correlated with varying l.r.e.e. enrichment characteristics.

## GEOCHEMISTRY OF INDIVIDUAL PROVINCES

### 1. Archaean

The preceding discussion has to some extent summarized the available data on Archaean high-magnesian mafic rocks. Perhaps the most important conclusion is that for many elements the geochemistry can be meaningfully interpreted despite extensive alteration. However, conclusions relating to elements such as Na, K, Rb and Ba are equivocal, because these elements are demonstrably mobile and their abundance patterns in any particular rock are quite erratic (see for example, Condie *et al.* 1977). Hart *et al.* (1970) propose that although the metamorphism is non-isochemical on a local scale, it can be regarded as isochemical on a regional scale. Their data on bulk samples suggest that compared with modern m.o.r.b., Archaean mafic rocks were more enriched in incompatible elements such as Rb, K and Cs. This implies that Archaean source regions were also more enriched than the source regions of m.o.r.b.

An independent method of comparing Archaean mafic rocks and m.o.r.b. has been suggested by Sun & Nesbitt (1977) who argue that at the level of melting involved in the production of high MgO liquids, the chondrite normalized La/Sm ratio ((La/Sm)<sub>N</sub>) of the liquid must be close to that of the source. This infers that (La/Sm)<sub>N</sub> will be useful in estimating relative abundances of other incompatible elements such as K, Rb, Ba and Sr. The data of Sun & Nesbitt (1978*b*) suggests that although the range of (La/Sm)<sub>N</sub> in Archaean mafic rocks is about the same as m.o.r.b., the average value (0.7–1.0) is higher than average m.o.r.b. (0.55). This suggests that the source for the average Archaean mafic rock was slightly more enriched in incompatible elements than the average source for m.o.r.b. In table 3, we compare our estimate of the ratios

of these elements for the two rock groups. These data support the overall conclusions of Hart *et al.* (1970) who based their values on large-scale sampling.

Table 3 also indicates that the ratios of elements such as Ti, Zr and P have changed very little since the Archaean, implying that at the level of melting involved, the behaviour of these elements is very similar.

TABLE 3. COMPARISON OF SOME ESTIMATED ELEMENTAL RATIOS FOR ARCHAEOAN BASALTS AND MODERN MID-OCEAN RIDGE BASALTS

	Archaean basalt	modern m.o.r.b.
$(La/Sm)_N$	0.7–1.3	0.4–0.7
Ti/Zr	110	110
$P_2O_5/Ce$	100	120
Sr/Ba	2	10
Rb/Sr	0.035	0.008
K/Rb	350	1046
K/Cs	5900	81000
K/Ba	30	110
$TiO_2/P_2O_5$	10	11

Although in the discussion of the Archaean data we have considered average  $(La/Sm)_N$  values of the source, it is clear that there are significant variations of the ratio within given rock suites. For example, the available data on Archaean rocks from Barberton, Abitibi and the Yilgarn of Western Australia (Sun & Nesbitt 1978*b*) show a pronounced variation not only between but also within these rock suites. In this respect, Archaean mafic rocks resemble modern m.o.r.b. which themselves show a considerable range in  $(La/Sm)_N$  even from one locality (see, for example, Langmuir *et al.* 1977). Although part of this variability can be attributed to the magmatic processes that produce the final liquid, it has been argued elsewhere (Sun *et al.* 1979) that mantle heterogeneity must be a major factor.

A similar conclusion can be reached about the source of Archaean mafic volcanics particularly in some of the Archaean high magnesian basalts (the s.t.b. of Sun & Nesbitt 1978*b*) which show extremely high  $(La/Sm)_N$  values. These basalt types occur within basaltic sequences with depleted l.r.e.e. patterns, indicating a heterogeneous source region. We conclude therefore that the mantle was already inhomogeneous 2.7–3.5 Ga ago.

## 2. Cape Smith

Within the Cape Smith lavas there is a systematic negative correlation of MgO with elements such as Ti (figure 1). This trend indicates that the range of MgO (8–24%) is attributable to olivine fractionation, a conclusion that is valid for all the suites of high-magnesian lavas studied (figure 1).

We can evaluate the Proterozoic lavas in terms of the parameters discussed for the Archaean lavas. For example, the Ti/Zr and  $TiO_2/P_2O_5$  ratios even in the most evolved lavas are essentially the same as those found in the Archaean (110 and 11 respectively). Furthermore, the lavas show quite a remarkable consistency in their  $Al_2O_3/TiO_2$  ratios with a value of 15 being maintained throughout the range of MgO composition. Since Ti/Zr is chondritic, we infer that the  $Al_2O_3/TiO_2$  ratio lower than chondritic is caused by Al depletion rather than Ti enrichment. Assuming that the source mantle had a chondritic Al/Ti ratio, we suggest that Al was retained by the source or extracted by a mineral phase(s) during crystal fractionation. The Al depletion

in these lavas is reflected in the value for other important ratios. For example, the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio ranges from 0.75 to 1.2 with an average value close to 1 and thus resembles komatiites (Nesbitt *et al.* 1979). In addition, the lavas have a slight but consistent heavy rare earth element (h.r.e.e.) depletion pattern ( $(\text{Yb}/\text{Gd})_N < 0.9$ ) and have  $\text{Sc}/\text{Zr}$  ratios (0.8) consistently less than the average value (1.4) for non-Barberton komatiites and chondrites. Again, since  $\text{Ti}/\text{Zr}$  is chondritic, we conclude that Sc is depleted in these melts relative to Zr. A similar conclusion can be made about V, since  $\text{Ti}/\text{V}$  ratios average 19 (range 16–20), whereas average non-Barberton Archaean komatiites have ratios of 14 (table 4).

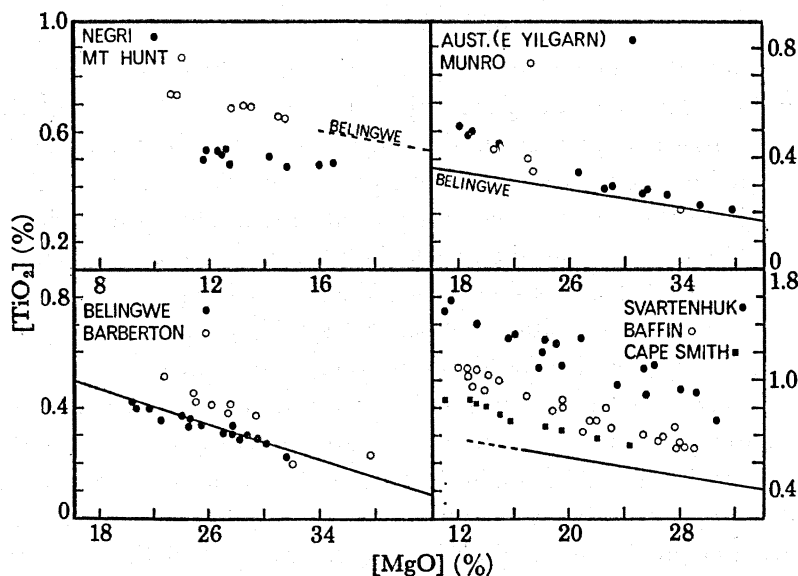


FIGURE 1.  $\text{MgO}-\text{TiO}_2$  plots for high-MgO liquids used in the study. The reference line on all four plots is drawn through the Belingwe data. Negri and Mt Hunt plots represent data on Australian spinifex textured basalts (Sun & Nesbitt 1978b).

TABLE 4. AVERAGE RATIOS FOR SOME IMPORTANT OXIDES AND ELEMENTS

	chondrite	s.t.p.k.†	Smith	Cyprus	Dyer	Padlop	Svart	Mariana	Vogel	m.o.r.b.	Negri
Ti/Zr	110	110	110	110–220	120	110	110	41	36	110	52
$\text{TiO}_2/\text{P}_2\text{O}_5$	0.1	11	13	10	9	10–17	9	6	6	9	7
Zr/Y	2.5	2.5	2.6	< 2	2.3	3	4	6	12	2	3.7
Sc/Zr	1.4	1.5	0.8	2.2	0.9	0.6	0.4	1	0.9	1	0.7
Ti/V	10	14	19	9	20	25	30	8	8	22	15
V/Zr	11	8.5	6	13	6	5	4	5	4	6	3.5
Ti/Sc	78	78	130	50	137	175	284	38	42	110	70
$\text{Al}_2\text{O}_3/\text{TiO}_2$	20	21	15	60	15	13	8	56	33	20	27
$\text{CaO}/\text{Al}_2\text{O}_3$	0.82	1	1	0.80	0.82	0.82	0.86	0.52	0.60	0.80	0.65

† These values are for s.t.p.k. of non-Barberton type, i.e. aluminous undepleted types of Nesbitt *et al.* (1979).

Despite the differences in Sc, V and h.r.e.e. between the Cape Smith lavas and Archaean komatiites, there can be little doubt that they should be classed as komatiites. In many respects they have several of the characteristics of the type-komatiites of Barberton. We are thus faced with exactly the same problem for these Proterozoic lavas as for the enigmatic Barberton komatiites. Nesbitt *et al.* (1979) discuss this problem and conclude that although specific source characteristics (see for example Cawthorn & Strong 1974) may be responsible for the Al



(h.r.e.e., etc.) depletion, a model in which garnet extraction is involved is more likely. Irrespective of the actual mechanism, we conclude that the Proterozoic Cape Smith lavas are komatiites, whose primary liquid composition did not reach the high-MgO contents of the Archaean equivalents but whose basic characteristics did not differ from Archaean (particularly Barberton type) lavas. Furthermore, in common with Archaean mafic lavas, the Cape Smith lavas have a spread of  $(La/Sm)_N$  ranging from slightly depleted to significantly enriched (1.5). Although this may be partly due to factors such as magma generation–fractionation processes (e.g. dynamic melting), we suggest that variable source characteristics are also responsible.

### 3. *Baffin Bay*

The Baffin Bay material comes from three localities, namely Cape Dyer and Padloping Island (Baffin Island) on the west side of the Bay and Svartenhuk (W Greenland) on the east side of the Bay. Clarke (1970) has pointed out that the range in MgO seen in these lavas is largely due to low pressure olivine fractionation. We have plotted our data and that of Clarke (1970) on a  $TiO_2$ –MgO diagram (figure 1) to demonstrate this point. The most obvious observation is that at a given MgO concentration, the Svartenhuk lavas are more enriched in  $TiO_2$ . This fact also applies to associated elements such as Zr, Y and P. Despite the systematic inter-lava variability in absolute abundances, ratios such as  $Ti/Zr$ ,  $TiO_2/P_2O_5$  show no differences and coincide with the values observed for Archaean high-magnesian lavas.

Clarke (1970) suggested that the chemical differences between the lavas on opposing sides of Baffin Bay were due to the effect of eclogite fractionation operating on the Svartenhuk lavas. This process not only results in an increase in the level of incompatible elements in the fractionated liquids but also produces differences in r.e.e. patterns. Subsequently, O’Nions & Clarke (1972) demonstrated that in the Svartenhuk lavas there was a depletion in heavy r.e.e. and proposed that variable amounts of partial melting or equilibrium fractionation of eclogite was responsible.

In general, our own r.e.e. data (Sun & Nesbitt, unpublished) on Svartenhuk, Padloping and Cape Dyer confirm the data of O’Nions & Clarke (1972). The Svartenhuk lavas have h.r.e.e. patterns that are strongly depleted ( $(Yb/Gd)_N$  about 0.6), whereas the Baffin Island samples have relatively flat h.r.e.e. The relative depletion in the h.r.e.e. between the two groups is also reflected in other elements. For example, the  $Sc/Zr$  ratio, although not chondritic in the Baffin Island rocks, is considerably higher than that of the Svartenhuk lavas (0.8 and 0.4 respectively). Similarly the  $Ti/V$  ratio, which is 14 in Archaean s.t.p.k. is 20–25 in the Baffin Island lavas and 30 in the Svartenhuk lavas. Since the  $Ti/Zr$  ratio is close to chondritic in all the lavas, we can assume that both Sc and V are relatively depleted in the Svartenhuk lavas compared with those on Baffin Island.

If we compare the  $Al_2O_3/TiO_2$  ratios of the lavas on either side of Baffin Bay, it is apparent that there are considerable differences in  $Al_2O_3$ . In the Baffin Island lavas, the  $Al_2O_3/TiO_2$  ratio ranges from 11 to 15 whereas it is 7–8 in the Svartenhuk lavas. This difference in  $Al_2O_3/TiO_2$  between the two groups thus reflects the differences in h.r.e.e. patterns and is a probable indication of garnet control. However, if we compare  $Al_2O_3/TiO_2$  ratios of Baffin Island lavas with those of Archaean lavas of comparable MgO and modern m.o.r.b. (with much less MgO), it is apparent that the Baffin Island material has unexpectedly low ratios. This suggests that in comparison with these other lavas, a considerable amount of an aluminous phase (pyroxene ?) was left in the residue of the Baffin Island lavas. This observation, together with the high

incompatible element content of these lavas (figure 1) suggests that depth and level of melting are important genetic factors controlling the differences. We therefore suggest that the amount of melting involved in the production of Baffin Bay lavas was significantly less than for Archaean lavas with comparable MgO, a feature probably produced by higher pressure (greater depth) conditions at the site of magma generation.

If variations in the amount of partial melting were responsible for the gross differences between Baffin Bay lavas and Archaean equivalents, perhaps the same mechanism can be used to explain the variation observed within the lavas themselves? For example, the failure to eliminate garnet from the source of the Svartenhuk lavas (O'Nions & Clarke 1972) could account for the observed geochemical differences. However, it is also clear that the amount of melting involved in the production of the Dyer-Padloping lavas was small and although garnet was eliminated some clinopyroxene may have remained. This view follows from the near-chondritic values for the CaO/Al<sub>2</sub>O<sub>3</sub> ratios observed in both the Svartenhuk and Baffin Island lavas. If Al was retained in the source then a compensating Ca bearing phase must have also been present, otherwise the Ca/Al ratio of the lavas would be greater than chondritic.

The r.e.e. data of O'Nions & Clarke (1972) and Sun & Nesbitt (unpublished) indicate variable l.r.e.e. in the Baffin Bay rocks, ranging from very depleted to mildly enriched patterns. Similar variation in l.r.e.e. is also found in Archaean lavas that have been sampled from the same volcanic sequence (see, for example, Sun & Nesbitt 1978*b*). Such patterns probably reflect some source variability although this is too difficult to evaluate in view of the small amounts of melting involved in the production of the lavas.

#### 4. Cyprus

The low-Ti lavas found within the Upper Pillow Lavas of the Troodos Complex were chosen for this study because of their relatively high MgO content. As the discussion will show, the choice was not a satisfactory one from the viewpoint of mantle evolution. The lavas are geochemically complex because both olivine and pyroxene are fractionating phases. Consequently it is not possible to view the lavas as primary liquids in which perhaps only one relatively simple phase (olivine) has settled out.

In the ten samples that we have analysed, MgO varies from 8 to 13% and TiO<sub>2</sub> from 0.2 to 0.65%. The depletion in Ti is accompanied by depletion in other incompatible elements (e.g. r.e.e., Zr, P, Nb and Y) but it is not altogether clear whether the depletion of these elements relative to each other is constant. For example, although the Ti/Zr ratio varies from 110 to 220 in our samples, the high values may be due to clinopyroxene accumulation (Pearce, personal communication 1978) rather than reflecting the primary composition of the liquid.

Overall, our view is that the relative depletion is constant and that ambiguities (such as large Ti/Zr values) are caused by crystal fractionation. Our reasoning is based on the observations of Sun *et al.* (1979) who show that for m.o.r.b. lavas there is a consistent relation between the r.e.e. and other incompatible elements. They show, for example, that in terms of incompatibility, Y = Ho, Ti = Eu, Zr = Sm, and P = Nd. It follows therefore, that if the Ti/Zr or Ti/P ratio is controlled by the melting (depletion) history, large ratios should be associated with strong l.r.e.e. depletion. This is not seen. For example, although P<sub>2</sub>O<sub>5</sub> concentrations are small (0.03–0.06) and therefore the analytical uncertainty large, the TiO<sub>2</sub>/P<sub>2</sub>O<sub>5</sub> ratio for these samples is always close to 10. This is the same value observed in s.t.p.k. Furthermore, sample 6aXT (Smewing & Potts 1976), which we have also analysed, shows strong l.r.e.e. depletion,

but has a Ti/Zr ratio of 115. Relative to Y, however, Zr shows a pronounced depletion, with the average Zr/Y ratio being less than 2, whereas the s.t.p.k. value is close to chondritic (2.5).

From the viewpoint of this study, the most important aspect of the geochemistry of the Cyprus lavas is the positive evidence of a complex depletion history. This has produced the prominent depletion in incompatible elements and is most easily recognized in the  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratio. For example, sample 6aXT (Smewing & Potts 1976), with an  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratio of 38, has 13% MgO and only  $4 \times$  chondrite abundances in the h.r.e.e. Such low abundances are seen only in Archaean s.t.p.k. with 23% MgO (Sun & Nesbitt 1978*b*), but these have chondritic  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios (20). Sample 6aXT also has a strong l.r.e.e. depletion so that to produce this and still deplete the total r.e.e., it seems probable that several melting episodes occurred. For example, one possible model would involve removal of a significant fraction of the l.r.e.e. from the source and then have at least one more major extraction episode in which all of the incompatible elements such as r.e.e., P, Zr, Nb, Y and Ti are depleted from the source. Re-melting of this source would produce lavas of the Cyprus, low-Ti, type.

Because of this complexity, it is difficult to interpret the low-Ti lavas in terms of an evolving mantle composition. To do this on Cyprus would require a study of those lavas with low Ti and high MgO, but near-chondritic  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios. What we can conclude from our study of the low-Ti lavas is that they do not have komatiitic characteristics and that they required specific tectonic conditions to produce melts from such a depleted source rock. Sun & Nesbitt (1978*a*) suggest that addition of water to the refractory residue is necessary to induce melting, whereas Duncan & Green (1979) have recently suggested that the low-Ti Cyprus lavas can be produced by the melting of a refractory peridotite which ascended from about 70 km.

##### 5. Cape Vogel and Mariana high-magnesian andesites (boninites)

The high- $\text{SiO}_2$ -high-MgO lavas of Cape Vogel (Dallwitz *et al.* 1966) and Mariana Trench (Anon. 1977) provide further samples of the Earth's mantle, which potentially provide information on their source. The rocks are characterized by low (less than  $10 \times$  chondrite) abundances of incompatible elements (Ti, P, r.e.e., etc.), low  $\text{Al}_2\text{O}_3$ , CaO and low  $\text{CaO}/\text{Al}_2\text{O}_3$ , Ti/Zr and  $\text{TiO}_2/\text{P}_2\text{O}_5$  ratios (table 4). These unusual characteristics are unlike those of the high-magnesian liquids already described. However, in many ways the boninites resemble the low-Ti lavas of Cyprus, particularly in the high  $\text{Al}_2\text{O}_3/\text{TiO}$  ratios (33–56) and the relative enrichment of V and Sc over Ti. Thus, the boninites have Ti/V and Ti/Sc ratios of 8 and 40 respectively, compared with Cyprus 9 and 50 (Archaean s.t.p.k. 14 and 79). However, the Cyprus lavas do not show the decoupling of Zr from Ti which characterizes the boninites. In all the lavas discussed so far (including Cyprus) the Ti/Zr ratio rarely drops below 100 and this close to chondritic value indicates that under normal melt producing conditions, the two elements are essentially coherent. In boninites, the coherence is broken by the relative enrichment of Zr over Ti (table 4).

The interpretation of Ti–Zr relations can take several forms. For example, if a Ti-bearing phase were residual in the source, this would explain the low Ti/Zr ratio, but it is difficult to predict exactly what this mineral might be since no Ti-rich phase is known to be on the liquidus of melts of this type. A modification of this explanation (Sun & Nesbitt 1978*a*) is based on the r.e.e. patterns of the boninites, which indicate the source for the lavas was a two (or more) component mixture. The patterns have a dish-shaped shape with an apparent depletion in the

middle r.e.e. and can be explained by the addition of one phase enriched in light r.e.e. to a source region that had previously been depleted in light r.e.e. In this model, the source region would have a Ti/Zr ratio of 110 and the general characteristics of the Cyprus lavas, i.e. high Al/Ti, V/Ti, Sc/Zr. To this depleted source would be added a second component which was depleted in Ti relative to Zr. Such a component could come from a deeper source which itself had a stable Ti-bearing mineral phase that would effectively decouple Ti from Zr.

Any model proposed for boninites must also be capable of producing the low CaO/Al<sub>2</sub>O<sub>3</sub> ratios (0.5–0.6) which apparently are characteristic of these rocks over a wide composition range. For example, Sun & Nesbitt (1978*a*) report ratios of 0.6 and 0.52 for lavas with 19 and 14% MgO respectively, and Kuroda & Shiraki (1975) report a value of 0.49 for a boninite lava with 8.5% MgO.

We have no ready explanation for this characteristic. The depletion of Ca relative to Al may be a function of the early history of depletion that the source undoubtedly experienced. However, the fact that the Cyprus lavas have normal CaO/Al<sub>2</sub>O<sub>3</sub> ratios indicates that this is not necessarily so. However, the alternative explanation, that the second component had a low CaO/Al<sub>2</sub>O<sub>3</sub> ratio, is equally unpalatable, because most low percentage partial melts with l.r.e.e. enriched fractions (e.g. kimberlites) have high CaO/Al<sub>2</sub>O<sub>3</sub> ratios. If both of these mechanisms are rejected, we have to resort to the process by which the final melt was produced. We suggest that a viable model for the production of boninites is by wet melting of an already depleted source, to which has been added a l.r.e.e. enriched phase. The lowering of the liquidus of the refractory source by the addition of water seems to be an essential parameter (Sun & Nesbitt 1978*a*). We therefore suggest that the Ca/Al ratio of the 'boninite liquid' (partial melt) was lower than that of its source, presumably owing to the relative stabilities of aluminous and calcic mineral phases in the source. Unfortunately, there is little in the currently available trace element data to support this latter suggestion strongly. For example, if the relative stabilities of garnet and/or clinopyroxene and/or orthopyroxene are the cause of the low CaO/Al<sub>2</sub>O<sub>3</sub> ratio, this should affect the V/Sc ratio of the resultant liquid. In fact, the ratio in boninites (*ca.* 5) is close to that of s.t.p.k. (5.6) and m.o.r.b. (6).

The implications of boninite geochemistry to mantle evolution are difficult to evaluate because we are uncertain of the relative abundance of these melts in the geological record. Lavas with such characteristics are not common and the closest analogy among high MgO lavas is the Archaean spinifex textured basalts (s.t.b.) described by Sun & Nesbitt (1978*b*). These rocks display the same high SiO<sub>2</sub> values and the low Ti/Zr ratio seen in the boninites. In addition, the r.e.e. patterns, although not identical, show the same mixing characteristics, with enriched l.r.e.e. In the Archaean examples, the amount and composition of the mixing phases were quite variable between localities, but apparently constant within one area (e.g. Negri Volcanics; Sun & Nesbitt 1978*b*). Furthermore, the amount of initial depletion suffered by the primary source was variable, such that in some s.t.b. the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> is about 30 while in others it is about 15. Our limited data suggest that in these rocks the degree of l.r.e.e. enrichment is positively related to the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio.

#### 6. *Mid-ocean ridge basalts*

We have reported elsewhere (Sun *et al.* 1979) our geochemical and isotopic data on ten samples of close to 'primitive' m.o.r.b. Here we give only our principal conclusions.

M.o.r.b. liquids with low TiO<sub>2</sub> (less than 0.8%), high MgO (9–11%) and Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and



CaO/TiO<sub>2</sub> ratios close to chondritic represent about 25% melting of a pyrolite mantle. The spread in (La/Sm)<sub>N</sub> (0.38–1.97) in the samples strongly supports the view of heterogeneity in the source. Despite this variation in the very incompatible elements, the liquids all show Ti/Zr close to chondritic (110), indicating that the mechanism responsible for producing source heterogeneity did not break the coherence of these two elements.

Sun *et al.* (1979) show that there is a pronounced difference in the normalized abundance patterns of the incompatible elements between those m.o.r.b. with depleted (normal or N type) and those with enriched (plume or P type) characteristics. In particular, while N type shows a progressive decrease in normalized abundances in the elemental sequence La, K, Nb, U, Th, Ba, Rb and Cs, the enriched type have an erratic pattern. Sun *et al.* (1979) suggest that P type m.o.r.b. are the product of melting of an N type source to which has been added an incompatible rich phase (phase B of Frey & Green 1974). The nature of the normalized abundance patterns can then be controlled not by the immediate mantle source, but by the source of the B phase.

To some extent, the mineralogical nature of the m.o.r.b. residue can be evaluated by using geochemical parameters. Sun *et al.* (1979) argue that since chondritic ratios of Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and CaO/TiO<sub>2</sub> are found in s.t.p.k. (of non-Barberton type) and some m.o.r.b. (those with low TiO<sub>2</sub>), this indicates that at the level of melting represented by m.o.r.b. no aluminous or calcic phases remain in the source. The progressive melting event represented by the sequence m.o.r.b. to s.t.p.k. thus probably represents a progressive melting of an olivine ± alumina-free orthopyroxene residue.

#### DISCUSSION AND CONCLUSIONS

In this study, we have examined a series of high-magnesian, low-alkali rocks that represent liquids whose age of eruption extends over a 3.5 Ga period. We have assumed that they represent large percentage melting of the mantle and that they are either primary or have lost only olivine during their ascent to the surface. The consistency of many of the elemental ratios and the fact that some are close to chondritic supports these assumptions. Herein lies one of the most important contributions that the study of Archaean spinifex textured high-magnesian ultramafic rocks has made to the understanding of mantle geochemistry.

In considering the liquids in relation to mantle heterogeneity, we can view the problem in terms of two extreme models. In the first model, the liquids originate from a completely homogeneous part of the mantle and the geochemical variations between the liquids can be explained by processes of magma generation, e.g. amount of melting, depth of melt–residue separation, nature of residual phases and fractionation history of the liquid. The second model assumes that the mantle is completely heterogeneous and that the variations observed in the liquids are largely the result of this heterogeneity.

Clearly, neither model is completely viable, but we suggest that the gross chemical variations can best be explained by magma generation processes acting on a source, which in terms of bulk chemistry can be considered homogeneous. However, it is clear both from published isotopic data and the nature of l.r.e.e. patterns within the same suite of lavas that the liquids cannot be considered to be coming from a totally homogeneous source. Suggestions as to the nature of the heterogeneity include a stratified mantle with an undepleted (or less depleted) mesosphere beneath a depleted lithosphere (see, for example, Sun & Hanson 1975), a ‘patchy’



distribution of enriched pockets or veins of varying dimensions and varying degrees of enrichment, sitting in a depleted upper mantle (see, for example, Hanson 1977) or a stratified low velocity zone (Green & Liebermann 1976).

All of these models can in effect be considered to be the result of melting processes. For example, a common model interpretation of P type m.o.r.b. data is one involving a long-term depletion event in the primary source, followed by the addition to the source of an incompatible rich (particularly l.r.e.e.) phase (phase B of Frey & Green 1974), just before the melting event (Sun *et al.* 1979). Thus in addition to the major fractionation processes (e.g. amount of melting) a depletion-enrichment process is operating and this combination may explain most of the variability of mafic lava chemistry. We can therefore infer that the combination of removal of large percentage melts from the mantle and the upward migration of silica undersaturated melts (or vapour phase) into the resultant depleted zones is a prime mechanism in the production of a heterogeneous mantle.

Data on Archaean ultramafic and mafic rocks (this paper and Sun & Nesbitt 1978*b*) suggest that these two processes were operating 3.5 Ga ago. Within Archaean mafic assemblages, there is abundant evidence of magma variability brought about by residual phase control and l.r.e.e. element variation in the source. Thus Sun & Nesbitt (1978*b*) conclude that although the Archaean mantle was probably not as depleted as that of the present day, it was as heterogeneous.

If we review the production of high-magnesian-low-alkali liquids through time, it is clear that both the degree of melting (reflected in the percentage of MgO achieved in the liquid) and the actual volume of liquid produced declined rapidly after the 2.7 Ga year greenstone forming event. The Cape Smith lavas (lower Proterozoic) represent (as far as we are aware) the last major eruption of komatiitic lavas, and in these the typical high MgO s.t.p.k. are absent. The occurrence of younger komatiites is a matter of komatiite definition, but when they occur they appear to be volumetrically insignificant. The komatiites of Gorgona Island, Colombia (Gansser *et al.* 1979), which are the youngest known komatiites (Lower Tertiary), come into this category. In many respects, the geochemistry of the Gorgona Island komatiites is remarkably similar to the Cape Smith lavas. For example, they display h.r.e.e. depletion accompanied by low  $\text{Al}_2\text{O}_3/\text{TiO}_2$  (18) and very high Ti/Sc (127), which indicates Sc depletion. Thus our interpretation of the limited data available for the Gorgona Island komatiites is that a small quantity of a phase such as garnet was residual in the source. Ratios such as  $\text{Ti}/\text{Zr} = 130$  and  $\text{TiO}_2/\text{P}_2\text{O}_5 = 11$  all indicate a 'normal' mantle source, but the limited r.e.e. data indicate a l.r.e.e. depletion.

One unusual feature of the Gorgona Island komatiites is the presence of spinifex textured olivine in a rock with relatively low MgO (16%) and this is presumably due to low  $\text{SiO}_2$  abundances. Thus these komatiites represent a relatively recent example of extensive mantle melting, and assuming a mantle with 0.2%  $\text{TiO}_2$ , they represent about 30% melting of a pyrolite source. The existence of such a liquid (without the h.r.e.e. depletion) was predicted by Green *et al.* (1978) based on an experimental study of m.o.r.b. They suggest that by extensive olivine loss during uprise, such liquids attain compositions typical of normal m.o.r.b. Thus, the Gorgona Island komatiite, which is believed to be part of an uplifted oceanic crust (Gansser *et al.* 1979) may provide the key to understanding the genetic link between komatiites and tholeiites (cf. Nesbitt *et al.* 1979).

We acknowledge the donation of samples from several colleagues and in particular we thank D. B. Clarke, W. Fahrigh, H. Lapierre, E. G. Nisbet, E. J. Schwarz, A. Sharaskin, M. J. Viljoen and R. P. Viljoen. This research was supported by the Australian Research Grants Committee and S.-S. Sun acknowledges a post-doctoral fellowship from this committee. R. W. Nesbitt acknowledges the use of facilities in the Institut de Géologie, Université de Rennes, during the writing of the manuscript.

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## Discussion

E. G. NISBET (*Department of Mineralogy and Petrology, Cambridge, U.K.*). I am unhappy about the criteria used to identify komatiitic ‘liquids’, as it seems likely that the chemistry of a coarse spinifex rock will be dominated by the spinifex minerals. Whatever way spinifex minerals grow from the liquid, they will not have the composition of that liquid, and thus any rock sample with

marked spinifex texture will not represent a 'liquid'. In finer-grained spinifex rocks it is possible that residual liquid may be trapped between and within the spinifex blades, but in rocks with coarser spinifex texture I should expect the rock composition as analysed to be very different from the composition of the original 'liquid'. We had the same problem in our Belingwe work, and there we specifically excluded coarser spinifex rocks. Our criteria were that rocks chosen to represent 'liquids' should ideally be phenocryst-poor and free from large spinifex or cumulate crystals; should have a very fine-grained or devitrified ground-mass (see, for example, Arndt *et al.* 1977, Plate 1D; Nisbet *et al.* 1977, Plate 1B); and if possible that there should be field evidence to suggest extrusion as pillows or flows. Rocks with well developed spinifex texture were excluded, although we did use some samples with poorly developed 'random' spinifex texture. Similarly, cumulate rocks in sills or thick flows were excluded (a fine example of this is NG. 179, collected from a sill/thick flow of bulk MgO of around 15–20%: NG. 179 is a clinopyroxenite, with SiO<sub>2</sub> 50.8%, MgO 18.7% and CaO: Al<sub>2</sub>O<sub>3</sub> = 7.7!) All of these rocks were judged by us *not* to represent 'liquids'.

However, we did study some rocks with random scattered spinifex olivine-'unsettled spinifex' textures, and these did have compositions close to the pillow lavas though, surprisingly, Na was high. So we would be prepared to accept rocks with these textures as close to 'liquids', though not as close as the phenocryst-poor, spinifex-poor lavas. Arndt *et al.* (1977, pp. 341 and 342) also looked at this. Of course, it could be argued that fine-grained rocks such as those that we used are often much more altered than coarser spinifex rocks and so are poor sources of data: we felt that our rocks displayed such strong chemical coherence that most elements must have been fairly immobile. But I would argue there is more chance of preserving original chemistry in fresh spinifex minerals. I suspect that there is no perfect answer to this problem!

R. W. NESBITT AND S.-S. SUN. We doubt whether anyone would disagree with Dr Nisbet's statement that spinifex minerals do not have the composition of the liquid. However, the basic question is whether the total mineral assemblage plus the devitrified glass represents a liquid. To enter that discussion is to enter the fields of what is the effect of alteration, what is a phenocryst and what is a xenocryst, and how large should the sample be? In this paper, we have attempted to demonstrate that many elemental ratios are consistent and interpretable and therefore represent the values of the liquid and in some cases their mantle sources. We are not really concerned with absolute abundances. Hence, although we have never utilized 'coarse spinifex rock' (contrary to Dr Nisbet's suggestion) we see no good reason why the same result could not be achieved (provided the sample is large enough). Our principal line of argument is that since olivine (the spinifex mineral) has very low distribution coefficients for most elements (other than Ni, etc.) its crystallization from the liquid will not affect the parameters in which we are interested. Thus in the analysis of a spinifex textured peridotitic komatite, olivine is simply acting as a diluent. The same reasoning can be applied to the rocks that Dr Nisbet quoted as being suitable for analysis (although we are surprised by his description of them as being 'phenocryst free') since they simply represent olivine plus liquid. The matter, of course, becomes critical if one is interested in the maximum MgO content achieved by a komatiitic liquid or if the spinifex growth involves minerals other than olivine (see specimen 422/99; Sun & Nesbitt 1978*b*).

M. J. O'HARA (*Department of Geology, The University of Wales, Aberystwyth, U.K.*). When the authors comment that production of true komatiites was restricted to the Archaean, would it

not be more accurate to say that eruption of true komatiites was restricted to the Archaean? The question of what is the real primary magma produced in more recent melting events is very much open to debate. The upper mantle sampled by Kimberlite diatremes in South Africa, for example, retains chemical variations indicating that komatiite is the only significant liquid to have been extracted (O'Hara *et al.* 1975). There is no imprint of the chemical variation which would have been caused by the removal of primary magma with the composition of the Karroo basalts. It is at least possible that komatiite was the primary magma parental to the Karroo volcanism.

There appears to be some discrepancy between the requirements of geochemists for 40–60% partial melting in the generation of komatiite and the 'field' evidence. Such extensive partial melting would tend to eliminate orthopyroxene from peridotite at lower pressures, yet the record of nodules in Kimberlite is one of komatiite extraction from an orthopyroxene-rich residuum. This is consistent with partial melting events at higher pressures (Howells *et al.* 1975), where large amounts of partial melting are no longer *required* to produce liquids with the major element chemistry of komatiites (O'Hara *et al.* 1975).

Could the authors' geochemical observations on komatiite be reconciled with 25–35% partial melting event leaving an olivine–alumina-poor orthopyroxene harzburgite residuum? What constraints can the authors place upon the composition of the source, and of the residual orthopyroxene for such a model?

#### References

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 O'Hara, M. J., Saunders, M. J. & Mercy, E. L. P. 1979 *Phys. Chem. Earth* **9**, 571–604.

R. W. NESBITT AND S.-S. SUN. Professor O'Hara's discussion raises three points.

1. We must admit the possibility that komatiitic liquids were produced in abundance after the Archaean but did not reach the surface. Professor O'Hara's question is an obvious one in view of the suggestion (O'Hara *et al.* 1975) that nodules in kimberlites contain evidence of komatiite extraction. We take it that the nodule 1032 is what Professor O'Hara regards as a possible komatiitic liquid. This is difficult to evaluate without trace element data. However, we note the TiO<sub>2</sub> content is low and the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio is higher than any komatiite that we have analysed. In terms of CaO/Al<sub>2</sub>O<sub>3</sub> ratio it cannot represent a Barberton komatiite but it could belong to the more abundant type (our AUPK).

2. We disagree with Professor O'Hara's suggestion that komatiite was the primary magma parental to Karroo volcanism. Much of our disagreement stems from what we are prepared to accept as a komatiite. In our definition, high MgO is certainly a criterion; but we would also regard low abundances of incompatible elements as being diagnostic. The Karroo basalts have unusually high abundances of incompatible elements (particularly K, Ti and Zr) and these levels cannot be derived by fractional crystallization of komatiitic liquids of Archaean type.

3. There is a circular argument involved in Professor O'Hara's discussion of the discrepancy between the requirements of geochemists and the 'field' (experimental?) evidence. Since he postulates that the nodules represent mantle material from which varying amounts of komatiitic liquid has been extracted, he therefore also postulates only small amounts of partial melting. He is of course drawn to this conclusion to reconcile the occurrence of orthopyroxene rich residues (the harzburgites). However, from the geochemical data on Archaean komatiites it is



clear that (a) large amounts of melting are involved and (b) orthopyroxene is either absent or present in small quantities. Our data on Archaean komatites are not consistent with a model involving an orthopyroxene rich harzburgite residue. However, there does seem to be a case for some orthopyroxene in the source in order to control the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio of komatiites (see Nesbitt *et al.* 1979).

J. V. SMITH, F.R.S. (*Department of the Geophysical Sciences, University of Chicago, U.S.A.*). Would the authors attribute low concentrations of chalcophilic elements to migration into a sulphur-rich outer core during accretion of the Earth? Such a conclusion would be consistent with a new model for heterogeneous accretion of the earth (J. V. Smith 1979, *Mineralog. Mag.* (in the press)), but might not be consistent with an oxygen-rich outer core as proposed by A. E. Ringwood (1977, *Geochem. J.* **11**, 111).

R. W. NESBITT AND S.-S. SUN. Unfortunately we have made very few quantitative measurements of the chalcophilic elements and therefore cannot comment on their abundance patterns in relation to the Earth models that Professor Smith mentions. However, it is clear that for some of the elements for which we have data, there is a systematic depletion. Phosphorus in particular shows a remarkable consistency in all high magnesian liquids such that with the exception of the l.r.e.e. enriched types, the  $\text{TiO}_2/\text{P}_2\text{O}_5$  ratio is always close to 10. Since we consider this to be the value for the bulk mantle this represents an order of magnitude greater than that observed in ordinary chondrites. Similarly, Archaean spinifex textured liquids of non-Barberton type (i.e. our AUPK) have high Ti/V ratios (about 14) compared with chondrites (10). Since Ti/Zr is chondritic in these liquids, we deduce that either the mantle is depleted in V or V is retained in the residue. Distribution coefficient data suggest that both olivine and orthopyroxene have higher values for Sc than V. However, since the Ti/Sc ratio for AUPK is chondritic, this suggests that neither of these minerals can control V sufficiently to affect the Ti/V ratio in the liquids. We are thus left to speculate that chromite is responsible. However, experimental evidence suggests that at this level of melting, chromite would not be residual in the source. We are therefore left with the possibility that the excess V is either not present in the Earth at all or it is in the core.