Depth and Degree of Melting of Komatiites

CLAUDE HERZBERG

Department of Geological Sciences, Rutgers University, New Brunswick, New Jersey Mineral Physics Institute, State University of New York, Stony Brook, New York

High pressure melting experiments have permitted new constraints to be placed on the depth and degree of partial melting of komatiites. Komatiites from Gorgona Island were formed by relatively low degrees of pseudoinvariant melting (< 30%) involving L + Ol + Opx + Cpx + Gt on the solidus at 40 kbar, about 130 km depth. Munro-type komatiites were separated from a harzburgite residue (L + Ol + Opx) at pressures that are poorly constrained, but were probably around 50 kbar, about 165 km depth; the degree of partial melting was < 40%. Komatiites from the Barberton Mountain Land were formed by high degrees ($\sim 50\%$) of pseudoinvariant melting (L + Ol + Gt + Cpx) of fertile mantle peridotite in the 80- to 100-kbar range, about 260- to 330- km depth. Secular variations in the geochemistry of komatiites could have formed in response to a reduction in the temperature and pressure of melting with time. The 3.5 Ga Barberton komatiites and the 2.7 Ga Munro-type komatiites could have formed in plumes that were hotter than the present-day mantle by 500° and 300°, respectively. When excess temperatures are this size, melting is deeper and volcanism changes from basaltic to komatiitic. The komatiites from Gorgona Island, which are Mesozoic in age, may be representative of komatiites that are predicted to occur in oceanic plateaus of Cretaceous age throughout the Pacific [Storey et al., 1991].

1. Introduction

Komatiites are high MgO volcanic rocks that can be roughly explained by high degrees of melting of mantle peridotite, typically 50 to 100 % [e.g., Viljoen and Viljoen, 1969; Green, 1972; Brooks and Hart, 1974; Cawthorn and Strong, 1974; Nesbitt and Sun, 1976; Bickle et al., 1977; Nisbet and Walker, 1982; Hess, 1990; Miller et al., 1991b]. But this interpretation is neither unique nor without its difficulties. Arndt [1977] pointed out the problem of forming komatiites in a single stage because basaltic melts are buoyant and they would segregate and drain from the source region before melting reached 20 to 30 %. Nisbet and Walker [1982] noted that this problem disappears at high pressures because olivine and komatiitic magmas are expected to have similar densities. The problem also disappears in the models of O'Hara et al. [1975] and Howells et al. [1975], who pointed out that initial melting at high pressures was likely to yield in a single stage komatiites instead of basalts. This high pressure origin has received considerable support from experimental data in the 100-kbar range [Herzberg and O'Hara, 1985; Takahashi, 1986; Wei et al., 1990; Herzberg et al., 1990].

Nesbitt et al. [1979] noted that wide variations exist in contents of CaO, Al₂O₃, and TiO₂, and subdivided komatiites into alumina-depleted and -undepleted types. If they were formed by very high degrees of melting, these differences can only be explained by differences in the composition of the source region [Cawthorn and Strong, 1974; Jahn et al., 1980; Herzberg and Ohtani, 1988; Anderson, 1989]. However, Arndt [1986] and Fujii et al. [1989] noted that these differences may not reflect the source, but instead are phase equilibrium-controlled at very high pressures. In order to test these possibilities, melting experiments have been run on compositions with a wide

Copyright 1992 by the American Geophysical Union.

Paper number 91JB03066. 0148-0227/92/91JB-03066\$05.00 range of CaO and Al_2O_3 contents in the 80- to 160-kbar range. A calibration has been made of the effect of pressure on CaO/(CaO + Al_2O_3) and MgO in komatiitic liquids formed on the solidus, and an examination has been made of the effect of FeO. It is now possible to simulate the melting of peridotite from 1 to 100 % and from 40 to 100 kbar, and the results are compared to the geochemistry of komatiites. This information is used to address the depths and degrees of melting, and the thermal state of the Earth during their formation.

These problems gain special significance now because komatiites have the potential of being probes into the major element geochemical structure of the mantle. If, for example, the Munro-type komatiites formed by melting in excess of 50 %, melting itself would have had to commence at lower mantle pressures (> 200 kbar [Miller et al., 1991b]), indicating a peridotite source region distributed throughout portions of the lower mantle during Archean times. Similarly, if the Barberton komatiites were formed by extensive melting, the source region must have been very different from mantle peridotite, possibly similar to piclogite in the transition zone [Anderson, 1989]. It is demonstrated in this paper that this kind of information cannot be obtained because the geochemistry of komatiites is determined largely by phase equilibrium processes rather than by the bulk composition of their source region.

2. EXPERIMENTAL METHOD AND RESULTS

With one exception, all experiments were carried out using the 2000-ton split sphere anvil apparatus at Stony Brook. A detailed description of the press, the sample assembly, and the techniques has been given in numerous papers [Gasparik, 1989, 1990; Herzberg et al., 1990; Herzberg and Gasparik, 1991], and will not be repeated here.

The starting materials were naturally occurring komatiites and several compositions in CaO-MgO-Al₂O₃-SiO₂ (CMAS), and they are listed in Table 1. The compositions and experiments in CMAS are identical to the ones reported by *Herzberg and Gasparik* [1991]. In both this and the companion study, melting

TABLE 1. Compositions of Starting Materials and Average Mantle Peridotite

	1	2	3	4	5	6
	C ₆₇ PX ₃₃	C ₅₀ PX ₅₀	PX	HSS-15	P9-118	Mantle
SiO ₂	53.14	54.58	58.92	46.77	44.26	44.47
TiO,	-	-	-	0.33	0.35	0.10
Al_2O_2	3.37	2.53	-	3.42	7.38	2.57
Fe ₂ O ₃	-	-	-	1.88	-	-
FeO	-	-	-	9.38	13.26	8.31
MnO	-	-	-	0.19	0.26	0.13
MgO	39.12	38.23	35.58	31.51	27.37	40.98
CaO	4.37	4.66	5.50	5.67	6.31	2.46
Na ₂ O	-	-	-	0.12	0.06	0.23
K ₂ O	-	-	-	0.08	0.08	0.05
Cr ₂ O ₃	-	-	-	0.34	0.48	0.43
NiO	-	-	-	0.27	0.20	0.27
Total	100.00	100.00	100.00	99.96	100.00	100.00
$CaO/(CaO + Al_2O_3)$	0.56	0.65	1.00	0.62	0.46	0.49

TABLE 2. Experimental Results

Starting	T Nominal	P	Time	Crystallization			
Material	°C	kbar	min	Sequence			
1	2000	80	4.0	L,Opx,Ol,Gt,Cpx [Ol + Cpx + Opx + Gt]			
1	2050	90	4.0	L,Opx,Ol,Gt,Cpx [Ol + Cpx + Opx + Gt]			
1	2070	100	3.0	L,Opx,Ol,Gt,Cpx [Ol + Cpx + Opx + Gt]			
1	2140	110	4.0	L,Opx,Ol+Gt,Cpx[Ol+Cpx+Opx+Gt]			
2	2080	100	4.0	L,Opx,Ol,Gt+Cpx [Ol + Cpx + Opx + Gt]			
2	2140	110	2.0	L,Opx,Ol,Gt,Cpx[Ol+Cpx+Opx+Gt]			
2	2220	130	5.0	L,Gt,Cpx2,Cpx1,Ol*[Ol+Cpx1+Cpx2+Gt]			
2	2240	140	4.0	L,Gt,Cpx2,Cpx1,O1 [Ol + Cpx1 + Cpx2 + Gt]			
3	2200	150	4.0	L,Cpx2,Cpx1 [Cpx1 + Cpx2]			
3	2240	160	4.0	L,Gt,Cpx1 [Gt]			
4	1920	80	4.0	L,Opx,Ol,Cpx,Gt [Ol + Cpx + Gt]			
4	1920	100	5.0	L,Opx,Gt,Ol,Cpx[Ol + Cpx + Gt]			
5	1600	29	60.0	L,Ol,Cpx,Opx,{Gt} [?]			

[Phases in square brackets] = subsolidus phase assemblage. $\{Gt\}$ = Garnet inferred, not observed. Cpx1 = High Ca Clinopyroxene.

experiments were performed on compositions that contain on the solidus the phase assemblage Liquid + Olivine + Orthopyroxene + Clinopyroxene + Garnet (L + Ol + Opx + Cpx + Gt) in the 80- to 160-kbar range. The purpose of the Herzberg and Gasparik [1991] study was to calibrate the compositions of coexisting garnets and pyroxenes that occur at all conditions in the upper mantle and transition zone. The starting material compositions were carefully selected in order to provide excess orthopyroxene at all conditions, and to provide the greatest probability of observing liquids that were multiply saturated in the greatest number of crystalline phases. In addition to highly precise equilibrium pyroxene and garnet compositions, these experimental data provide improved constraints on the compositions of the liquids for the solidus

assemblage L + Ol + Opx + Cpx + Gt. The purpose of this paper is to present these liquid data in light of the komatiite problem.

Starting materials were loaded into rhenium containers, and 10 mm size assemblies were used. These were then fired at 1000°C for 1 hour prior to running in order to expell all water. Run conditions ranged from 80 to 160 kbar, and from 2000 to 2240°C nominal. Run durations were typically 3 to 5 min. Thin sections were made of the run products, and the garnet and pyroxene compositions were determined by electron probe analysis [Herzberg and Gasparik, 1991].

Of particular interest here is the crystallization sequence, or the order of the phases as they appear from the hot spot to the cold end. These are listed in Table 2. The nomenclature L,

^{*} Opx transforms to Cpx2, a low Ca clinopyroxene, between 110 and 120 kbar [Herzberg and Gasparik, 1991].

Opx, Ol, Gt, Cpx [Opx + Ol + Gt + Cpx] refers to this crystallization sequence, which is a short-hand notation for L; L + Opx; L + Opx + Ol; L + Opx + Ol + Gt; L + Opx + Ol+ Gt + Cpx; the subsolidus phase assemblage is given in brackets [Opx + Ol + Gt + Cpx]. The nominal temperatures given in Table 2 are temperatures recorded by the thermocouple. The thermocouple junction is located close to but to one side of the hot spot, and the temperature it reads is valid at one point along the temperature gradient. This is 50°C within 0.7 mm of the hot spot, increasing to about 250°C to the cold end of the capsule, about 2 mm distant [Herzberg et al., 1990]. In most experiments the nominal temperature is slightly above the solidus temperature [Herzberg and Gasparik, 1991], and the crystalline phases of interest are usually distributed within 1 mm of the hot spot where the temperature gradient is minimal. The liquidus and solidus temperatures differ by 100-150°C, and it is within this temperature range where the crystallization sequence can be observed.

A source of some concern involves the acquisition of phase equilibrium information in a temperature gradient, and again a detailed discussion of this problem appears in Herzberg et al. [1990]. The major effect is the expulsion of some intergranular melt toward the hot spot and solution-precipitation of the crystalline phases, observations that were originally made and discussed by Lesher and Walker [1988] from piston-cylinder experiments. The concern is that this process could affect the liquidus phase and crystallization sequence. For experiments that range from seconds to 10 min., we have observed no changes in the liquidus phase, in agreement with the treatment of Lesher and Walker [1988]. However, for liquids that are multiply saturated in two or more crystalline phases, these phases are not always distributed in the cotectic proportions that would be expected from crystallization in the absence of a temperature gradient. Rather, some phases concentrate in bands that parallel the isotherms for experiments greater than 2 - 3 minutes in duration [see Figures 7, 10, & 19 in Herzberg et al., 1990]. These phases are ordered along the temperature gradient in a way that reflects the crystallization sequence. experiments containing only three crystalline phases, the liquidus phase is obvious, the second phase appears at and below the solidus, and the third phase is distributed between these two bounding phases. A more complicated case involves four crystalline phases. A good example involves the case of peritectic melting in the 80 kbar experiment on natural komatiite The crystallization sequence is HSS-15 (Table 2). L,Opx,Ol,Cpx,Gt, [Ol + Cpx + Gt].Orthopyroxene is completely absent in the subsolidus, but is abundant and ubiquitous throughout the crystallization interval. Identical observations were reported by O'Hara and Yoder [1967] on the melting of a mixture of olivine + garnet + clinopyroxene at 30 kbar by a series of isothermal piston-cylinder experiments, each with a minimal temperature gradient. The melting relation proposed by O'Hara and Yoder [1967] is L + Opx = Ol + Cpx+ Gt, identical to the one reported by us at 50 and 100 kbar [Herzberg et al., 1990] (see below) based on observations of the isobaric crystallization sequence and the compositions of coexisting pyroxenes. We have now obtained internally consistent isobaric phase diagrams from experiments done on a wide range of different starting material compositions, and have encountered no complications arising from the temperature

In two important experiments, a pair of phases were observed to appear simultaneously along an isotherm. These are O1 + Gt at 2140°C and 110 kbar, and Gt + Cpx at 2080°C and 100 kbar (Table 2). In the latter experiment, olivine was observed several tens of degrees up the temperature gradient, indicating a close approach to simultaneous crystallization of olivine, clinopyroxene, and garnet for this composition at the solidus. Experiments like these yield the most information on the T-P-X disposition of cotectics and invariant points, and these are discussed below.

A 29 kbar experiment on a natural komatiite is also reported in Table 2. This was done with the piston-cylinder apparatus in 1980 at the Johnson Space Center. The purpose of this and others like it was to determine the partitioning of Fe and Mg between olivine and liquid; a full reporting of these low pressure data will be made elsewhere in conjunction with new data in the 100-kbar range. The low pressure experiment is included in this paper because it provides a constraint on the compositions of liquids along the high pressure solidus.

3. DISCUSSION OF RESULTS

3.1. The System CaO-MgO-Al₂O₃-SiO₂

The locations of the cotectics and invariant points are projected in Figures 1-4. These figures are very similar to the ones published previously by *Herzberg et al.* [1990], differing in that the phase boundaries are much more tightly constrained. In particular, it has been possible to position accurately the important parameter CaO/(CaO + Al₂O₃) for liquids on the solidus (L + Ol + Opx + Cpx + Gt), and this was done by observing simultaneous crystallization of clinopyroxene + garnet at the solidus.

It was determined previously that the generation of liquids coexisting with the four crystalline phases Ol + Opx + Gt + Cpx at 30 and 40 kbar is peritectic and takes the form L + Opx = Ol + Gt + Cpx [Davis, 1964; Davis and Schairer, 1965; O'Hara and Yoder, 1967]. This peritectic reaction was also observed at 50 and 100 kbar [Herzberg et al., 1990], and our new results support this earlier work (Figure 1). The extensive solubility of enstatite in clinopyroxene at melting conditions yields a small tetrahedron of Ol + Opx + Cpx + Gt, thereby restricting the stabilization of orthopyroxene-bearing assemblages to compositions that are fairly silica-rich, such as chondrite. Liquids generated by melting at 50 and 100 kbar are located outside this tetrahedron, to the enstatite-poor side of the plane Ol + Cpx + Gt. The experiments on natural komatiite HSS-15 at 80 and 100 kbar illustrate the peritectic melting behaviour as well (Table 2; point #4 in Figure 1).

Figure 2 shows that fractionation of orthopyroxene can yield liquids with lower silica contents by crystallization down the cotectic L + Ol + Gt + Cpx which degenerates to a thermal minimum. The exact location of this thermal minimum has not yet been determined. However, the evidence presently available indicates that it is more siliceous than mantle peridotite analogues in CMAS, similar to the peritectic points [Herzberg et al., 1990].

Presnall and Gasparik [1990] concluded that the silica contents at these peritectics were still too low, based on the location of their 165 kbar eutectic L + Fo + Opx on the binary Mg₂SiO₄ - MgSiO₃ (Figure 2). They argued that the peritectic point located by us is in error because it would require an implausibly strong rotation of the L + Fo + Opx cotectic, as indicated also in Figure 2. But this criticism is actually erroneous because it stems from a distortion in the diopside

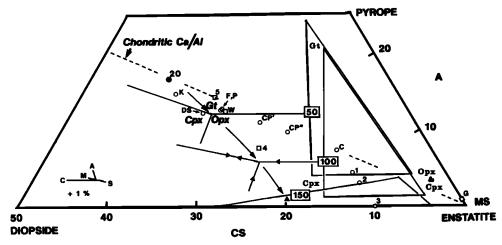


Fig. 1. A projection to and from olivine (M₂S) into part of the plane CS-MS-A (mole percent) [O'Hara, 1968], modified after Herzberg et al. [1990]. Garnet and pyroxene compositions at the pressures indicated (kilobars) are from Herzberg and Gasparik [1991]. The crystallization fields and cotectics are strictly valid for the system CaO-MgO-Al₂O₃-SiO₂. DS is 40 kbar invariant point from Davis and Schraier [1965]; F is 54 kbar invariant point from Fujii et al. [1989]; W is natural komatiite M620 from Wei et al. [1990]. K (komatiite), P (peridotite), C (chondrite), and CP (chondrite-peridotite mixtures) are compositions and experimental results reported in Herzberg et al. [1990]. Compositions 1, 2, 3, 4, and 5 are listed in Table 1.

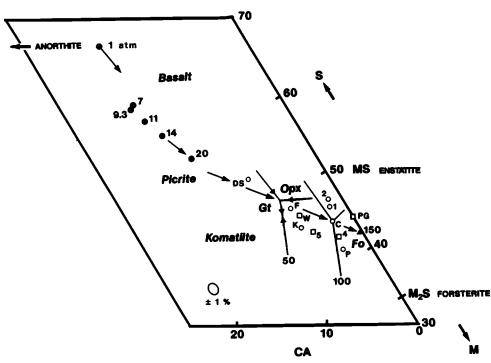


Fig. 2. A projection to and from diopside (CMS₂) into part of the plane CA-M-S (mole percent) [O'Hara, 1968], modified after Herzberg et al. [1990]. Solid circles are the compositions of liquids formed by isobaric invariant melting on the solidus in CaO-MgO-Al₂O₃-SiO₂: 1 atm from Longhi [1987] and 7 to 20 kbar from Presnall et al. [1979]. Other symbols as for Figure 1. PG is eutectic in MgSiO₃-Mg₂SiO₄ at 165 kbar from Presnall and Gasparik [1990]. Crystallization fields and cotectic boundaries are strictly valid for the system CaO-MgO-Al₂O₃-SiO₂ (kbar), and may or may not be saturated in clinopyroxene.

projection. This point is illustrated better in Figure 3, a projection from Al_2O_3 into a part of the plane CaO-MgO-SiO₂. It can be seen that pressure does indeed rotate the cotectic L + Fo + Opx rather substantially, and that the peritectic invariant points at 100 to 150 kbar have contents of silica that are very similar to those on the forsterite-enstatite join.

At 50 kbar the crystallization field of orthopyroxene is very extensive (Figure 1), and orthopyroxene will participate in the melting of mantle peridotite (L + Ol + Opx + Cpx + Gt; Figure 1) [Herzberg et al., 1990]. Pressure causes the orthopyroxene crystallization field to contract, and at 100 kbar

it is absent for mantle peridotite which will melt to the assemblage L+Ol+Gt+Cpx on the solidus. Initial melting is strictly pseudoinvariant because the liquid is unlikely to be perfectly coincident in composition with the thermal minimum. These initial liquids and the thermal minimum are probably enriched in SiO_2 compared to mantle peridotite (Figure 2), and progressive melting will cause a reduction in these silica contents by migration up the cotectic L+Ol+Gt+Cpx (Figure 2).

Figure 4 is a projection from enstatite into a plane that contains forsterite - diopside - pyrope. It is geologically very useful because the compositions of most mantle peridotites and

komatiites are contained close to this plane, so that ambiguities stemming from distortions are minimized. The advantage of viewing things this way is that we can now concentrate on the contents of CaO and Al_2O_3 , and how these change with pressure. The most important observation is that pressure greatly expands the crystallization field of garnet at the expense of both olivine and clinopyroxene (Figure 4), and garnet can be seen to expand at the expense of orthopyroxene as well (Figure 1). This causes a very pronounced increase to occur in CaO/(CaO + Al_2O_3) for liquids that are multiply saturated in Cpx + Gt, and this is shown in Figure 5.

The experimental data in CMAS position CaO/(CaO + Al₂O₃) at 0.65 and 100 kbar (Table 2; 2080°C and 100 kbar). Near 160 kbar, this value increases to 1.0, based on the stabilization of majorite garnet in the alumina-free system CMS;

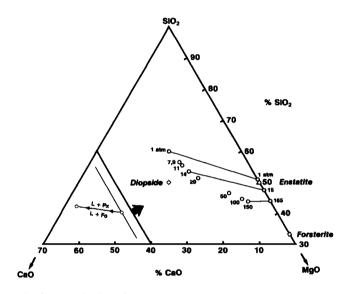


Fig. 3. A projection of invariant points and the cotectic equilibrium L + Fo + Px from alumina (Al₂O₃) into part of the plane CaO-MgO-SiO₂. Data on the join MgO-SiO₂: 1 atm from Andersen [1915]; 15 kbar from Taylor [1973]; 165 kbar from Presnall and Gasparik [1990].

a thermodynamic analysis of these results positions it more precisely at 158 kbar [Herzberg and Gasparik, 1991]. At 140 kbar, CaO/(CaO + Al₂O₃) is constrained to be greater than 0.79; this was determined from solidus garnets occurring without clinopyroxene, data reported in Herzberg et al. [1990] together with the equilibrium constant that describes the partitioning of CaO and Al₂O₃ between garnet and liquid [Herzberg and Gasparik, 1991]. Included in Figure 5 are experimental data in natural FeO-bearing systems from many sources. The important observation is that these additional components have no effect, a point discussed in more detail below.

At pressures greater than or equal to 158 kbar, pyroxenes cannot crystallize in the melting interval for any composition because of the extensive crystallization field of majorite garnet. Alumina is absent in liquids generated on the solidus (i.e., $CaO/(CaO + Al_2O_3) = 1.0$), but it can be present in liquids located between the liquidus and solidus. This condition is likely to persist until about 180 kbar where calcium perovskite has been predicted to become stabilized relative to majorite garnet [Gasparik, 1990]. At pressures greater than this, liquids on the solidus will contain Al_2O_3 once again. A better understanding of these very high pressure phase relations must await the acquisition of additional experimental data.

The phase equilibrium data reported here and in *Herzberg* et al. [1990] for the system CMAS have permitted for the first time estimates of the absolute compositions of the liquids for the equilibrium L + Ol + Opx + Cpx + Gt in the 50- to 100-kbar range. They were determined by randomly varying the liquid composition at 50 and 100 kbar until the isobaric invariant points were internally consistent with both the high pressure data (Figures 1-4) and the low pressure data of *Presnall et al.* [1979]. These liquid compositions are listed in Table 3, together with a rough estimate of the 150 kbar liquid. The latter was estimated in part by the value of unity for CaO/(CaO + Al₂O₃) at 158 kbar (Figure 5).

We are now in a position to evaluate the full range of liquid compositions on the solidus to 150 kbar, and the results are shown in Figure 6. The experimental data at 1 atm to 20 kbar [Longhi, 1987; Presnall et al., 1979] provide an important low pressure reference frame for understanding the high pressure

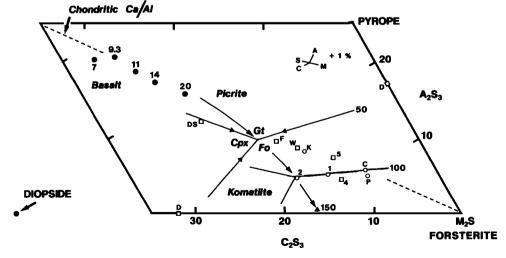


Fig. 4. A projection to and from enstatite (MS) into part of the plane $M_2S - C_2S_3 - A_2S_3$ (mole percent) [O'Hara, 1968], modified after Herzberg et al. [1990]. Symbols as for Figures 1 and 2. The crystallization fields and cotectic boundaries are strictly valid for the system CaO-MgO-Al₂O₃-SiO₂, and may or may not be saturated in orthopyroxene.

data, and demonstrate that discontinuous changes occur in all oxide components at phase boundaries. These are especially evident at around 9 kbar, where plagioclase peridotite transforms to spinel peridotite [Presnall et al., 1979] and at 22 kbar where spinel peridotite transforms to garnet peridotite (Figure 6). The lowest concentrations of SiO₂ are 47 to 48 % at 22 kbar, and at higher pressures there is a steady increase to about 52 % at 150

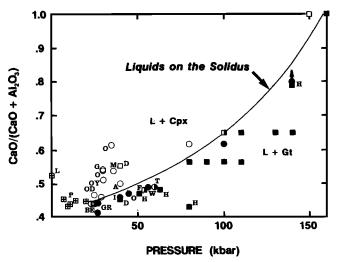


Fig. 5. CaO/(CaO + Al₂O₃) by weight for liquids on the solidus as a function of pressure. Squares are data in CaO-MgO-Al₂O₃-SiO₂, circles are data in natural FeO-bearing systems. Solid symbols are liquid + garnet; open symbols are liquid + clinopyroxene; half open/half solid symbols are liquid + garnet + clinopyroxene. Squares with crosses are solidus liquids in CaO-MgO-Al₂O₃-SiO₂ at 1 atm (L; Longhi [1987]) and 7 to 20 kbar (P; Presnall et al. [1979]). Unlabelled symbols are data reported in this paper. Other data sources: A, Arndt [1976]; B, Bertka and Holloway [1988]; D, Davis [1964]; E, Elthon and Scarfe [1984]; F, Fujii et al. [1989]; G, Falloon et al. [1988]; GR, Green and Ringwood [1967]; H, Herzberg et al. [1990]; I, Ito and Kennedy [1967]; M, Mysen and Kushiro [1976]; O, Howells et al. [1975]; OD, Obata and Dickey [1976]; OY, O'Hara and Yoder [1967]; T, Takahashi [1986]; W, Wei et al. [1990]. The 40 kbar invariant point in CMAS estimated by Davis and Schairer [1965] coincides with data point A. Data of Kushiro et al. [1968] and Takahashi and Kushiro [1983] on peridotite HK66 $[CaO/(CaO + Al_2O_3) = 0.38]$ are anomalous because they show clinopyroxene stable relative to garnet (L + Cpx) from 30 to 50 kbar; this indicates a possible error in their reported bulk composition.

kbar. Pressure causes a continuous increase in MgO to contents that are typical of komatiite analogues in CMAS, and it tends to decrease the content of CaO, and most notably Al_2O_3 , which drops to zero at 158 kbar. The low contents of alumina are particularly relevant to the aluminum-depleted komatiites from the Barberton Mountain Land.

The concentrations of these four oxide components at pressures greater than 22 kbar have been fitted to the polynomial:

$$SiO_2(wt\%) = a + bP + cP^2 + dP^3$$

The coefficients a, b, c, and d are listed for each oxide component in Table 4. It is important to note that these equations are only valid for liquids that are buffered by the four crystalline phases Ol + Opx + Cpx + Gt. Many naturally-occurring peridotites and peridotite analogues contain orthopyroxene on the solidus at 22 to 50 kbar, but loose it at pressures much higher than 80 kilobars. When this occurs, melting is along a cotectic L + Ol + Cpx + Gt (see above), and the liquids will have contents of SiO_2 that are less and contents of MgO that are somewhat greater than those shown in Figure 6.

3.2. Natural Complex Systems

For ultramafic rocks such as komatiites and peridotites, the major difference between the analogue system CMAS and natural complex systems is the presence of iron. The system CaO-MgO-FeO-Al₂O₃-SiO₂ (CMFAS) therefore represents about 98-99 % of the geochemistry of these rocks in nature. Several experiments were run on natural komatiite compositions. One is P9-118, an alumina-undepleted komatiite from Munro Township donated to the author by Nicholas Arndt. The other is HSS-15, an alumina-depleted komatiite from the Barberton Mountain Land, originally described by Smith and Erlank [1982]. Melting experiments were reported for HSS-15 by Wei et al. [1990], and samples were donated to the author by Reidar Tronnes. The reason why additional experiments were run on the Barberton sample is because no distinction was reported between clinopyroxene and orthopyroxene in the experiments of Wei et al. [1990]. The distinction is important because it is the observation of multiple saturation in garnet and clinopyroxene that determines the parameter CaO/(CaO + Al₂O₃) for liquids on the solidus. The compositions of these komatiite starting

TABLE 3. Compositions of Liquids on the Anhydrous Solidus

	Pressure, kbar										
	1atm	7	9.3	11	14	20	50	100	150		
SiO ₂	55.40	50.62	49.57	49.13	48.88	48.23	49.5	51.2	52.4		
Al_2O_3	15.20	18.95	20.54	19.72	18.45	17.47	10.0	4.2	0.5		
MgO	12.40	14.66	14.30	15.69	17.47	20.22	30.5	36.8	40.2		
CaO	17.00	15.76	15.59	15.47	15.20	14.08	10.0	7.8	6.9		

¹ atm from Longhi [1987]; 7-20 kbar from Presnall et al. [1979] normalized to 100%; and 50-150 kbar from this work.

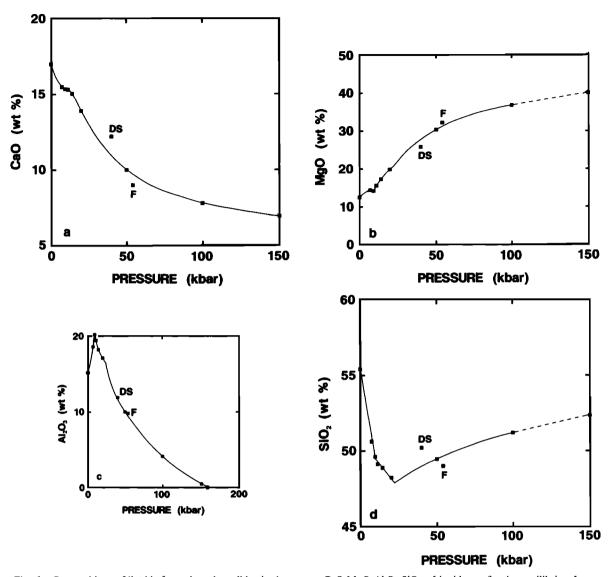


Fig. 6. Compositions of liquids formed on the solidus in the system CaO-MgO-Al₂O₃-SiO₂. Liquids are for the equilibria: L + Fo + Opx + Cpx + Anorthite (1 atm to 9.3 kbar [Longhi, 1987; Presnall et al., 1979]); L + Fo + Opx + Cpx + Spinel (9.3 to 22 kbar [Presnall et al., 1979]); L + Ol + Opx + Cpx + Garnet (22 to 158 kbar; Table 3). DS, Davis and Schairer [1965]; F, Fujii et al. [1989].

TABLE 4. Coefficients for Liquids on the Anhydrous Solidus in the system CaO-MgO-Al₂O₃-SiO₂ and at Pressures in the Garnet Stability Field (L + Ol + Opx + Cpx + Gt)

		· .	-/10-3\	4/10-6\	
		b	c(10³)	d(10°)	
SiO ₂	46.15	0.0913	-0.561	1.54	
Al ₂ O ₃	26.04	-0.4775	3.677	-10.86	
MgO	9.21	0.6562	-5.415	16.12	
CaO	18.60	-0.2699	2.299	-6.80	

 SiO_2 (wt%) = a + bP + cP² + dP³ ...where P is in kbar

materials are given in Table 1, and the experimental results are included in Table 2.

In the 80 kbar experiment on HSS-15, clinopyroxene occurs above the solidus, and garnet is restricted to temperatures at and below the solidus; the opposite was observed at 100 kbar.

These results are shown in Figure 5. The pressure at which multiple saturation occurs in garnet and clinopyroxene is located between these brackets, and is valid for $CaO/(CaO + Al_2O_3)$ of HSS-15, that being 0.62. This is exactly the value that is predicted by the experimental data in the simple system CMAS.

Most garnet synthesis experiments in natural complex systems have been done on komatiite, peridotite, and eclogite compositions restricted to the 23- to 40-kbar range, and the results are included in Figure 5. The important observation is that the addition of FeO neither expands nor contracts the crystallization field of garnet with respect to clinopyroxene. This is illustrated by the data of Bertka and Holloway [1988] on a very iron-rich garnet lherzolite composition that is appropriate for Mars. The minimum melt at 23 kbar has the following properties: 23.3 % FeO; 12.7 % MgO; CaO/(CaO + Al₂O₃) = 0.44. In the iron-free system CMAS, it is predicted that CaO/(CaO + Al₂O₃) = 0.44 at 23 kbar. It can be seen that the parameter CaO/(CaO + Al₂O₃) is common to both CMAS and all geochemical systems of interest.

Addition of FeO does not affect the crystallization field of garnet with respect to clinopyroxene presumably because it lowers the freezing temperatures of the iron-free end-members CaMgSi₂O₆ and Mg₃Al₂Si₃O₁₂ about equally. The major effect of FeO is to lower the SiO₂ content of a liquid at an isobaric invariant point. In the very FeO-rich composition reported by Bertka and Holloway [1988], SiO₂ = 41.9 % for the liquid (L + Ol + Opx + Cpx + Gt; 23 kbar). This compares with about 48 % in the system CMAS (Figure 6d) and 44.4 % in CMFAS when MgO is replaced by FeO in the appropriate proportions. This effect is also observed in other ways. For komatiite HSS-15 at 100 kbar (point #4 in Figures 2 & 4), the crystallization sequence in CMAS is predicted to be L,Opx,Ol,Gt,Cpx. This differs from the observed crystallization sequence L,Opx,Gt,Ol,Cpx, demonstrating that FeO expands the crystallization field of garnet at the expense of olivine. Liquids at isobaric invariant points in CMAS have slightly higher CaO, Al₂O₃, and SiO₂ than those found in nature. An estimate of these effects is now made.

As a first step in extending CMAS to CMFAS, MgO was replaced by FeO using the distribution coefficient $K_D = (\text{MgO/FeO})_{\text{Liquid}} \times (\text{FeO/MgO})_{\text{Ohvane}}$. The value of K_D is 0.34 at 30 to 40 kbar [Bickel et al. 1977], and remains fairly constant in the 100-kbar range [Takahashi, 1986; C. Herzberg, unreported data, 1991]. The initial liquid compositions were calculated by mass balance with olivine of a known composition, this being Fo₉₀ for average mantle peridotite [Boyd, 1989], and Fo₇₅ for a presumed Martian mantle olivine [Bertka and Holloway, 1988]. This first step will yield a liquid composition that projects to the same location as that in CMAS. In the second step, the contents of SiO₂, Al₂O₃, and CaO were lowered because FeO contracts the crystallization field of olivine as discussed above. The Bertka and Holloway [1988] data were used to parameterize this effect, and the results are:

$$SiO_2 = [a + bP + cP^2 + dP^3] \times [1 - 0.46(FeO/MgO)]$$

where the coefficients a, b, c, and d are valid for the system CMAS (Table 4), and FeO/MgO (wt.%) is for the composition of olivine in the source region. Similarly, the reductions in CaO and Al_2O_3 were parameterized by the following:

$$Al_2O_3 = [a + bP + cP^2 + dP^3] \times [1 - 0.69(FeO/MgO)]$$

 $CaO = [a + bP + cP^2 + dP^3] \times [1 - 0.69(FeO/MgO)]$

The algorithm is simple because CMAS can be extended to CMFAS by the introduction of two constant parameters (i.e., 0.46 and 0.69), and two adjustable parameters, the composition of olivine in the source and the degree of partial melting; a copy of it can be obtained from the author as a computer program. Again the liquids so calculated are valid only for initial melting at pressures in the garnet stability field.

Table 5 shows that the calculated iron-rich initial melt composition of Bertka and Holloway is in excellent agreement with the observed composition. The melting of mantle peridotite on Earth at 25 kbar will generate picrite, and Table 5 shows that the calculated composition is also in very good agreement with that determined experimentally by *Elthon and Scarfe* [1984].

Initial liquids formed at 50 kbar contain 23.2 to 25.3 % MgO and 13.7 to 10.7 % FeO, depending on the degree of partial melting (Table 5). At 100 kbar, MgO ranges from 27.4 to 30.4 %. These compare with 24 % MgO at 40 kbar, determined experimentally by Litvin [1989]. Liquids generated at 50 and 100 kbar invariant points are distinctly komatiitic in composition, and their significance to the Earth will be addressed below. These liquid compositions are now projected in Figures 7a & b in order to demonstrate the effect of FeO on expanding the crystallization fields of garnet, clinopyroxene, and orthopyroxene at the expense of olivine.

Use of liquid compositions in CMAS are actually very successful when applied to naturally occurring rocks with a terrestrial FeO/MgO. Simple substitution of MgO for FeO without accounting for a contraction of the crystallization field of olivine results in contents of SiO₂, Al₂O₃, and CaO that are too high by 1.7 %, 0.3 %, and 0.6 %, respectively (absolute), at 100 kbar; MgO and FeO are too low by 2 % and 0.6 %, respectively. However, these small differences can yield very different crystallization sequences. For example, the system CMAS predicts the crystallization sequence L,Opx,Ol,Gt,Cpx for HSS-15 at 100 kbar. This compares with L,Opx,Gt,Ol,Cpx, a crystallization sequence that is both experimentally observed (Table 2) and predicted in CMFAS (Figure 7).

At the present time, the largest discrepancy between calculated and observed liquid compositions is for the Elthon and Scarfe [1984] picrite at 25 kbar (Table 5). Although the disagreement is not understood, accepting it at face value illustrates that the calculated and observed liquid compositions differ by no more than the following relative amounts: +/- 5 %

TABLE 5.	Compositions of Liquids on the Anhydrous Solidus in the System CaO-MgO-FeO-Al ₂ O ₃ -SiO ₂
	and at Pressures in the Garnet Stability Field (L + Ol + Opx + Cpx + Gt)

Pressure 23 kbar		25		50			100			
% Mel	ting 1		1		1	20	40	1	20	40
Fo	0.	75	0.9	0	0.90	0.91	0.93	0.90	0.92	0.93
	Calc.	Obs.*	Calc.	Obs.#	Calc.	Calc.	Calc.	Calc.	Calc.	Calc.
SiO ₂	42.0	41.9	45.5	47.9	45.7	45.9	46.2	46.1	46.7	47.0
Al ₂ O ₃	11.9	11.9	14.5	13.8	8.7	8.8	8.9	3.6	3.6	3.7
FeO	23.4	23.3	10.7	9.9	13.7	12.1	10.7	16.2	14.0	12.1
MgO	13.1	12.7	17.5	16.6	23.2	24.4	25.3	27.4	29.0	30.4
CaO	9.6	9.4	11.8	10.9	8.7	8.8	8.9	6.7	6.7	6.8

^{*} From Bertka and Holloway [1988].

[&]quot; From Elthon and Scarfe [1984].

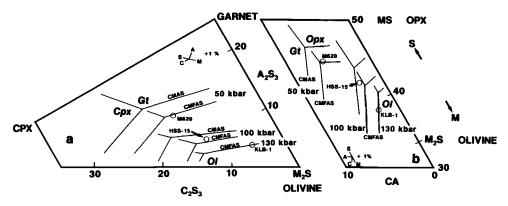


Fig. 7. Pseudoinvariant points and cotectic boundaries in the system CMFAS compared to CMAS (Figures 2 and 4). Experimental work on KLB-1 [Herzberg et al., 1990] show the crystallization sequence L,Gt,Ol,Cpx at 140 kbar; multiple saturation in olivine + garnet (L + Ol + Gt) has not been determined, but will not be much lower than 130 kbar.

for SiO₂, Al₂O₃, and MgO; +/-8 % for FeO and CaO (Table 5). The most serious difficulty is with SiO₂. The value offered by Elthon and Scarfe [1984] is 47.9% substantially higher than the calculated value (45.5 %). But this high SiO₂ is probably incorrect because it predicts a crystallization field of olivine (L + Ol) at 27 to 30 kbar for which orthopyroxene (L + Opx) was observed instead for the binary diopside-pyrope in CMAS, the FeO-bearing composition Cpx₂₅Opx₂₅Gr₅₀ (A3/10596) [O'Hara and Yoder, 1967], and the picrite of Green and Ringwood [1967]. Mysen and Kushiro [1977] also reported very low silica contents at 20 kbar. It is concluded, therefore, that initial melting in the 25 kbar range yields picritic liquids (~16 - 17 % MgO) with low SiO₂ (45 - 46 %; Table 5).

The component Na₂O will reduce the amount of MgO that is contained in liquids on the solidus because it reduces the solubility of olivine in silicate liquids [Herzberg, 1979]. At 15 kbar, the addition of 3.5 % Na₂O to the system CMAS can reduce MgO from about 17 % to 10 %, and it also contributes to a lowering of SiO₂ [D. C. Presnall, personal communication 1991]. This will cause an important uncertainty in estimating the MgO content of initial liquids in which Na2O is concentrated, a problem that is likely to be important for small melt fractions (i.e., 1-2 %). However, this problem is not likely to be important in interpreting most komatiites because they typically contain less 0.5 % Na2O, and most of them were formed by degrees of melting that exceeded 25 % (see below). But the reader should be cautioned that liquids on the solidus in the system CMFAS (Table 5) will be too high in MgO, especially for low melt fractions that contain several percent Na₂O.

4. DEPTH AND DEGREE OF MELTING OF KOMATITES

4.1. Geochemical Types of Komatiites

In Figure 8 are projected the compositions of 668 peridotites from our world data base [Herzberg et al., 1988, 1990] together with 255 komatiites. The komatiite data base is from too many sources to list, but a sampling includes Nesbitt and Sun [1976], Nesbitt et al. [1979], Arndt et al. [1977], Viljoen and Viljoen [1969], Smith and Erlank [1982], Pyke et al. [1973], and Nisbet et al. [1987]. The peridotites are the so-called "oceanic" types [Boyd, 1989]; these include all samples with the exception of the "continental" types which are the coarse-grained and low temperature xenoliths from sourthern Africa. The average of the 668 peridotites is listed in Table 1,

and is very close to the average of 384 spinel lherzolites compiled by Maaloe and Aoki [1977].

The komatiites are divided into two populations. One is the alumina-depleted type komatiite [Nesbitt et al., 1979] which is characteristic of the Barberton Mountain Land and Pilbara, and are these have ages of about 3.5 Ga [Jahn et al., 1982; Gruau et al., 1990a]. The second is the alumina-undepleted type which is most commonly found in other cratons and is typically younger (e.g., 2.7 Ga [Gruau et al., 1990a]); these are well represented by komatiites from the Munro Township in the Abitibi greenstone belt in Canada [Arndt et al., 1977]. The alumina-undepleted character of the Munro komatiites is revealed by their ratio of CaO/(CaO + Al₂O₃) (by weight) that averages 0.49 (see appendix; CaO/Al₂O₃ = 0.99), essentially identical to average mantle peridotite [Herzberg et al., 1990]. The contents of CaO and Al₂O₃ are indicated in Figure 8 by the coordinates C₂S₃ and A₂S₃, the chondritic value included for reference. The alumina-depleted character of the Barberton komatiites is manifest by high CaO/(CaO + Al₂O₃), and this is clearly evident in Figure 8b.

Komatiites from the Gorgona Islands have a major element geochemistry that is similar to Munro [Gansser et al., 1979; Echeverria, 1982; Aitken and Echeverria, 1984], and they are important because of they are Mesozoic in age [Walker et al., 1991]. In detail, however, they are slightly lower in both CaO/(CaO + Al₂O₃) and MgO compared to Munro-type komatiites.

An analysis now follows of the depths and degrees of partial melting that were involved in the formation of the Munrotype, Barberton, and Gorgona komatiites. The depths of melting have been estimated from CaO/(CaO + Al₂O₃). The degrees of partial melting have been estimated by mass balancing the compositions of the liquid and crystalline phases with the bulk composition being melted, so that melting is strictly equilibrium. The compositions of garnet, clinopyroxene, and orthopyroxene at all temperatures and pressures of interest are now very well known, particularly along the solidus, and the compositions used in this analysis have been retrieved from the equations of Herzberg and Gasparik [1991]. The compositions of the liquids on the solidus depend on both pressure and the degree of partial melting, and these were computed for the system CMFAS. For advanced levels of melting (e.g., L + Ol and L + Ol + Opx), the compositions of the liquids were estimated from the disposition of the cotectics, and these are shown in Figures 9a,

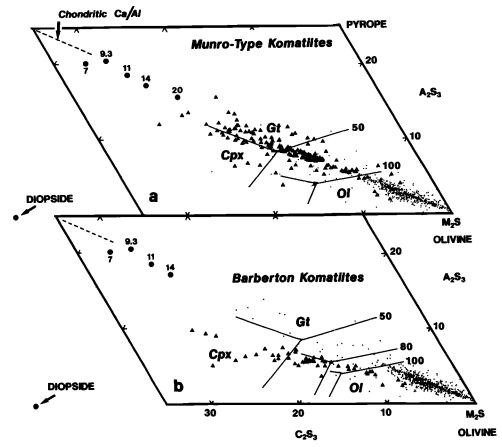


Fig. 8. A projection of liquidus phase boundaries in CMFAS from Figure 7, mantle peridotite (dots), and komatiites (triangles).

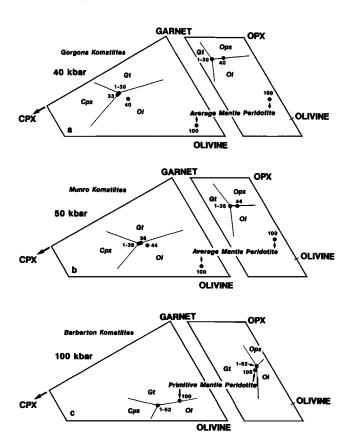


Fig. 9. A projection of liquids formed by the melt percentages shown at (a) 40, (b) 50, and (c) 100 kbar. Average mantle peridotite is given in Table 1. Primitive mantle peridotite is Ib8 of Stosch and Seck [1980].

9b, and 9c for the Gorgona, Munro-type, and Barberton komatiites respectively.

4.2. Gorgona Komatiites

The parameter CaO/(CaO + Al_2O_3) is restricted to 0.46-0.47 [Echeverria, 1982; Aitken and Echeverria, 1984], indicating a pressure of melting of about 36 kbar. There is some indication that CaO has been removed because of alteration (see below and appendix), so the pressure of melting was probably somewhat higher.

At 40 kbar, the partial melting of average mantle peridotite on the solidus will involve the assemblage L + Ol + Opx + Cpx + Gt, and the degree of melting will range from about 1 to 30 %. In CMFAS the liquids formed will have 20 to 23 % MgO and a low content of SiO_2 (i.e., 45 - 46 %). The Gorgona komatiites are relatively high in Na_2O (i.e., about 0.8 % [Aitken and Echeverria, 1984]), indicating that these MgO contents are overestimated by 1 to 2 %(see above). Nevertheless, the Gorgona komatiites are very similar to these primary liquid compositions, except that they have been modified by addition and subtraction of olivine (Figure 10).

When the degree of partial melting exceeds 30 %, garnet is the first phase to be consumed (L + Ol + Opx + Cpx). CaO and Al_2O_3 will change slightly until the degree of partial melting reaches 33 %, at which point $CaO/(CaO + Al_2O_3)$ of the liquid is 0.49, defined by the peridotite source. Progressive melting will exhaust clinopyroxene and melting will proceed up the harzburgite cotectic L + Ol + Opx. Orthopyroxene will remain in the residue until the degree of melting reaches 40 %. It is during the progressive melting of harzburgite where the largest

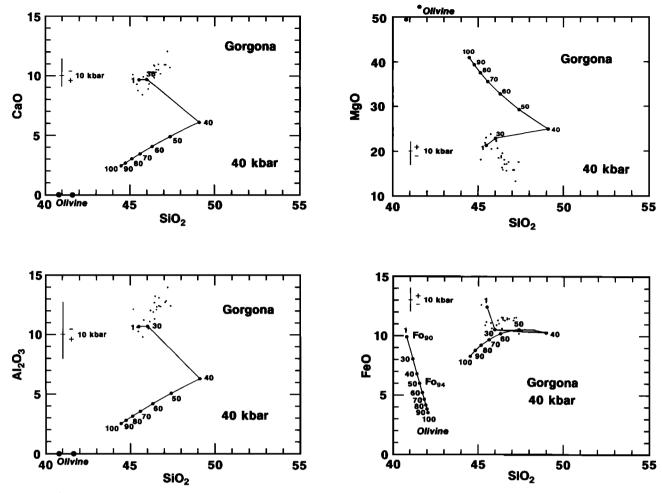


Fig. 10. Liquid compositions formed by 1 to 100 % melting of average mantle peridotite at 40 kbar, compared to the geochemistry of Gorgona komatiites (weight %). Phase relations are shown in Figure 9a. Liquids are valid for the system CMFAS; Na₂O will lower MgO (see text).

changes occur in the composition of the liquid, particularly for CaO, Al_2O_3 , and SiO_2 (Figure 10). The content of SiO_2 increases because of the dissolution of orthopyroxene in the melt, and reaches a maximum of 49%. Mysen and Kushiro [1977] documented similar changes at 20 kbar; liquids formed by < 2 % melting are nepheline normative with 44 to 45 % SiO_2 ; liquids formed by 35 % melting and in equilibrium with harzburgite (L + Ol + Opx) have 51 % SiO_2 . Large variations were also reported for CaO and Al_2O_3 [Mysen and Kushiro, 1977].

Inspection of Figure 10 demonstrates that most of the Gorgona komatiites were formed by pseudoinvariant melting that did not exceeded 30 %. Garnet is expected to have been a residual phase for most komatiites (L + Ol + Opx + Cpx + Gt), and this is consistent with the observation of depletions in the heavy rare earth elements (Gd/Yb >1 [Aitken and Echeverria, 1984]). Again, the pressure of partial melting was 40 kbar, about 130 km depth.

4.3. Munro-Type Komatiites

Inspection of Figure 8a shows that many of the Munro-type komatiites are similar in composition to liquids at the 50 kbar pseudoinvariant point L + Ol + Opx + Cpx + Gt. The content of MgO is 23 to 25 % (Table 5), and it is therefore possible to interpret these as primary magmas. The spectrum of

compositions radiate to and from olivine, consistent with the addition and removal of olivine from a 50 kbar partial melt. But this interpretation is neither unique nor without its difficulties.

Another possibility is that the Munro komatiites were all residual liquids formed by extensive (L + Ol) or total (L) melting of mantle peridotite. Figure 8a shows that they could have formed by fractionation of variable amounts of olivine from a liquid with the composition of mantle peridotite. Most of the Munro-type komatiites have contents of MgO that exceed 24 %. and these project to the olivine-rich side of the 50 kbar pseudoinvariant point (Figure 8a). Although some can be explained as olivine cumulates in a 50 kbar partial melt, Bickle [1982] has demonstrated that komatiites having 27 to 30 % MgO could have been cumulate-free liquids. Since these highly magnesian liquids are not coincident with a high pressure invariant point, the logical interpretation is that they formed by very high degrees of melting. For the cases where melting is total (L), high (L + Ol), or moderate (L + Ol + Opx), the contents of CaO and Al₂O₃ in komatiites are inherited from the peridotite source. And since CaO/(CaO + Al₂O₃) for average mantle peridotite and partial melts at 50 kbar are similar purely by chance, it is possible to conclude that komatiites plot near the 50 kbar invariant point also by chance.

We therefore have two possible interpretations for the Munro komatiites based strictly on CaO/(CaO + Al₂O₃). Either they were partial melts from 50 kbar that had experienced

olivine addition and subtraction, or they were all residual liquids formed by variable olivine removal from an extensively melted peridotite source. This problem is important to resolve because Miller et al. [1991b] the implications are enormous. demonstrated that mantle peridotite would have to melt at pressures in the lower mantle (> 200 kbar) in order to be totally or extensively molten at the surface. This in turn would place profound constraints on the composition of the lower mantle. However, a komatiite formed by lower degrees of melting at 50 kbar does not constrain the geochemical structure of the source region. In order to evaluate which of these two possibilities is erroneous, a more detailed examination is now made of the partial melting possibility, with degrees of partial melting that range from 1 % to 100 %. The phase diagram is shown in Figure 9b, and the results are shown in Figure 11.

An additional complication that has made the Munro-type komatiites difficult to understand is that there is such a wide range of compositions, with SiO₂ that ranges from 44 % to 51 %, and CaO and Al₂O₃ that both range from 4% to 10% (Figure 11). This variation cannot be explained simply by olivine addition and removal from a single parental composition or by alteration (see appendix). However, Figure 11 shows that this spectrum of compositions can be explained by addition and subtraction of olivine from a spectrum of liquids formed by 35 to 44 % melting of average mantle peridotite.

At 50 kbar, the partial melting of average mantle peridotite on the solidus will involve the assemblage L + Ol + Opx + Cpx + Gt and the degree of melting will range from about 1 to 35 %. The geochemical characteristics of these initial liquids are $CaO/(CaO + Al_2O_3) = 0.50$; MgO = 23 to 25 %; and SiO_2 = 45 - 46 %. When the degree of partial melting exceeds 35 %, clinopyroxene is the first phase to be consumed (L + Ol + Onx + Gt: Figure 9b). CaO and Al₂O₃ change slightly until the degree of partial melting reaches 36 %, at which point CaO/(CaO + Al₂O₃) of the liquid is 0.49, defined by the peridotite source. Progressive melting will proceed up the harzburgite cotectic L + Ol + Opx after garnet has been exhausted. This scenario is very similar to the one discussed above for the origin of the Gorgona komatiites at 40 kbar. It is during the progressive melting of harzburgite where large changes occur for CaO, Al2O3, and SiO2 in the liquid (Figure 10), even though CaO/(CaO + Al₂O₃) remains at 0.49, defined by the peridotite source. Changes in MgO are more modest, increasing from 25 % to 27 %. The content of SiO₂ increases to 49 %, and this increase occurs because orthopyroxene is being dissolved into the melt. Further melting will involve only olivine (L + Ol), and its dissolution will cause SiO₂ to drop. Inspection of Figure 11 shows that most Munro-type komatiites can be described by addition and subtraction of olivine from liquids that had harzburgite in the residue (i.e., L + Ol + Opx),

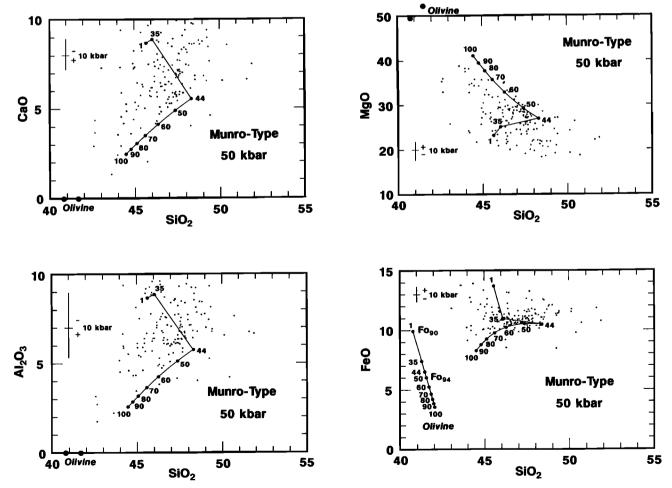


Fig. 11. Liquid compositions formed by 1 to 100 % melting of average mantle peridotite at 50 kbar, compared to the geochemistry of Munro-type komatiites (weight %). Phase relations are shown in Figure 9b. Liquids are valid for the system CMFAS.

and that the degree of partial melting ranged from about 35 to 44 %. The absence of garnet in the residue is consistent with the rare earth evidence, which shows no depletions in the heavy rare earth elements [Arth et al., 1977; Jahn et al., 1980].

Although this analysis has been restricted to the partial melting of average mantle peridotite, it is also possible that the source region contained a considerable amount of harzburgite sensu stricto (Ol + Opx) in addition to lherzolite (Ol + Opx + Cpx + Gt)[D. Canil, personal communication, 1991]. If correct, the spectrum of Munro komatiites could have formed by degrees of melting that were lower than the estimates given above, that is < 40%.

So far we have considered melting at 50 kbar; but inspection of Figure 10 illustrates that this scenario could have operated also at 40 kbar. For liquids that have a harzburgite residue (L + Ol + Opx), the parameter CaO/(CaO + Al₂O₃) is defined largely by the composition of the source region. In this case, pressure information is lost because Munro komatiites could have had harzburgite residues from 25 to 80 kbar. The actual pressure of melting is therefore subject to considerable uncertainty. However, a number of lines of evidence indicate that 50 kbar is probably realistic. If the pressure was as low as 25 kbar or so, initial liquids and those for harzburgite residues will be too low in MgO. Conversely, if the pressure of melting was near 80 kbar, the SiO₂ content would be too high (Table 5, Figure 12).

It is also possible to explain the geochemistry of the Munro komatiites as residual liquids from high degree (L + Ol) or from total melts (L), but it requires some special circumstances. Although not explicity shown in Figure 11, residual liquids formed by fractional crystallization of olivine from a liquid having the composition of average mantle peridotite would define a track similar to, but not identical with, the equilibrium L + Ol track (44 - 100 %; Figure 11). There would be only one way to explain a komatiite that did not have a composition on this track. For a komatiite that is low in both MgO and SiO₂, that is one with the characteristics of an initial melt at 50 kbar (i.e., 24 % MgO and 46 % SiO₂), the source region would have to be lower in SiO₂ than average mantle peridotite.

Our world data base of 668 peridotites yields an average of 44.47 +/- 2 % (two standard deviations), so there exist real variations in silica in the mantle. If these high degree melting arguments are applied to the Gorgona komatiites, which are Munro-like in that CaO/(CaO + Al₂O₃) is similar to mantle peridotite, then we may anticipate wide variations in their geochemistry also. But inspection of Figure 10 shows that the geochemistry of the Gorgona komatiites is quite restricted. This means that if indeed they were formed by high degrees of melting instead of by pseudoinvariant melting, the source region must have been very homogeneous with respect to the major elements.

We are left with the unfortunate conclusion that the geochemistry of the Munro-type komatiites is compatible with both very high (e.g., 100 %) and moderate degrees (35 - 44 %) of partial melting. But the essential difficulty with the high melt fraction scenario is that it would have required a unique source region to explain each Munro komatiite and fails, therefore, on grounds of improbability.

4.4. Barberton Komatiites

When initial melting occurs at pressures that are greater than 50 kbar, the liquids will begin to have affinities with the Barberton komatiites, characteristically high in CaO/(CaO + But before we can proceed with an igneous interpretation of these rocks, an assessment must be made of the effect of alteration on CaO/(CaO + Al₂O₃) [Smith and Erlank, 1982]. This has been the subject of considerably scrutiny by de Wit et al. [1987], and an expansion of their discussion is given in the appendix. Alteration by circulating hydrothermal solutions tends to strip from a rock significant amounts of CaO and SiO₂, a process that appears to have affected the Barberton komatiites more than most Munro-types. Removal of CaO is usually not accompanied by a local gain in CaO, so the system is open on an outcrop scale; alteration therefore tends to lower SiO₂ and CaO/(CaO + Al₂O₃). Pressures estimated from CaO/(CaO + Al₂O₃) will therefore be minimum possible bounds. The samples projected in Figure 8b are the least altered, about 50 % of the Barberton data base (appendix).

Figure 8b demonstrates that many Barberton komatiites have the compositions of liquids at a pseudoinvariant point involving L + Ol + Gt + Cpx in the 80- to 100-kbar range; the spectrum of komatiites radiate to and from olivine, indicating that some are liquids that have gained and lost olivine. Partial melting at 100 kbar has been modeled, and the results are shown in Figure 9c and Figure 12. Melting involves the assemblage L + Ol + Gt + Cpx and, although orthopyroxene does not participate, the modeling was simplified by using an intial liquid composition for the peritectic equilibrium L + Ol + Opx + Cpx + Gt. As explain above, use of this composition will result in MgO that is too low and SiO_2 that is too high, a problem that will not seriously affect the conclusions that follow.

A 1 % melt fraction will have about 3.5 % Al₂O₃ and 27 % MgO (Table 5), but does not quite match the geochemistry of Barberton komatiites because SiO2 is too low (Table 5; Figure 12). To increase SiO₂ to the levels observed, the degree of partial melting must have been high. But because orthopyroxene is not involved, the only way this can be achieved is by high degrees of pseudoinvariant melting on the solidus (L + Ol + Gt + Cpx) involving a source region that was also fairly high in SiO₂. Although the composition of the source region does not directly affect the composition of liquids formed on the solidus, it does affect the degree of partial melting that is possible. Higher degree initial melts will be higher in MgO, MgO/FeO, and SiO₂ (Table 5), even for liquids that are strictly pseudoinvariant. Average mantle peridotite is not a good source region because pseudoinvariant melting could not have exceeded 35 %. But for the primitive mantle peridotite chosen, which is Ib8 of Stosch and Seck [1980], initial melting can reach up to 52 % (Figure 9c). The liquid produced has about 31 % MgO and 47 % SiO₂ (Figure 12), and successfully reproduces the geochemistry of many Barberton komatiites. Again the spectrum of komatiites can be explained by olivine addition and substraction from this composition.

Melting in excess of 52 % is very unusual. Clinopyroxene will be first phase to be consumed, and advanced melting will proceed up the cotectic L+Ol+Gt (Figure 9c). When this occurs, there will actually be an increase in Al_2O_3 in the liquid because the Al_2O_3 content of the primitive mantle source is higher than initial Barberton liquids (Figure 12). Barberton komatiites could not have formed from these high degree liquids. The next phase to be consumed is predicted to be olivine, and garnet will be the liquidus phase for Ib8 at 100 kbar (Figure 9c). However, the crystallization interval of garnet only (L+Gt) is likely to be only some tens of degrees, and the liquid trajectory

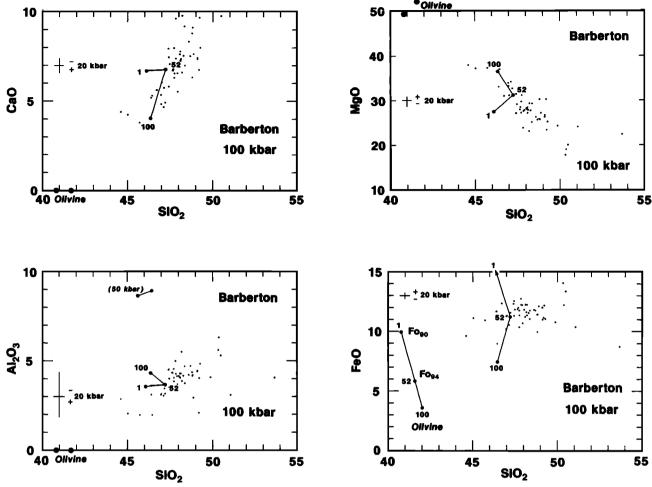


Fig. 12. Liquid compositions formed by 1 to 100 % melting of primitive mantle peridotite [Ib8 Stosch and Seck, 1980], compared to the geochemistry of Barberton komatiites (weight %). Phase relations are shown in Figure 9c. Liquids are valid for the system CMFAS.

from 52 to 100 % melting in Figure 12 was treated as if lb8 was multiply saturated in olivine and garnet (L + Ol + Gt) at all temperatures between the liquidus and the solidus.

A Barberton komatiite formed as a partial melt at 100 kbar would have had garnet in the source region (i.e., L + Ol + Gt + Cpx). The importance of garnet was discussed in the pioneering articles of Green [1975], Sun and Nesbitt [1978], Nesbitt et al., [1979], and Jahn et al., [1982], and this was based on the observation that high CaO/(CaO + Al₂O₃) is accompanied by depletions in the heavy rare earth elements (e.g., high Gd/Yb). However, there has been less agreement has to the mechanism by which garnet was removed. The general possiblities that have been discussed are (1) garnet was retained as the residual phase or fractionated somehow during the time of melting [Green, 1975; Sun and Nesbitt, 1978; Ohtani, 1984; Arndt, 1986], (2) the source region had inherited the geochemical signature of a prior stage of garnet removal by, for example, removal in an early magma ocean, and garnet did not necessarily play a role during magma genesis [Jahn et al., 1982; Cawthorn and Strong, 1974; Ohtani et al., 1989]. The nearly chondritic initial isotopic ratios reported for both hafnium [Gruau et al., 1990a] and neodymium [Gruau et al., 1990b] in Barberton komatiites is strong support for the residuum interpretation. This is in complete accord with our phase equilibrium results which show that garnet was fractionated as a residual phase (L + Ol + Gt + Cpx) during partial melting.

5. Effects Of Decompression On The Geochemistry Of Komatiite

Although isobaric phase diagrams like Figure 9 are useful for examining how the geochemistry of a komatiite is affected by advanced melting above the solidus, they are geophysically unrealistic because the melting of mantle peridotite cannot proceed from initial to total isobarically. It is triggered when the mantle advects adiabatically and intersects the solidus, and the parcel of magma will follow a new adiabatic T-P path which connects the temperatures and pressures of melt initiation on the solidus to eruption temperature at the surface. These concepts were applied to the generation of basaltic magmas at low pressures [McKenzie, 1984; McKenzie and Bickle, 1988], and more recently to the generation of komatiites at elevated pressures [Miller et al., 1991a, b].

Adiabatic T-P trajectories for komatiite magmas are shown in Figure 13. The komatiites formed on the solidus at 40 to 100 kbar have been connected to eruption temperatures by means of the adiabatic trajectories given in *Miller et al.* [1991b]. Figure 13 differs from the work of *Miller et al.* [1991b] only in that the melting temperatures for KLB1 determined at Stony Brook [Herzberg et al., 1990; McFarlane et al., 1990] are higher than those reported by Takahashi [1986]. The important point is that the adiabatic dT/dP trajectories approximately parallel dT/dP for the olivine liquidus at pressures below about 50 kbar. If they

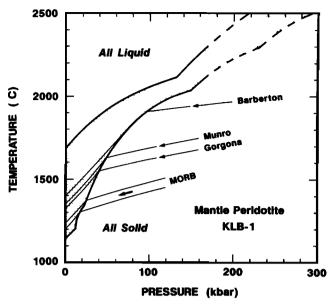


Fig. 13. Adiabatic trajectories and depths of melting inferred for Gorgona, Munro, and Barberton komatiites. The solidus and liquidus temperatures for KLB1 are based on experimental data of *Takahashi* [1986] adjusted to higher temperatures observed by *Herzberg et al.* [1990] and *McFarlane et al.* [1990] and unreported data. Broken lines are extrapolated solidus and liquidus locations. Adiabatic trajectories are based on the work of *Miller et ql.* [1991b]. MORB adiabat is bounded between the 1280°C potential temperature of *McKenzie and Bickle* [1988] and slightly higher temperatures indicated by garnet in the source region [Salters and Hart, 1989]. Deflections in the adiabats due to the olivine-modified spinel transformation are not shown.

are precisely parallel then it follows that olivine can be neither melted nor crystallized, and there can be no change in the melt fraction with decompression. Additionally, the composition of the erupted magma would be identical to the primary magma formed on the solidus. This may explain why many Gorgona and Barberton komatiites are so geochemically similar to their primary magmas formed at 40 and 100 kbar respectively. The principal modifications have been in terms of olivine addition and subtraction, a process that could have occurred by settling after eruption on the surface.

A reduction in pressure simultaneously lowers dT/dP of the adiabats [McKenzie and Bickle, 1988; Miller et al., 1991b] and raises dT/dP of the olivine liquidus (Figure 13). This combined effect can result in an increased melt fraction with decompression, the magnitude of which will depend on a precise location of the adiabat; these are difficult to determine with precision for trajectories that are located between the liquidus and solidus [Miller et al., 1991b]. This kind of information is needed in order to understand how the Munro komatiites could have evolved from initial melts to larger melt fractions in equilibrium with harzburgite; at 50 kbar the melt fraction must increase from 35 % to 44 % (Figure 11). But at 40 kbar, the melt fraction needed to form similar high SiO₂ komatiite magmas drops to about 40 % (Figure 10). The wide spectrum of Munro komatiite compositions can then be explained by melting that varied from 35 % at 50 kbar to 40 % at 40 kbar. The important point is that small increases in melting attending adiabatic decompression can cause large changes in the geochemistry of komatiites when harzburgite is either the source or the residue from a more fertile source.

The 80 to 100 kbar pressures of melting for the Barberton komatites are similar to the 80 to 90 kbar pressure of neutral

buoyancy between olivine and magmas [Agee and Walker, 1988; Miller et al., 1991a]. It is within this high pressure region where melting could be mostly equilibrium rather than fractional [Herzberg, 1984]. The density contrast will increase upon adiabatic decompression, and this will create opportunities for the melt to fractionate by segregation into pools [Arndt, 1986]. The 80 to 100 kbar inferred from the geochemistry of the Barberton komatiites could be recording only the final stages in equilibrium melting prior to separation of the liquid from its matrix, and the actual pressure of melt initiation may have been even greater.

6. FORMATION OF KOMATTITES IN PLUMES

Thermal models point to an Archean mantle with a mean temperature that was only 100 to 150°C higher than at present [Turcott, 1980; Jarvis and Campbell, 1983; Campbell and Jarvis, 1984], and komatiites could have formed by melting in hot rising plumes [Jarvis and Campbell, 1983; Arndt, 1986; Campbell et al., 1989; Miller et al., 1991a,b]. These would have differed from present-day hot spots to the extent that the plumes intersected the solidus greater depths. An obvious corollary to this model is that the Earth was largely solidified throughout the Archean, and this has considerable support in the isotopic compositions of the earliest Archean basalts, komatiites, and continental crust. The mantle source regions of these rocks had high Sm/Nd [Shirey and Hanson, 1986; McCulloch and Compston, 1981], and this is most simply interpreted as a depletion event caused by approximately 10 to 20 % partial melting of a fully solidified mantle soon after the Earth first formed [Arndt, 1986; Chase and Patchett, 1988; Galer and Goldstein, 1991; Smith and Ludden, 1989]. Although there is considerable evidence for a magma ocean stage of Earth history [Wetherill, 1990, Stevenson, 1987; Herzberg and Gasparik, 1991], the isotopic data and thermal modeling [Miller et al., 1991b] indicate that it solidified early, well before the onset of the Archean [see also Arndt, 1986].

The formation of the Barberton komatiites at pressures equal to or greater than the 80 to 90 kbar pressure of neutral buoyancy between olivine and magmas [Agee and Walker, 1988; Miller et al., 1991a] demonstrates that there existed no density barrier to the eruption of komatiitic magmas in the Archean. If komatiites formed by percolation in a passive matrix like present-day MORB volcanism [e.g., Takahashi, 1990], it is difficult to understand how they could have erupted to the surface from 300 km depth. Arndt [1986] and Miller et al. [1991a,b] addressed this dilema by considering an origin in mantle plumes or diapirs. Thermal buoyancy drives a plume because the temperature in it is higher than that of ambient mantle outside, and the plume will continue to rise even if a parcel of komatiite liquid within it is denser than a coexisting olivine crystal. The work of Miller et al. [1991a] indicates that komatiite and peridotite liquids have lower densities than the present-day bulk mantle to 400 kbar, a possible exception being a similarity in densities at around 133 kbar. komatiites contained within a hot plume would have been less dense than the ambient mantle at 100 kbar.

Compared to the present-day Earth, excess temperatures in a 3.5 Ga Barberton plume would have been about 500°C, and excess temperatures in a 2.7 Ga Munro plume about 250 to 300°C (Figure 13). However, if the Archean mantle was 100 to 150°C hotter than at present [Jarvis and Campbell, 1983; Turcotte, 1980], excess temperatures in Archean plumes would have been correspondingly lower, about 150 to 350°C above

ambient mantle temperatures. These are very similar to 200 to 300°C excess temperatures that have been recommended for the present-day Hawaiian and Icelandic plumes [Sleep, 1990; McKenzie, 1984; Griffiths and Campbell, 1991; Watson and McKenzie, 1991; Liu and Chase, 1989].

Melt initiation will occur at 40 kbar if present-day plumes have an excess temperature that is 200° above the 1280°C MORB potential temperature [McKenzie and Bickle, 1988; Figure 13], and the primary magmas produced will be Gorgona-type komatiites with about 20 % MgO. But the volcanic rocks from Hawaii are typically basaltic instead. Clague et al. [1991] reported 15 % MgO in Hawaiian picritic glasses, and recommended a primary magma with 17 % MgO. These have CaO/(CaO + Al₂O₃) and a major element chemistry that is similar to liquids formed at 25 to 30 kbar [Elthon and Scarfe, 1984; Table 5], indicating an excess temperature of only about 100-150° for Hawaii.

Attention is drawn to the possibility that the Gorgona komatiites were formed in plumes that rivaled the Munro plume in depth of melting. This is of special interest because Re-Os age dating [Walker et al., 1991] constrains the Gorgona komatiites to be 155 +/- 43 Ma, late Jurassic to early Cretaceous. Walker et al. [1991] noted the coincidence in this age with the breakup of Pangea, and suggested that this event could have been caused by large-scale mantle upwelling. The error bars permit an equally intriguing possibility; that the Gorgona komatiites are early to mid Cretaceous in age (120 Ma). If correct, they may have been a part of the Caribbean Plateau [Storey et al., 1991] formed by the Galapagos hot spot [Duncan and Hargraves, 1984]. An early Cretaceous age is also the time of formation of the gigantic oceanic plateaus in the Pacific [Larson, 1991; Tarduno et al., 1991]. At the present time, there is no information on the composition of the oceanic crust below such plateaus as Ontong Java. However, in addition to basalts, komatiites of Cretaceous age may be fairly abundant in oceanic plateaus throughout the Pacific, and may provide a good analogue for understanding komatiites in Archean greenstone belts [Storey et al., 1991].

Attention has also been drawn to possible secular variations in the geochemistry of komatiites [Jahn et al., 1982]. High CaO/(CaO + Al2O3) and Gd/Yb characterize the early Archean komatiites from Barberton and the Pilbara block, and these have ages of about 3.5 Ga [e.g., Gruau et al., 1990a]. Munro-type komatiites with mantle-like CaO/(CaO + Al₂O₃) and Gd/Yb were formed in the late Archean, about 2.7 Ga ago [Nesbitt et al., 1979; Jahn et al., 1982; Gruau et al., 1990a], and the Gorgona komatiites are Mesozoic in age. The similarity in conditions of melting between the Gorgona and Munro komatiites (Figure 13), and the possibility of Munro-like volcanism in the Pacific of Cretaceous age, point to an interior that cooled marginally over the last 2.5 billion years. Secular cooling appears to have been expressed mainly in the early part of the Archean.

7. CONCLUSIONS

High pressure melting experiments on compositions in the system $CaO-MgO-Al_2O_3-SiO_2$ demonstrate that liquids on the solidus are komatiitic in the 50-to 150-kilobar pressure range. The effect of pressure is to expand the stability field of garnet at the expense of olivine, clinopyroxene, and orthopyroxene. This causes a very pronounced increase to occur in $CaO/(CaO + Al_2O_3)$ for liquids that are multiply saturated in Cpx + Gt,

demonstrating that it is a good indicator of depth of melting. Addition of FeO does not affect CaO/(CaO + Al₂O₃) of liquids at an isobaric invariant point, but it lowers the contents of CaO, Al₂O₃, and SiO₂. The MgO contents of liquids on the solidus are about 24 % at 50 kbar and 30 % at 100 kbar.

The melting of peridotite from 1 to 100 % has been simulated at a range of high pressures, and the liquids so produced have been compared to the geochemistry of komatiites. Komatiites from Gorgona Island can be understood as relatively low degree partial melts (< 30 %), the products of pseudoinvariant melting involving L + Ol + Opx + Cpx + Gt on the solidus at 40 kilobars, about 130 km depth.

Munro-type komatiites are more difficult to understand. They have CaO/(CaO + Al₂O₃) that is similar to low degree melts at 50 kbar (L + Ol + Opx + Cpx + Gt), moderate degree melts (L + Ol + Opx), or high degree melts (L; L + Ol). Because of this problem, the depth of melting for the Munro-type komatiites cannot be rigorously determined. And unlike the Gorgona komatiites, they contain a wide range of values for CaO, Al₂O₃, and SiO₂, variations that cannot be attributed simply to olivine addition and subtraction. This spectrum of compositions can be understood as liquids coexisting with a harzburgite residue (L + Ol + Opx) formed by <40%melting of either average mantle peridotite or of harzburgite sensu stricto. Although the pressure of melting cannot be rigorously constrained, it was probably around 50 kbar, about 165 km depth. The difficulty with the high degree melting scenario (L + Ol) is that it would have required a unique source region to explain each Munro komatiite and fails, therefore, on grounds of improbability.

Komatiites from the Barberton Mountain Land have high $CaO/(CaO + Al_2O_3)$ and are similar to liquids formed by about 50 % pseudoinvariant melting (L + O1 + Gt + Cpx) of fertile mantle peridotite in the 80- to 100-kbar range (260- to 330-km).

Komatiites have been reasonably interpreted as the products of extensive or total melting of the mantle because they have a geochemistry that can be roughly explained by the removal of olivine from peridotite. But the results of this work point to problems with this interpretation. Instead, they can be more easily explained as partial melts (< 50 % melting) with a geochemistry that was determined by high pressure crystal-liquid phase equilibria. An important corollary is that komatiites cannot be used to place constraints on the geochemistry of their source region, except in the most rudimentary way. This is unfortunate because it means that they cannot be used to probe the structure of the mantle, and address important questions concerning the geochemical properties of seismic discontinuities.

Secular variations in the geochemistry of komatiites could have formed in response to a reduction in the temperature and pressure of melting with time. The 3.5 Ga Barberton komatiites and the 2.7 Ga Munro-type komatiites could have formed in plumes that were hotter than the present-day mantle by 500° and 300°, respectively. When excess temperatures are this size, melting is deeper and volcanism changes from basaltic to komatiitie. The komatiites from Gorgona Island, which are Mesozoic in age, may be representative of komatiites that are predicted to occur in oceanic plateaus of Cretaceous age throughout the Pacific [Storey et al., 1991].

APPENDIX

With the exception of the extremely fresh komatiites from Zimbabwe [Nisbet et al., 1987], most have been

metamorphosed to greenschist and amphibolite facies and have suffered variable amounts of alteration by hydrothermal solutions. An evaluation of these effects is required before confidence can be placed in any igneous interpretation. Smith and Erlank [1982] documented some possible problems in understanding CaO and Al₂O₃ in the Barberton komatiites, and de Wit et al. [1987] have documented important evidence for widespread mobilization of Ca and Si, amongst others elements.

The effects of alteration on the geochemistry of volcanic rocks have been examined by laboratory experimentation and by carefully controlled field studies, and the reader is referred to the excellent discussion of this work in de Wit et al. [1987]. Experimental studies have monitored geochemical changes in seawater before and after reaction with rhyolite, andesite, basalt, and peridotite at elevated temperatures and pressures [e.g., Hajash and Chandler, 1981; Bischoff and Dickson, 1975; Hajash, 1975]. The results demonstrate that important quantities of Ca and Si can be removed from basalts and peridotites and Mg can be added. Studies have also been made on samples of fresh and hydrothermally altered pillow basalts from the Mid-Atlantic Ridge [Humphris and Thompson, 1978], and the results agree with the experimental work in that Si and Ca can be leached from the rock while Mg can be taken up. One of the important findings of the field studies is that mobilization of these elements is not confined to a hand specimen or outcrop scale. While leaching of Ca can be accompanied by localized precipitation, in general the system is open on an outcrop scale. This process has added important quantities of Si and Ca to the world's oceans, and resulted in the deposition of Fe, Mn, Cu, and Zn on the sea floor [Von Damm et al., 1985; Hart, 1973; Reed, 1983].

These studies agree that Ca and Si are more mobile than Al in hydrothermal solutions. A positive correlation of CaO/Al₂O₃ and SiO₂ is therefore an indication of alteration. This is observed for the Barberton komatiites in Figure A1, and this supports the suggestion of de Wit et al. [1987] that Ca and Si have indeed been removed from the komatiites. The Munro komatiites are notable for having CaO/Al₂O₃ equal to 1.0 [e.g., Jahn et al., 1982] and, unlike the Barberton komatiites, Figure A2 shows that it is largely independent of SiO₂. It can be concluded from these comparisons that the Barberton komatiites were more severly affected by alteration than the Munro-types.

Addition and subtraction of olivine from a komatiitic magma cannot change CaO/Al₂O₃. Pseudoinvariant melting can yield high pressure liquids with CaO/Al₂O₃ and SiO₂ that are higher than liquids generated at lower pressures. But to account for the spectrum of compositions in Figure A1 would require a range of pressures than span over 100 kbar, and is unreasonable on geological grounds. One other igneous process than can potentially explain the data is by advanced melting through the sequence $L + Ol + Cpx + Gt \longrightarrow L + Ol + Gt \longrightarrow L$ + Ol. In projection, highly magnesian komatiites from Barberton would differ from the others in having Munro-like CaO/Al₂O₃. This observation was originally made by Smith and Erlank [1982], and correctly dismissed as another artifact of alteration because no change was observed for Al₂O₃/TiO₂. This parameter is shown also in Figure A3. It can be seen that for Barberton komatiites having CaO/Al₂O₃ > 1.5, the ratio Al₂O₃/TiO₂ is typically around 11, and this contrasts with about 20 for Munro-type komatiites [Jahn et al., 1982; Gruau et al., 1990a]. But for Barberton komatiites having $CaO/Al_2O_3 < 1.5$, the ratio Al₂O₂/TiO₂ stays either unchanged or it increases to

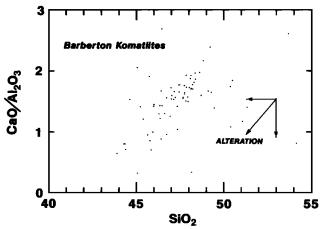


Fig. A1. CaO/Al₂O₃ (weight % ratio) versus SiO₂ for Barberton komatiites.

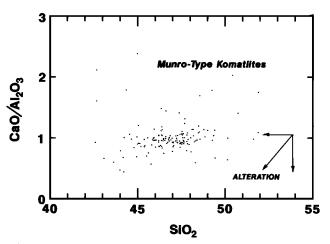


Fig. A2. CaO/Al₂O₃ (weight % ratio) versus SiO₂ for Munro-type komatiites.

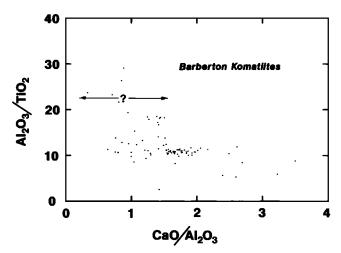


Fig. A3. Al_2O_3/TiO_2 versus CaO/Al $_2O_3$ (weight % ratios) for Barberton komatiites.

over 20. It is this part of the Barberton population that is suspect of being altered, and the highly scattered data have no obvious igneous explanation. Barberton komatiites with unusually high Al₂O₃/TiO₂ may be bad analyses [N.T. Arndt,

personal communication, 1991] or they may be an artifact of Ti removal during hydrothermal alteration. Barberton komatiites having $\text{CaO/Al}_2\text{O}_3 > \text{than 1.5}$ are about 50 % of the population, and are probably the least altered of the data base. The high pressure igneous interpretation offered above has been based on these "clean" Barberton samples.

Inspection of Figure 12 shows that the clean Barberton komatiites can be explain as liquids formed by about 52 % pseudoinvariant melting at around 100 kbar. But a detailed examination of these plots shows that while this adequately explains MgO, Al₂O₃, and SiO₂ the contents of CaO that are predicted are mostly higher than those that are observed even for the clean Barberton data set. Although these differences are certainly within the experimental error of the high pressure data base, they may indicate that even the clean Barberton komatiites have lost some CaO.

Acknowledgments. This research was supported by NSF grant EAR 89-16836 to C. Herzberg. The results on garnet and pyroxene were reported by Herzberg and Gasparik [1991], and supported in part by NSF EAR 90-03748 to T. Gasparik. The high pressure experiments reported in this paper were performed in the Stony Brook High Pressure Laboratory which is jointly supported by the National Science Foundation (EAR 89-17563) and the State University of New York at Stony Brook. Thanks are extended to Nick Arndt and Dan McKenzie for critical comments on a first draft of this paper, and to Tibor Gasparik and Paul Hess for discussions.

REFERENCES

- Agee, C.B., and D. Walker, Static compression and olivine floatation in ultrabasic silicate liquid, J. Geophys. Res., 93, 3437-3449, 1988.
- Aitken, B.G., and L.M. Echeverria, Petrology and geochemistry of komatiites and tholeiites from Gorgona Island, Colombia, Contrib. Mineral. Petrol., 86, 94-105, 1984.
- Anderson, D.L., Composition of the Earth, Science, 243, 367-370, 1989.
- Andersen, O., The system anorthite-forsterite-silica, Am. J. Sci., 4th ser., 39, 407-454, 1915.
- Arndt, N.T., Melting relations of ultramafic lavas (komatiites) at 1 atm and high pressure, *Year Book Carnegie Inst. Washington*, 75, 555-562. 1976.
- Arndt, N.T., Ultrabasic magmas and high-degree melting of the mantle, Contrib. Mineral. Petrol. 64, 205-221, 1977.
- Arndt, N.T., Komatiites: a dirty window to the Archean mantle, Terra Cognita, 6, 59-66, 1986.
- Arndt, N.T., A.J. Naldrett, and D.R. Pyke, Komatiitic and iron-rich tholeiitic lavas of Munro Township, Northeast Ontario, J. Petrol., 18, 319-369, 1977.
- Arth, J.G., N.T. Arndt, and A.J. Naldrett, Genesis of Archean komatiites from Munro Township, Ontario: trace element evidence, Geology, 5, 590-594, 1977.
- Bertka, C., and J.R. Holloway, Martian mantle primary melts: an experimental study of iron-rich garnet lherzolite minimum melt composition, *Proc. Lunar Planet. Sci. Conf.*, 18, 723-739, 1988.
- Bickle, M.J., The magnesium contents of komatiitic liquids, In: Komatiites, edited by N.T. Arndt, and E.G. Nisbet, pp. 479-494, George Allen and Unwin, London, 1982.
- Bickle, M.J., C.E. Ford, and E.G. Nisbet, The petrogenesis of peridotitic komatiites: evidence from high-pressure melting experiments, *Earth Planet. Sci. Lett.*, 37, 97-106, 1977.
- Bischoff, J.L., and F.W. Dickson, Seawater-basalt interaction at 200°C and 500 bars: implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry, *Earth Planet. Sci. Lett.*, 25, 385-397, 1975.

- Boyd, F.R., Compositional distinction between oceanic and cratonic lithosphere, Earth Planet. Sci. Lett., 96, 15-26, 1989.
- Brooks, C., and S.R. Hart, On the signficance of komatiite, Geology, 2, 107-110, 1974.
- Campbell, I.H., and G.T. Jarvis, Mantle convection and early crustal evolution, *Precambrian Res.*, 26, 15-56, 1984.
- Campbell, I.H., R.W. Griffiths, and R.I. Hill, Melting in an Archaean mantle plume: heads it's basalts, tails it's komatiites, *Nature*, 339, 697-699, 1989.
- Cawthorn, R.G., and D.F. Strong, The petrogenesis of komatiites and related rocks as evidence for a layered upper mantle, Earth. Planet. Sci. Lett., 23, 369-375, 1974.
- Chase, C.G., and P.J. Patchett, Stored mafic/ultramafic crust and early Archean mantle depletion, Earth Planet. Sci. Lett., 91, 66-72, 1988.
- Clague, D.A., W.S. Weber, and J.E. Dixon, Picritic glasses from Hawaii, Nature, 353, 553-556, 1991.
- Davis, B.T.C., The system Diopside-Forsterite-Pyrope at 40 kilobars, Year Book Carnegie Inst. Washington, 63, 165-171, 1964.
- Davis, B.T.C, and J.F. Schairer, Melting relations in the join diopside-forsterite-pyrope at 40 kilobars and at one atmosphere, Year Book Carnegie Inst. Washington, 64, 123-126, 1965.
- de Wit, M.J., R.A. Hart, and R.J. Hart, The Jamestown ophiolite complex, Barberton mountain belt: a section through 3.5 Ga oceanic crust. J. African Earth Sci., 6, 681-730, 1987.
- Duncan, R.A., and R.B. Hargraves, Plate tectonic evolution of the Caribbean region in the mantle reference frame, The Caribbean -South American plate boundary and regional tectonics, Mem. Geol. Soc. Am., 162, 81-93, 1984.
- Echeverria, L.M., Komatiites from Gorgona Island, Colombia, in: *Komatiites*, edited by N.T. Arndt and E.G. Nisbet, pp. 199-209, George Allen and Unwin, London, 1982.
- Elthon, D., and C.M. Scarfe, High-pressure phase equilibria of a high-magnesia basalt and the genesis of primary oceanic basalts, Am. Mineral., 69, 1-15, 1984.
- Falloon, T.J., D.H. Green, C.J. Hatton, and K.L. Harris, Anhydrous partial melting of a fertile and depleted peridotite from 2 to 30 kb and application to basalt petrogenesis, J. Petrol., 29, 1257-1282, 1988.
- Fujii, T., M. Tachikara, and K. Kurita, Melting experiments in the system CaO-MgO-Al₂O₃-SiO₂ to 8 GPa: Constraints to the origin of komatiites, Eos Trans. AGU, 70, 483, 1989.
- Galer, S.J.G., and S.L. Goldstein, Early mantle differentiation and its thermal consequences, Geochim. Cosmochim. Acta, 55, 227-240, 1991.
- Gansser, A., V.J. Dietrich, and W.E. Cameron, Palaeogene komatiites from Gorgona Island, *Nature*, 278, 545-546, 1979.
- Gasparik, T., Transformation of enstatite-diopside-jadeite pyroxenes to garnet, Contrib. Mineral. Petrol., 102, 389-405, 1989.
- Gasparik, T., Phase relations in the transition zone, J. Geophys. Res., 95, 15,751-15,769, 1990.
- Green, D.H., Archean greenstone belts may include terrestrial equivalents of lunar maria?, Earth Planet. Sci. Lett., 15, 263-270, 1972.
- Green, D.H., Genesis of Archean peridotitic magmas and constraints on Archean geothermal gradients and tectonics, Geology, 3, 15-18, 1975.
- Green, D.H., and A.E. Ringwood, The genesis of basaltic magmas, Contrib. Mineral. Petrol., 15, 103-190, 1967.
- Griffiths, R.W., and I.H. Campbell, On the dynamics of long-lived plume conduits in the convecting mantle, *Earth. Planet. Sci. Lett.*, 103, 214-227, 1991.
- Gruau, G., C. Chauvel, N.T. Arndt, and J. Cornichet, Aluminum depletion in komatiites and garnet fractionation in the early Archean mantle: Hafnium isotopic constraints, Geochim. Cosmochim. Acta, 54, 3095-3101, 1990a.
- Gruau, G., C. Chauvel, and B.M. Jahn, Anomalous Sm-Nd ages for the early Archean Onverwacht Group Volcanics: Significance and petrogenetic implications, Contrib. Mineral. Petrol., 104, 27-34. 1990b.
- Hajash, A., Hydrothermal processes along mid-ocean-ridges: an

- experimental investigation, Contrib. Mineral. Petrol., 53, 205-226, 1975.
- Hajash, A., and G.W. Chandler, An experimental investigation of hightemperature interactions between seawater and rhyolite, andesite, basalt and peridotite, Contrib. Mineral Petrol., 78, 240-254, 1981.
- Hart, R.A., Geochemical and geophysical implications of the reaction between seawater and the oceanic crust, Nature, 243, 76-78, 1973.
- Herzberg, C.T., The solubility of olivine in basaltic liquids: an ionic model, Geochim. Cosmochim. Acta, 43, 1241-1251, 1979.
- Herzberg, C.T., Chemical stratification in the silicate Earth, Earth Planet. Sci. Lett., 67, 249-260, 1984.
- Herzberg, C., and T. Gasparik, Garnet and pyroxenes in the mantle: a test of the majorite fractionation hypothesis, J. Geophys. Res., 96, 16, 263-16,274, 1991.
- Herzberg, C.T., and M.J. O'Hara, Origin of mantle peridotite and komatiite by partial melting, Geophys. Res. Lett., 12, 541-544, 1985.
- Herzberg, C.T., and E. Ohtani, Origin of komatiite at high pressures, Earth Planet. Sci. Lett., 88, 321-329, 1988.
- Herzberg, C.T., M. Feigenson, C. Skuba, and E. Ohtani, Majorite fractionation recorded in the geochemistry of peridotites from South Africa, Nature, 332, 823-826, 1988.
- Herzberg, C., T. Gasparik, and H. Sawamoto, Origin of mantle peridotite: constraints from melting experiments to 16.5 GPa, J. Geophys. Res., 95, 15,779-15,803, 1990.
- Hess, P.C., Komatiites and the Archean mantle (abstract), Proc. Lunar Planet. Sci. Conf., 21, 501-502, 1990.
- Howells, S., C. Begg, and M.J. O'Hara, Crystallization of some natural eclogites and garnetiferous ultrabasic rocks at high pressure and temperature, *Phys. Chem. Earth*, 9, 895-902, 1975.
- Humphris, S.E., and G. Thompson, Hydrothermal alteration of oceanic basalts by seawater, Geochim. Cosmochim. Acta, 42, 107-125, 1978.
- Ito, K., and G.C. Kennedy, Melting and phase relations in a natural peridotite to 40 kilobars, Am. J. Sci., 265, 519-538, 1967.
- Jahn, B.-m., P. Vidal, and G.R. Tilton, Archean mantle heterogeneity: evidence from chemical and isotopic abundances in Archean igneous rocks, Philos. Trans. R. Soc. London A, 297, 353-364, 1980.
- Jahn, B.-m., G. Gruau, and A.Y. Glikson, Komatiites of the Onverwacht Group, S. Africa: REE geochemistry, Sm/Nd age and mantle evolution, Contrib. Mineral. Petrol., 80, 25-40, 1982.
- Jarvis, G.T., and I.H. Campbell, Archean komatiites and geotherms: solution to an apparent contradiction, Geophys. Res. Lett., 10, 1133-1136, 1983.
- Kushiro, I., Y.. Syono, and S. Akimoto, Melting of a peridotite nodule at high pressures and high water pressures, J. Geophys. Res., 73, 6023-6029, 1968.
- Larson, R.L., Latest pulse of Earth: evidence for a mid-Cretaceous superplume, Geology, 19, 547-550, 1991.
- Lesher, C.E., and D. Walker, Cumulate maturation and melt migration in a temperature gradient, J. Geophys. Res., 93 10, 295-10, 311, 1988.
- Litvin, Y.A., High pressure melting relations in the garnet-lherzolitic system olivine-orthopyroxene-clinopyroxene-garnet, Phase Transformations at high pressures and high temperatures: applications to geophysical and petrological problems, Abstracts of the second Japan-USSR Symposium, Misasa, 48-50, 1989.
- Liu, M., and C.G. Chase, Evolution of midplate hot spot swells: numerical solutions, J. Geophys. Res., 94, 5571-5584, 1989.
- Longhi, J., Liquidus equilibria and solid solution in the system CaAl₂Si₂O₈ Mg₂SiO₄ CaSiO₃ SiO₂ at low pressure, Am. J. Sci., 287, 265-331, 1987.
- Maaloe, S., and K. Aoki, The major element composition of the upper mantle estimated from the composition of lherzolites, Contrib. Mineral. Petrol., 63, 161-173, 1977.
- McCulloch, M.T., and W. Compston, Sm-Nd age of Kambalda and Kanowna greenstones and heterogeneity in the Archaean mantle, Nature, 294, 322-327, 1981.
- McFarlane, E.A., M.J. Drake, and C. T. Herzberg, Magnesiowustite/ melt and majorite/melt partitioning and the early thermal history of

- the Earth, (abstract), Proc. Lunar Planet Sci. Conf., 22, 1990.
- McKenzie, D.P., The generation and compaction of partial molten rock, J. Petrol., 25, 713-765, 1984.
- McKenzie, D., and M.J. Bickle, The volume and composition of melt generated by extension of the lithosphere, J. Petrol., 29, 625-679, 1988.
- Miller, G.H., E.M. Stolper, and T.J. Ahrens, The equation of state of a molten komatiite, 1, Shock wave compression to 36 GPa, J. Geophys. Res., 96, 11,831-11,848, 1991a.
- Miller, G.H., E.M. Stolper, and T.J. Ahrens, The equation of state of a molten komatiite, 2, Application to komatiite petrogenesis and the Hadean mantle, J. Geophys. Res., 96, 11,849-11,864, 1991b.
- Mysen, B.O., and I. Kushiro, Compositional relations of coexisting phases with degree of melting of peridotite in the upper mantle, Am. Mineral., 62, 843-865, 1977.
- Nesbitt, R.W., and S.-S. Sun, Geochemistry of Archaean spinifextextured peridotites and magnesian and low-magnesian tholeiites, Earth Planet. Sci. Lett., 31, 433-453, 1976.
- Nesbitt, R.W., S.-S. Sun, and A.C. Purvis, Komatiites: geochemistry and genesis, *Can. Mineral.*, 17, 165-186, 1979.
- Nisbet, E.G., N.T. Arndt, M.J. Bickle, W.E. Cameron, C. Chavel, M. Cheadle, E. Hegner, T.K. Kyser, A. Martin, R. Renner, and E. Roeddler, Uniquely fresh 2.7 Ga komatiites from the Belingwe greenstone belt, Zimbabwe, Geology, 15, 1147-1150, 1987.
- Nisbet, E.G., and D. Walker, Komatiites and the structure of the Archaean mantle, Earth Planet. Sci. Lett., 60, 105-113, 1982.
- Obata, M., and J.S. Dickey Jr., Phase relations of mafic layers in the Ronda Peridotite, *Year Book Carnegie Inst. Washington*, 75, 562-566, 1976.
- O'Hara, M.J., The bearing of phase equilibria studies in synthetic and natural systems on the origin and evolution of basic and ultrabasic rocks, *Earth Sci. Rev.*, 4, 69-133, 1968.
- O'Hara, M.J., and H.S. Yoder, Jr., Formation and fractionation of basic magmas at high pressures, Scou. J. Geol., 3, 67-117, 1967.
- O'Hara, M.J., M.J. Saunders, and E.P.L. Mercy, Garnet-peridotite, primary ultrabasic magma and eclogites; interpretation of upper mantle processes in kimberlite, *Phys. Chem. Earth*, 9, 571-604, 1975.
- Ohtani, E., Generation of komatiite magma and gravitational differentiation in the deep upper mantle, *Earth Planet. Sci. Lett, 67,* 261-272, 1984.
- Ohtani, E., I. Kawabe, J. Moriyama, and Y. Nagata, Partitioning of elements between majorite garnet and melt and implications for petrogenesis of komatiite, *Contrib. Mineral. Petrol.*, 103, 263-269, 1989.
- Presnall, D.C., and T. Gasparik, Melting of enstatite (MgSiO₃) from 10 to 16.5 GPa and the forsterite (Mg₂SiO₄) majorite (MgSiO₃) eutectic at 16.5 GPa: implications for the origin of the mantle, J. Geophys. Res., 95, 15,771-15,778, 1990.
- Presnall, D.C., J.R. Dixon, T.H. O'Donnell, and S.A. Dixon, Generation of mid-ocean ridge tholeites, J. Petrol., 20, 3-35, 1979.
- Pyke, D.R., A.J. Naldrett, and O.R. Eckstrand, Archean ultramafic flows in Munro Township, Ontario, Geol. Soc. Am. Bull., 84, 955-978, 1973.
- Reed, M.H., Seawater-basalt reaction and the origin of greenstones and related ore deposits, Econ. Geol., 78, 466-485, 1983.
- Salters, V.J.M., and S.R. Hart, The hafnium paradox and the role of garnet in the source of mid-ocean-ridge basalts, *Nature*, 342, 420-422, 1989.
- Shirey, S.B., and G.N. Hanson, Mantle heterogeneity and crustal recycling in Archean granite-greenstone belts: evidence from Nd isotopes and trace elements in the Rainy Lake area, Superior Province, Ontario, Canada, Geochim. Cosmochim. Acta, 50, 2631-2651, 1986.
- Sleep, N., Hotspots and mantle plumes: some phenomenology, J. Geophys. Res., 95, 6715-6736, 1990.
- Smith, A.D, and J.N. Ludden, Nd isotopic evolution of the precambrian mantle, Earth Planet. Sci. Lett., 93, 14-22, 1989.
- Smith, H.S., and A.J. Erlank, Geochemistry and petrogenesis of

- komatiites from the Barberton greenstone belt, South Africa, In: Komatiites, edited by N.T. Arndt and E.G. Bickle, pp. 347-397, George Allen and Unwin, London, 1982.
- Stevenson, D.J., Origin of the moon the collision hypothesis, Annu. Rev. Earth Planet. Sci. 15, 271-315, 1987.
- Storey, M., J.J. Mahoney, L.W. Kroenke, and A.D. Saunders, Are oceanic plateaus sites of komatiite formation?, Geology, 19, 376-379, 1991
- Stosch, H.-G., and H.A. Seck, Geochemistry and mineralogy of two spinel peridotite suites from Dreiser Weiher, West Germany, Geochim. Cosmochim. Acta, 44, 457-470, 1980.
- Sun, S.-S., and R.W. Nesbitt, Petrogenesis of Archaean ultrabasic and basic volcanics: evidence from rare earth elements, *Contrib. Mineral. Petrol.*, 65, 301-325, 1978.
- Takahashi, E., Melting of a dry peridotite KLB-1 up to 14 GPa: Implications on the origin of peridotitic upper mantle, J. Geophys. Res., 91, 9367-9382, 1986.
- Takahashi, E., Speculations on the Archean mantle: missing link between komatiite and depleted garnet peridotite, J. Geophys. Res., 95, 15, 941-15, 954, 1990.
- Takahashi, E., and I. Kushiro, Melting of a dry peridotite at high pressures and basalt magma genesis, Am. Mineral., 68, 859-879, 1983.
- Tarduno, J.A., W.V. Sliter, L. Kroenke, M. Leckie, H. Mayer, J.J. Mahoney, R. Musgrave, M. Storey, and E.L. Winterer, Rapid formation of Ontong Java plateau by Aptian mantle plume volcanism, Science, 254, 399-403, 1991.
- Taylor, H.J.C., Melting in the system MgO-Al₂O₃-SiO₂ at 15 kb, Geol. Soc. Am. Bull., 84, 1335-1348, 1973.

- Turcotte, D.L., On the thermal evolution of the Earth, Earth Planet. Sci. Lett., 48, 53-58, 1980.
- Viljoen, R.P., and M.J. Viljoen, Evidence for the composition of the primitive mantle and its products of partial melting from a study of the rocks of the Barberton Mountain Land, Geol. Soc. S. Afr. Spec. Publ., 2, 275-296, 1969.
- Von Damm, K.L., J.M. Edmond, B. Grant, C.I. Measures, B. Walden, and R.F. Weiss, Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise, Geochim. Cosmochim. Acta, 49, 2197-2220, 1985.
- Walker, R.J., L.M. Echeverria, S.B. Shirey, and M.F. Horan, Re-Os isotopic constraints on the origin of volcanic rocks, Gorgona Island, Colombia: Os isotopic evidence for ancient heterogeneities in the mantle, Contrib. Mineral. Petrol., 107, 150-162, 1991.
- Watson, S., and D. McKenzie, Melt generation by plumes: a study of Hawaiian volcanism, J. Petrol., 32, 501-537, 1991.
- Wei, K., R.G. Tronnes, and C.M. Scarfe, Phase relations of aluminum-undepleted and aluminum-depleted komatiites at pressures of 4-12 GPa, J. Geophys. Res., 95, 15,817-15,828, 1990.
- Wetherill, G., Formation of the Earth, Annu. Rev. Earth Planet. Sci., 18, 205-256, 1990.
- C. Herzberg, Department of Geological Sciences, Rutgers University, Wright Laboratory, Busch Campus, New Brunswick, NJ 08903.

(Received March 31, 1991; revised November 18, 1991 accepted December 10, 1991.)