Mantle-derived sapphirine

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ABSTRACT. A xenolith from the Delegate breccia pipe (New South Wales, Australia) contains sapphirine in equilibrium with aluminous clinopyroxene, garnet, and plagioclase (An_{48}). This unusual assemblage probably developed from a clinopyroxene ($\pm$spinel$\pm$plagioclase) cumulate during cooling from $> 1400\,°C$ to $c.\ 1000\,°C$ at pressures near 15 kbar. The sapphirine is close to the $7:9:3$ composition, suggesting that bulk composition is more important than P-T conditions in determining the stoichiometry of natural sapphirines. A similar occurrence of sapphirine has also been recorded in mantle-derived xenoliths from the Stockdale kimberlite in Kansas. Re-examination of sapphirine granulites from Finero suggests that their primary assemblages and origin may have been similar to those of the Delegate xenolith. Sapphirine is clearly stable under upper-mantle conditions in Ca-Al-Mg-rich bulk compositions.

SAPPHIRINE is found in Mg, Al-rich rocks from many high-temperature granulite terranes. Experimental work suggests that it may also be stable under upper-mantle conditions, if appropriate bulk compositions are available (Ackermand et al., 1975). However, observational evidence to confirm this suggestion is rare. Sapphirine has been reported from the contact zones of several alpine-type peridotites (Monchoux, 1972) but in parageneses and geological associations which strongly suggest a crustal origin. Metagabbros associated with the Finero peridotite of the Ivrea zone of the NW Italian Alps locally contain sapphirine which may be of upper-mantle origin (see below), but these assemblages have been extensively modified during uplift and emplacement of the peridotites (Lensch, 1971; Sills et al., 1983).

The best evidence on the paragenesis of sapphirine in the upper mantle could, in principle, be obtained from the study of xenoliths in volcanic rocks. The mineral assemblages in such xenoliths are generally not modified, because of their rapid ascent to the surface (Ozawa, 1984; Spera, 1985), and may thus escape the complex symplectite

formation that affects many sapphirine-bearing rocks. The only previous report of sapphirine from xenoliths of mantle origin is from the Stockdale kimberlite, Kansas (Meyer and Brookins, 1976). Sapphirine occurs here as rims on spinel, in garnet-clinopyroxene granulite xenoliths.

This paper reports the occurrence of sapphirine in equilibrium with clinopyroxene, garnet, and plagioclase, in a xenolith from the basaltic breccia pipes at Delegate, NSW, Australia (36° 50′ S., 148° 45′ E.; Wass and Irving, 1976). This occurrence extends the documented stability range of natural sapphirines in terms of pressure, temperature, and bulk composition.

Geological setting

The two breccia pipes at Delegate consist of massive and brecciated nephelinites, dated by K-Ar at about 140-160 Ma (Lovering and White, 1969). The heavily altered matrix contains abundant xenoliths of garnet clinopyroxenites ('fassaite eclogite'), garnet granulites, and two-pyroxene granulites. Chemical and microstructural data suggest that the garnet pyroxenites and at least some garnet granulites are derived from pyroxenites by exsolution and recrystallization of complex clinopyroxenes ($\pm$spinel) (Lovering and White, 1969; Griffin et al., 1984).

Geothermobarometry indicates that the garnet clinopyroxenites and garnet granulites have equilibrated at upper-mantle depths of 40-65 km, while the two-pyroxene granulites come from the lower crust (25-35 km) (O'Reilly and Griffin, 1985). Irving (1974) experimentally reproduced the mineral assemblages of some garnet pyroxenites at 1050-1100 °C, 16-17 kbar.

The xenolith described here was collected from the Delegate no. 2 pipe (Lovering and White, 1969) by students and staff of the Australian National

University, Canberra (specimen no. 38926). It was donated for this study by Mr George Halford.

Petrography

The xenolith is subangular with rounded edges and measures approximately $8 \times 5 \times 3$ cm. It is medium-grained (~ 3 mm) and equigranular. A faint cm-scale banding is defined by variations in the content of pale orange garnet in a green matrix. It was originally described in hand specimen as a garnet peridotite.
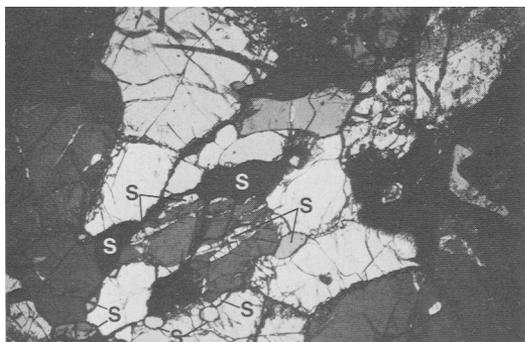

FIG. 1. Photomicrograph (crossed polars) showing sapphirine as polygonal interstitial grains and as elongated blebs within clinopyroxene. Sapphirine is marked 'S'. Garnet is evident at centre right of the field. Width of field is 13 mm.

The thin section shows a well-equilibrated mosaic microstructure (fig. 1) made up of clinopyroxene (86%), plagioclase (7.5%), garnet (4%), and sapphirine (2.5%). Clinopyroxene forms equidimensional grains 1–5 mm across; it shows no twinning, exsolution, or optically visible zoning. Grain boundaries are locally sieve-textured due to incipient melting. Plagioclase grains are 1–5 mm across, unzoned, and have some albite twinning; they are locally altered to sericite. Sapphirine occurs as pale blue, nearly colourless, rounded 0.5–1 mm grains, devoid of twinning or alteration. These grains are commonly included in clinopyroxene, but also occur as discrete grains in contact with plagioclase and garnet without any sign of reaction rims. One small clinopyroxene grain contains three roughly lamellar grains of sapphirine in parallel alignment. Garnet occurs as 0.5 mm isolated grains, and as larger grains containing inclusions of all the other phases.

Locally, the xenolith has apparently reacted with the host magma, and clinopyroxene and garnet have broken down to a fine-grained mixture of clinopyroxene, plagioclase, and green spinel where the nephelinite has penetrated the xenolith.

Chemistry

The analysis of the xenolith differs only slightly from that calculated from the modal analysis (Table I); the differences suggest that the analysed portion was slightly richer in plagioclase and garnet than the thin section. The norm is dominated by Di, An, and Ne, since the rock is rich in Ca and Al compared with most basaltic rocks. It is similar to the sapphirine-bearing xenoliths from the Stockdale pipe (Meyer and Brookins, 1976; Table I), but is considerably more magnesian (mg = 90, compared with 77–79). Some of the other Delegate rocks are nearly as aluminous as no. 38926, but none are quite as calcic; hence, most of them are Hy-normative rather than Ne-normative.

Table I Compositions of sapphirine-bearing xenoliths and Finero granulites

	38926	38926*	1128d*	1128p*	Aver.granul.**	38926
	Delegate		Stockdale		Finero (n=6)	+10% Spin
SiO$_2$	47.23	47.3	46.6	45.0	44.8	43.6
TiO$_2$	0.21	0.2	0.3	0.1	0.1	0.2
Al$_2$O$_3$	19.08	19.4	15.7	20.1	24.2	23.8
FeO	2.79	2.4	8.5	7.9	3.4	3.7
MnO	0.03	-	-	-	0.05	-
MgO	9.99	9.8	12.9	11.5	12.0	11.2
CaO	16.24	18.4	14.8	13.7	13.5	15.0
Na$_2$O	2.64	2.5	1.4	1.7	1.6	2.4
K$_2$O	0.07	-	-	-	0.05	-
P$_2$O$_5$	0.04	-	-	-	-	-
l.o.i	1.24	-	-	-	-	-
Σ	99.56	100.1	100.2	100.0	99.7	99.9
Xmg	90	91	79	77	89	88
Ne	8.3	11.0	1.8	3.6	3.2	11.0
Ab	7.1	0.9	8.6	7.7	7.6	-
An	40.0	41.7	36.6	47.2	58.7	54.2
Di	31.8	39.1	29.6	16.7	6.5	14.4
Ol	9.6	6.4	21.2	22.8	22.4	18.5
Il	0.4	0.4	0.6	0.2	0.2	0.4
Mt	0.7	0.6	2.1	1.9	0.8	0.9
Ni	734				411	700
Cr	1287				462	1600
V	133				18	120
Rb	17				-	15
Sr	238				(109) n=5 159 n=6	214
Ba	211				24	190
Zr	3				11	3
Y	5				2	4

* Calculated from modal analysis and mineral compositions

** Sills et al. (1983)

Norms calculated with Fe^{3+}/Fe^{2+} = 0.20

Mineral analyses are presented in Table II. All phases are homogeneous within analytical uncertainty ($\pm 1\%$ for major elements, $\pm 5\%$ for minor elements).

Table II Mineral analyses

Delegate sapphirine granulite 38926

	CPX (n=6)	GNT (n=4)	PLAG (n=4)	SAPPHIRINE (n=4)
SiO_2	47.72	42.17	56.87	13.88
TiO_2	0.29	0.0	0.0	0.0
Al_2O_3	16.97	24.28	27.67	64.60
Cr_2O_3	0.10	0.0	0.0	0.41
FeO	2.41	7.20	0.0	3.39
MnO	0.0	0.20	0.0	0.10
MgO	10.01	18.38	0.0	18.71
CaO	20.20	8.38	9.82	0.0
Na_2O	2.41	0.0	5.73	0.0
K_2O	0.0	0.0	0.22	0.0
	100.11	100.61	100.31	100.99
	6 Ox	12 Ox	8 Ox	10 Ox
Si	1.715	2.980	2.543	0.802
Al^{IV}	0.285	0.020	0.457	2.198
Al^{VI}	0.434	2.002	1.002	2.198
Ti	0.008	0.000	0.000	0.000
Cr	0.003	0.000	0.000	0.019
Fe	0.072	0.425	0.000	0.164
Mn	0.000	0.012	0.000	0.000
Mg	0.536	1.936	0.000	1.610
Ca	0.778	0.634	0.471	0.000
Na	0.168	0.000	0.497	0.000
K	0.000	0.000	0.013	0.000
Σ Cat	3.999	8.009	4.983	6.991

Cell Parameters

a	9.641 ± 1
b	8.782 ± 1
c	5.267 ± 1
β	106.43 ± 1

Analyses done by WDS electron microprobe at Macquarie University.

n = number of points analysed.

XRD analysis by R. Oberti (University of Pavia).

The clinopyroxene is one of the most aluminous terrestrial fassaites known, with $c.18\%$ Tschermak's component (CaTs) and 15% jadeite component (Jd). Sackij *et al.* (1983) report a clinopyroxene containing 19.7% Al_2O_3 (as $c.23\%$ CaTs, 29% FeTs, and 6% TiTs); this occurs in a cpx + gnt + plag + spin + sphene xenolith from the Udnachaya kimberlite pipe. The cell parameters of our clinopyroxene have been determined, using single-crystal diffraction, by R. Oberti (Table II). A calculation of the site populations, based on the microprobe analysis and the mean atomic number in the octahedral sites yields a $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of 0.43. The resulting $Mg/(Mg + Fe^{2+})$ ratio is

0.93. A detailed discussion of the crystal chemistry of this unusual pyroxene will be presented elsewhere. Other Delegate fassaites are more ferrous, less aluminous, and less calcic. The sieved margins are lower in Na and Al than host pyroxenes. Similar phenomena are observed in garnet lherzolite xenoliths from kimberlite pipes, and are ascribed to decompression melting (Carswell, 1975).

The garnet $(Py_{64.5}Alm_{14}Gros_{21.1}Spes_{0.4})$ is more magnesian and more calcic than most from Delegate. The plagioclase $(An_{48}Ab_{50.7}Or_{1.3})$ is more calcic than those from the other Delegate garnet granulites.

The sapphirine is an aluminous variety, close to the $7:9:3$ 'end-member' composition (fig. 2). The charge balance of the analysis suggests that it contains no Fe^{3+}.

The phases in the secondary-breakdown patches are a heterogeneous clinopyroxene, poor in Na and Al; plagioclase ranging from An_0 to An_{30}; and spinel with mg = 70–80 and very low Cr_2O_3.

P–T conditions

O'Reilly and Griffin (1985) constructed a geotherm using thermobarometric data on well-equilibrated garnet websterite xenoliths from two maars in western Victoria. They also demonstrated that P–T estimates for xenoliths from many other localities in eastern Australia (including four samples from Delegate) are consistent with this geotherm. For the present xenolith, T can be estimated using the cpx–gnt thermometer of Ellis and Green (1979), and P can be derived from the xenolith-based geotherm. This procedure gives about 1005 °C, 14 kbar, a somewhat lower P and T than Irving's (1974) experimental duplication of mineral assemblages in Delegate garnet pyroxenites. Temperatures for spinel peridotite xenoliths from southeastern Australia range from $c.850$ °C to $c.1100$ °C, while granulite xenoliths inferred to be derived from the lower crust give T estimates of 750–875 °C (O'Reilly and Griffin, 1985). The P–T estimate for the sapphirine-bearing xenolith no. 38926 therefore indicates that it was derived from deep in the upper mantle, near the inferred spinel peridotite–garnet peridotite transition.

Meyer and Brookins (1976) estimated P–T conditions of equilibration for the Stockdale xenoliths of 800–1000 °C and 10–14 kbar. Our recalculation of their data for a sapphirine-bearing two pyroxene-garnet granulite (assuming Fe = FeO) yields a T of 1000 °C. However, the unusually high Al_2O_3 (8.5 wt. %) of the orthopyroxene in this sample gives an impossibly low P (0–2 kbar) (Ellis and Green, 1979; Wood, 1974). This may reflect disequilibrium between garnet and orthopyroxene. Anastasiou
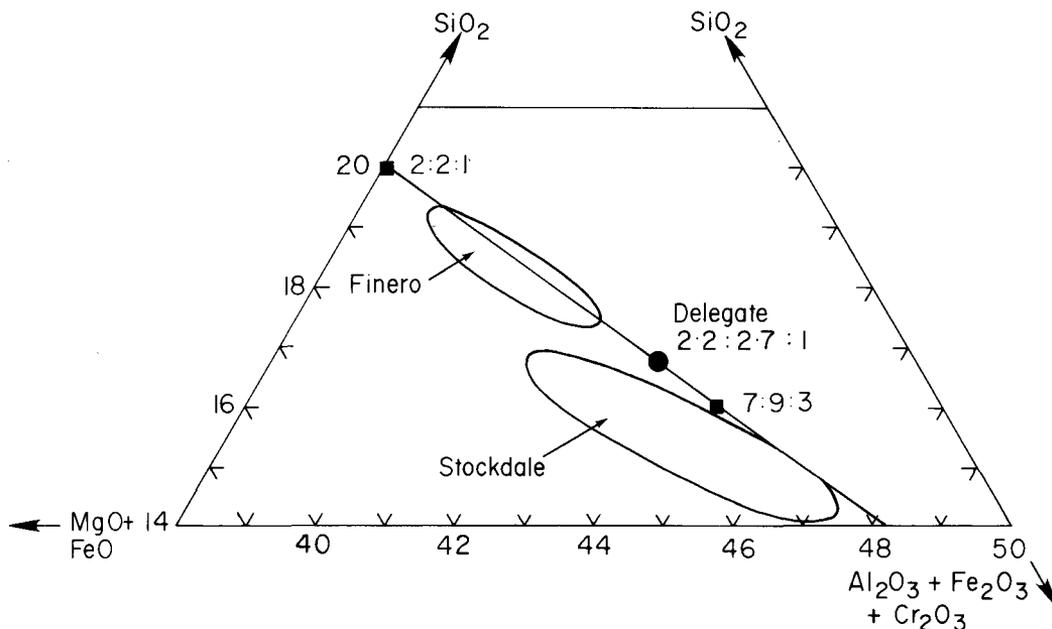
FIG. 2. Sapphirine analyses (see text for details) from the Finero outcrops, the Stockdale xenoliths and Delegate (this study) plotted on part of the triangle $SiO_2-(MgO+FeO)-(Al_2O_3+Fe_2O_3+Cr_2O_3)$ mol. %. 2:2:1 etc. are proportions of Mg:Al$_2$:Si respectively, referring to the sapphirine end-member compositions: $(Mg,Fe^{2+})_2$ $(Al,Fe^{3+}, Cr)_4$ $SiO_{10}-(Mg,Fe^{2+})_7$ $(Al,Fe^{3+}, Cr)_{18}$ Si_3O_{40}.

and Seifert (1972) measured similar Al_2O_3 contents in the orthopyroxene coexisting with sapphirine + cordierite in experimental runs at $T = 1000$–$1050\,°C$.

The P–T estimate for sample 38926 lies well within the stability field of sapphirine in dry systems (Ackermand et al., 1975). Schreyer and Seifert (1969) found that $P > 15$ kbar was necessary for the coexistence of sapphirine + pyrope, but the presence of Ca and Fe, as in the present rock, would stabilize garnet at lower pressure. Hensen and Green (1973) found that the assemblage garnet + sapphirine is stable above an invariant point at $c.7.5$ kbar, $1150\,°C$ in pelitic compositions. Ackermand et al. (1975) pointed out that sapphirine would only be stable in very Mg-, Al-rich bulk compositions in the upper mantle; our sample meets this constraint.

Discussion

Sapphirine stoichiometry. Taylor (1973) synthesized sapphirine from a range of bulk compositions at $1400\,°C$, 15 kbar; all of the synthesized sapphirines have silicic compositions, near the 2:2:1 end member. This agrees with several earlier studies,

which show that all sapphirines synthesized at $P > 8$ kbar are also near 2:2:1. This observation led Schreyer and Abraham (1975) to suggest that the aluminous compositions are only stable at low P, and that peraluminous compositions may be metastable. Sills et al. (1983) suggest that the more Si-rich sapphirine compositions in the Finero occurrences are indicative of high P.

However, the sapphirine found in the present sample is aluminous, despite being formed at high pressure, and several of the sapphirines from the Stockdale xenoliths are peraluminous (fig. 2). High P and T alone are therefore not sufficient to produce 2:2:1 sapphirines. Bulk composition probably plays an important role as well. Another reason for the discrepancy may lie in the polymorphism of sapphirine; synthetic sapphirines are known to have different thermodynamic properties from natural examples (Seifert, 1974).

Evolution of the assemblage. The garnet pyroxenites from Delegate and other eastern Australian localities show abundant microstructural and chemical evidence of their evolution from complex primary igneous clinopyroxenes, through exsolution and recrystallization (Lovering and White, 1969; Griffin et al., 1984). The exsolved phases
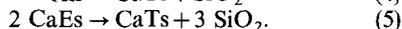
include orthopyroxene, spinel, plagioclase, and garnet; possible primary spinels are rimmed and replaced by garnet. Sample 38926 represents a Mg, Al, Ca-rich end member of the chemical spectrum defined by these other pyroxenites; we regard it as genetically related to them, and formed by the same processes. Lovering and White (1969) proposed the following exsolution/reaction sequence during cooling to explain the mineralogy of the Delegate garnet pyroxenites:

$$\text{cpx A} \rightarrow \text{cpx B} + \text{spin} + \text{opx} + \text{plag} \rightarrow$$
$$\text{gnt} + \text{cpx C}. \quad (1)$$
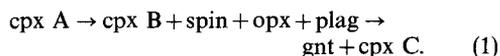
In a still more Ca, Al-rich bulk composition at high P, we might expect further reactions of the type:

$$8 \text{ Spin} + 3 \text{ An} + \text{SiO}_2 \rightarrow$$
$$\text{Di} + 2 \text{ CaTs} + \text{Sa}(7:9:3). \quad (2)$$
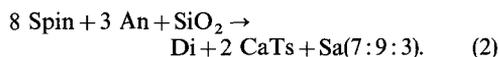
The small amount of SiO_2 required could be provided by reactions such as:

$$\text{Ab} \rightarrow \text{Jd} + \text{SiO}_2. \quad (3)$$
$$\text{An} \rightarrow \text{CaTs} + \text{SiO}_2. \quad (4)$$
$$2 \text{ CaEs} \rightarrow \text{CaTs} + 3 \text{ SiO}_2. \quad (5)$$

All of these reactions would be favoured in undersaturated, Ca-rich compositions. Reaction (5) is based on the observed solid solution of the calcium-escola end member $(Ca_{0.5}AlSi_2O_6)$ in pyroxenes of the Di–CaTs–An system at high P, T (Wood, 1976). The reaction of spinel to produce sapphirine is consistent with the petrographic relations in the Stockdale xenoliths (Meyer and Brookins, 1976). This sequence of reactions can explain the modal composition and mineral chemistry of sample 38926, if the original rock was a clinopyroxene ± spinel ± plagioclase cumulate, formed at $P = c.15$ kbar and cooled isobarically from $T > 1400\,°C$ to $T \approx 1000\,°C$ (cf. Green, 1966).

Analogues in alpine peridotite? Xenoliths only rarely offer direct evidence (in the form of composite xenoliths) of spatial relationships between rock types at depth. We can only speculate on the processes which might have produced the enrichment of Mg in the present sample, relative to other Delegate pyroxenites. One obvious suggestion is that it represents partial reaction between the original magma (or its cumulates) and the inferred peridotite host rock. Such exchange of material between pyroxenite veins and lherzolite has been documented in xenoliths (Irving, 1980; Wilshire, 1984; Griffin *et al.*, 1984) and in peridotite massifs (Wilshire and Pike, 1975). Alternatively, the Mg, Ca-rich rocks may represent early clinopyroxene + spinel cumulates from a primitive magma.

A possible analogy may be drawn with the Finero massif, N. Italy, where sapphirine, garnet, clinopyroxene, and plagioclase occur in horn-blende granulites and pyroxenites near the contact of garnetiferous metagabbro and hornblende lherzolite. The sapphirine-bearing rocks are richer in Al and poorer in Ca than sample 38926 (Table I). Sills *et al.* (1983) suggest that the protoliths of the sapphirine-bearing rocks were olivine + plagioclase ($\pm$ hbl $\pm$ spin) cumulates, metamorphosed to plag + cpx + spin $\pm$ hbl and then to cpx + gnt + plag + sa $\pm$ hbl $\pm$ sp. This evolution is interpreted as reflecting cooling and burial from $c.1200\,°C$, 7 kbar to $c.900\,°C$, 9 kbar. The high-P mineralogy has been extensively modified by symplectite formation during later uplift.

We find it difficult to accept this scenario, especially the low-pressure protoliths (olivine + plagioclase). The Sr contents of the rocks are low (only one is over 130 ppm), and there is no obvious correlation of Sr with normative feldspar content. The normative feldspar is extremely calcic (An_{86-100}), which is typical of rocks containing CaTs-rich pyroxene (Lovering and White, 1969; Griffin *et al.*, 1984). Sills *et al.* argue against the presence of primary clinopyroxene because V contents are low; this argument is only valid if the host magma was primitive and had low f_{O_2}, an assumption for which there is no evidence. There is at best a poor correlation of Ni with normative olivine.

The composition of the sapphirine-bearing rocks from Finero can be roughly duplicated by adding small amounts of spinel (no. 395 of Sills *et al.*) to our sample 38926. Addition of minor plagioclase further improves the fit. We therefore suggest that the protoliths at Finero may have been cpx + spinel + plag cumulates. This removes the constraint of low-P (< 10 kbar) origin, and eliminates the need to postulate burial during cooling of the protolith, as proposed by Sills *et al.* (1983).

Sills *et al.* (1983) suggest that hornblende was present in the Finero rocks from the magmatic, or at least early metamorphic, stage, and that reactions involving hbl were involved in the production of sapphirine. From their descriptions, and our own work at Finero, we do not find the petrographic evidence for this suggestion to be convincing. The amphibole may have been introduced into the metagabbros at the same time that amphibole and phlogopite were formed in the adjacent peridotites. Prior to this metasomatic event, the mineral assemblages, and evolutionary history, of the sapphirine-bearing rocks may have resembled those of the Delegate and Stockdale xenoliths.

Conclusions

Available evidence indicates that the occurrence of sapphirine in the upper mantle is restricted to

rocks rich in Ca, Al, and Mg, where the stable assemblage is aluminous clinopyroxene + plagioclase + garnet + sapphirine ($\pm$opx$\pm$hbl). These rocks may originate as clinopyroxene + spinel ($\pm$plagioclase) cumulates; their high Mg/(Mg + Fe) may reflect wall-rock reaction with the host peridotite or early cumulate origin from Mg-rich magmas. High-pressure sapphirines may be either silicic or aluminous; the controls on crystal chemistry need further study.

This study emphasizes the advantages of comparisons between xenoliths in volcanic rocks and tectonically emplaced ultramafic massifs. The petrographic and chemical relationships in the latter may be obscured by deformation, reaction, and recrystallization during uplift, but the spatial relationships of rock types in these massifs are useful in interpreting the more pristine mineral assemblages found in the xenoliths.

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