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Ultradeep (Greater Than 300 Kilometers), Ultramafic Upper Mantle Xenoliths

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Geophysical discontinuities in Earth's upper mantle and experimental data predict the structural transformation of pyroxene to garnet and the solid-state dissolution of pyroxene into garnet with increasing depth. These predictions are indirectly verified by omphacitic pyroxene exsolution in pyropic garnet-bearing xenoliths from a diamondiferous kimberlite. Conditions for silicon in octahedral sites in the original garnets are met at pressures greater than 130 kilobars, placing the origin of these xenoliths at depths of 300 to 400 kilometers. These ultradeep xenoliths support the theory that the 400-km seismic discontinuity is marked by a transition from peridotite to eclogite.

DIAMONDIFEROUS KIMBERLITES are widely recognized as hosts for a rich source of xenoliths from Earth's upper mantle (*1*). Study of these accidental inclusions have provided critical data on the composition, age, and evolution of parts of the upper mantle as well as on the origin of diamonds (*2*). The deepest samples from the upper mantle are considered to be sheared garnet lherzolites (composed mostly of olivine, orthopyroxene, and clinopyroxene) that were sampled by kimberlites from the stable mantle lithosphere at depths no greater than 180 km (*3*). Whether the mobile and deeper asthenosphere is ever sampled in kimberlite eruptives remains uncertain (*4*). A precise knowledge of the mineralogy and petrology of the deeper (>200 km) upper mantle is needed to account more rationally for the nature of seismic discontinuities and other geophysical properties and for verification of the results of high-pressure experiments (*5*).

Direct access to ultradeep samples is also required in the face of the growing debate on the nature of subduction in the Archean and on whether downgoing oceanic crustal slabs become buoyant at the 650 km discontinuity (*6, 7*) or continue to the core-mantle boundary (*8*). Subducted oceanic crust, which is largely basaltic in composition, is predicted to transform to eclogite (Na-rich clinopyroxene and Fe-Ca-Mg-rich garnet) with increasing depth, but eclogites in kimberlites may also form by low-pressure partial melting of garnet lherzolite (*9*). The origin of eclogites is by no means settled (*10*), nor are the propositions that the deeper asthenosphere is composed of piclogite [olivine-bearing eclogite (*11*)] or alternatively of garnetite [garnet and the solid-state transformation of pyroxene to the garnet structure, (*12*)], both of which require high temperatures and depths exceeding 300 km.

Conversion of low-pressure pyroxene to the garnet structure, or the solid-state dissolution of pyroxene in garnet, requires that some of the Si in fourfold tetrahedral (Si^{IV}) coordination at low pressure be converted to sixfold octahedral (Si^{VI}) coordination, which is indicative of high pressure (*13*). Because the ratio of Si to O in pyroxene is 4:12 rather than the garnet value of 3:12, the chemical signature of this high pressure substitution is more than 3 Si atoms per 12 O atoms (*14, 15*). Although solid solution of pyroxene in garnet was demonstrated experimentally more than 20 years ago (*16*), naturally occurring analogs have only recently been recognized in diamond inclusions from South Africa (*17*) and Brazil (*18*).

We have now identified xenoliths similar to the mineral inclusions from diamond that have eclogitic affinities and large concentrations of omphacite (diopside-jadeite solid solution) exsolved in pyropic garnet. The xenoliths were collected from coarse (1 to 5 cm) heavy media concentrates resulting from commercial diamond recovery at the Jagersfontein kimberlite, 230 km southeast of Kimberley, South Africa (*19*). Two xeno-

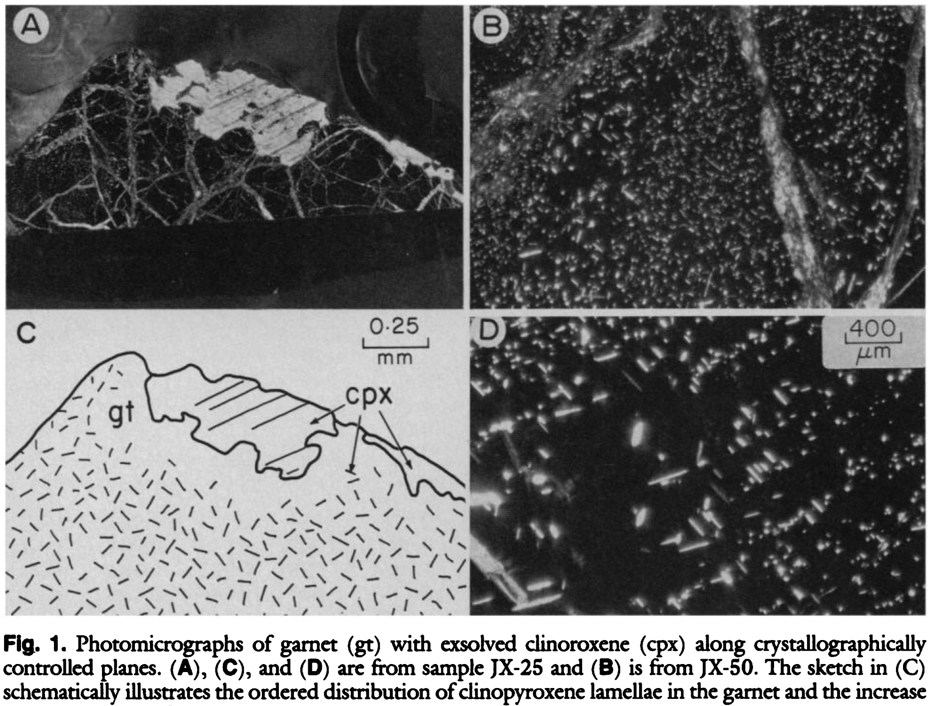

Fig. 1. Photomicrographs of garnet (gt) with exsolved clinoroxene (cpx) along crystallographically controlled planes. (**A**), (**C**), and (**D**) are from sample JX-25 and (**B**) is from JX-50. The sketch in (C) schematically illustrates the ordered distribution of clinopyroxene lamellae in the garnet and the increase in the number of lamellae with distance from the larger clinopyroxene grain; note the irregular geometry of the grain boundary contact between garnet and clinopyroxene and the lamellae-free diffusion zone. Bright veinlets are cracks filled by secondary calcite, mica, and amphibole. The millimeter scale applies to (A), (B), and (C), and the micrometer scale to (D).

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liths (JX-25 and JX-50) were recognized as unusual because they have large (1 by 2 cm) single crystals of intensely purple garnet and bright apple-green clinopyroxene, unlike the more common lherzolite and eclogite xenoliths derived from the upper mantle. Sample JX-25 is dominantly garnet (95%) with associated clinopyroxene (5%), whereas JX-50 has approximately 60% garnet and 40% clinopyroxene. Garnets in both samples contain abundant clinopyroxene lamellae 5 to 50 μm in width and up to 200 μm in length. Lamellae are either spindle-shaped or octagonal prismatic basal sections. Although unevenly distributed, the overall lamellar pattern is distinctly triangular in form (Fig. 1); the shape and orientation suggest that the pyroxene is due to exsolution along the {111} garnet planes. These are dominant glide planes, and in a periodic cylindrical packing model for garnet (*20*) (Fig. 2), the cylinders correspond to linear arrays of octahedrally coordinated Al that are oriented at 60° and 120°. The diffusion rate of Al in silicate minerals is slow (*21*); hence, these arrays are inherently conducive to the diffusion capture of Na, Ca, and Mg, and thus the nucleation and growth of Al^{VI}-rich pyroxene (that is, omphacite). In both specimens, large single clinopyroxene crystals (0.25 mm width) occur adjacent to garnet; the grain-boundary contact is cuspate and sealed (Fig. 1A). In sample JX-25 the garnets do not contain exsolution lamellae in a zone 100 to 200 μm wide adjacent to these pyroxenes (Fig. 1C); the lamellae increase in concentration with distance away from this zone to a maximum of approximately 30% by volume. This distribution is further evidence that the lamellae originated by exsolution rather than by epitaxial replacement or accidental inclusion of lamellar clinopyroxene in garnet. Sample JX-25 has irregular inclusions of garnet in the larger clinopyroxene, whereas JX-50 has lamellar and globular garnet along (010) and exsolved orthopyroxene along (100) in its larger clinopyroxene; the clinopyroxene is deformed and exhibits undulose extinction.

Electron microbeam analyses (*22*) of these assemblages (Table 1) show that compositions of the garnet in the two samples differ largely in Fe:Mg ratio; Cr_2O_3 is minor but differs by a factor of 2 to 3. Host garnet and lamellar globular garnet in clinopyroxene are similar in composition in each sample, as are the lamellar and attached clinopyroxenes. Both garnet and clinopyroxene are unzoned. These compositional and exsolution features suggest that the assemblage in each sample is in equilibrium; the larger clinopyroxenes in JX-25 may be derived exclusively from the host garnet by exsolution, but the proportion of discrete clinopyroxene that resulted by exsolution in JX-50 is uncertain. Pyroxene-substituted garnet inclusions in diamonds from Brazil (*17*) also have associated clinopyroxene (with up to 45 mole percent jadeite component) and are similar to JX-25 and JX-50 in texture and mineralogy. One population of the Brazil diamonds is composed of homogeneous garnet but with 3.1 to 3.4 Si atoms per 12 O atoms; similar garnets have been reported from the Monastery kimberlite (*17*) and from Jagersfontein (*23*), where occluded garnets have Si values of 3.1 and 3.3 per 12 O atoms. If JX-25 is used as an example, and clinopyroxene (cpx) is recombined into host garnet (gt) at various proportions to infer the original garnet composition (*24*) the Si contents for $Gt_{80}Cpx_{20}$ and $Gt_{70}Cpx_{30}$ are 3.149 and 3.238, respectively, on the basis of 12 O atoms (Table 2). We regard $Gt_{70}Cpx_{30}$ in JX-25 and $Gt_{80}Cpx_{20}$ in JX-50 as conservative estimates of the original garnet compositions. These compositions are depleted in Al and are remarkably similar to a diamond inclusion garnet (B9-17) with excess Si from Monastery (*17*).

Table 1. Electron microprobe analyses in weight percent (above) and cations per 12 O atoms (below). Garnet, Gt; clinopyroxene, Cpx; orthopyroxene, Opx; H, Gt host; C, Gt or Opx in large Cpx; L, lamellar Cpx in Gt; A, attached, large Cpx.

Component or cation	JX-25				JX-50				
	Gt(H)	Gt(C)	Cpx(L)	Cpx(A)	Gt(H)	Gt(C)	Cpx(L)	Cpx(A)	Opx(C)
SiO_2	42.23	42.52	54.08	53.93	41.75	41.34	54.61	55.25	57.31
TiO_2	0.04	0.00	0.09	0.05	0.14	0.05	0.18	0.08	0.11
Al_2O_3	23.54	23.82	2.42	2.22	23.67	23.51	3.74	4.49	0.75
Cr_2O_3	1.54	1.00	1.20	0.78	0.50	0.70	0.74	0.59	0.00
FeO	7.70	7.54	1.76	1.37	9.91	10.26	2.77	2.37	6.40
MnO	0.48	0.00	0.02	0.10	0.42	0.34	0.03	0.00	0.04
MgO	20.38	21.05	15.40	16.02	19.66	19.49	15.14	14.78	34.41
CaO	4.56	4.51	22.39	22.28	4.13	3.87	19.12	19.10	0.24
Na_2O	0.06	0.04	2.33	2.17	0.00	0.05	2.69	2.75	0.08
K_2O	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.02	0.00
Totals	100.52	100.48	99.71	98.95	100.18	99.61	99.03	99.43	99.34
Si	2.979	2.986	3.940	3.949	2.973	2.966	3.973	3.984	3.973
Ti	0.002	0.000	0.005	0.003	0.007	0.003	0.010	0.004	0.006
Al	1.957	1.971	0.208	0.192	1.986	1.988	0.321	0.382	0.061
Cr	0.085	0.056	0.069	0.045	0.028	0.040	0.040	0.034	0.000
Fe	0.454	0.443	0.107	0.084	0.590	0.616	0.169	0.143	0.371
Mn	0.029	0.000	0.001	0.006	0.025	0.021	0.002	0.000	0.002
Mg	2.143	2.203	1.672	1.748	2.087	2.084	1.642	1.589	3.555
Ca	0.345	0.339	1.748	1.748	0.315	0.297	1.490	1.476	0.018
Na	0.008	0.005	0.329	0.308	0.000	0.007	0.379	0.384	0.011
K	0.000	0.000	0.001	0.003	0.000	0.000	0.001	0.002	0.000
Totals	8.002	8.003	8.081	8.086	8.012	8.021	8.027	7.998	7.997

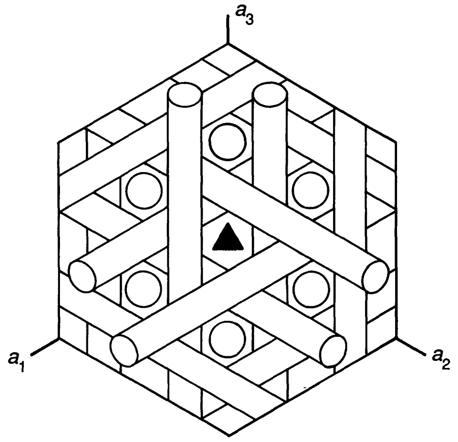

Fig. 2. Sketch of the cylindrical stacking model for garnet (*20*) viewed down a triad axis (solid triangle); a_1, a_2, and a_3 are crystal axes. Rod orientations are {111}, and the rods connect Al^{VI} sites in the garnet structure; these parts of the structure are compositionally and crystallographically amenable to clinopyroxene exsolution as illustrated in Fig. 1.

The conditions at which xenoliths JX-25 and JX-50 were once homogeneous pyroxene-substituted garnets must be inferred from experiments on simplified systems. The substitution of enstatite ($MgSiO_3$) in pyrope ($Mg_3Al_2Si_3O_{12}$) has been determined experimentally in the Mg-Al-Si-O (MAS) system (*14*, *23*), and garnet compositions of $Gt_{70}Cpx_{30}$ are stable at pressures of 100 to 120 kbar. Synthetic systems that incorporate calcium (CMAS) predict pressures approaching 100 kbar (*15*, *26*), or in excess of 100 kbar [120 to 130 kbar (*27*)]. Systems with sodium and calcium (NCMAS), however, extend the garnet stability field to lower pressures (*27*). Experiments on harzburgite and model pyrolite (*28*) show that garnets with excess Si are formed at ~120 kbar in harzburgite and at ~100 to 120 kbar in pyrolite. Experiments on garnet solid solutions appropriate to the precise compositions in JX-25 and JX-50 have not been done; however, in experiments on closely related compositions (*27*), the first appearance of garnet is at ~133 kb and 1650°C, and with increasing pressure the stability and the proportion of garnet and pyroxene solid solution in garnet is greatly increased (*27*, p. 401). Pressures of 140 to 150 kbar are estimated for JX-25 and JX-50, but such pressures are probably too high because the effects of Fe and Cr on the complex NCMAS system are unknown (*29*). Furthermore, we cannot demonstrate that the pyroxene-substituted garnets in JX-25 and JX-50 were originally in equilibrium with discrete pyroxene; our estimate of 30% pyroxene solid solution may also be slightly high. Homogenization experiments on the pyrope-omphacite assemblage are required to establish firmly the minimum pressure and temperature of equilibration. Notwithstanding these uncertainties, we consider that 120 to 130 kbar is reasonable, and this value would place the origin of the xenoliths at a depth of about 400 km. This depth is equivalent to a major seismic discontinuity and would be consistent with the transformation of garnet + pyroxene (eclogite) to garnetite (*6, 7, 30*); this depth is also significantly greater than that of other xenoliths typically present in kimberlites. Xenoliths JX-25 and JX-50, however, have disproportionated from garnetite to pyrope + omphacite. A suitable geobarometer is not available for this bimineralic assemblage, but because the partitioning of Fe and Mg is strongly temperature dependent, one can estimate an equilibration temperature by assuming a value for pressure (*31*). We have assumed that the samples equilibrated in the lithosphere long enough to achieve long-range ordering and solid-state exsolution equilibrium. At 45 kbar, the temperature of equilibration is ~900° to 1000°C.

Apart from the diamond inclusions, remarkably similar garnet and clinopyroxenes have been described in eclogite xenoliths from the Roberts Victor kimberlite in South Africa (*32*) and the Koidu kimberlite in Sierra Leone (*33*), and in olivine-bearing clinopyroxenite and websterite xenoliths from the Bellsbank kimberlite fissure complex in South Africa (*34*). These samples all contain omphacite and chrome pyrope. The garnets contain 1 to 2% Cr_2O_3 by weight, unlike those in typical eclogites (0 to 0.2% Cr_2O_3), but in several other respects (for example, concentrations of FeO, CaO, MgO, and TiO_2 and CaO/Cr_2O_3 ratios, the garnets resemble the ultramafic inclusion suite in diamonds (*35*) that are generally assumed to be derived from depleted lithosphere. Xenoliths similar to JX-25 and JX-50 are distinctive: the pyroxene is Na-rich and eclogitic, the garnet is Mg-rich and ultramafic, and accessory orthopyroxene is commonly present. These xenoliths are refractory and have on average (by weight) 19% MgO, 14% Al_2O_3, and 1% Cr_2O_3; they are also relatively rich in SiO_2 (48%), CaO (11%), FeO (6%), Na_2O (1%), and K_2O (0.3%). We propose that they also originated at deep levels (>100 kbar) in the upper mantle.

Table 2. Reconstituted clinopyroxene solid solutions in garnet and xenolith bulk compositions in weight percent (above) and cations per 12 O atoms (below). The estimated bulk composition of JX-25 is equivalent to $Gt_{70}Cpx_{30}$. The bulk composition of JX-50 is based on a bulk modal proportion of $Gt_{60}Cpx_{40}$. Zero-pressure densities used in the calculations are from (*24*).

Component or cation	JX-25		JX-50		
	$Gt_{70}Cpx_{30}$	$Gt_{80}Cpx_{20}$	$Gt_{70}Cpx_{30}$	$Gt_{80}Cpx_{20}$	Bulk
SiO_2	45.50	44.38	45.17	43.99	48.94
TiO_2	0.05	0.05	0.15	0.15	0.16
Al_2O_3	17.72	19.70	18.37	20.19	13.35
Cr_2O_3	1.44	1.47	0.57	0.54	0.64
FeO	6.07	6.62	8.01	8.66	5.92
MnO	0.36	0.39	0.32	0.36	0.21
MgO	19.01	19.47	18.45	18.87	17.13
CaO	9.48	7.80	8.12	6.75	12.52
Na_2O	0.68	0.47	0.72	0.47	1.34
K_2O	0.003	0.002	0.003	0.002	0.006
Totals	100.31	100.35	99.88	99.98	100.21
Si	3.2376	3.1491	3.2340	3.1436	
Ti	0.0257	0.0026	0.0082	0.0082	
Al	1.4860	1.6475	1.5503	1.7004	
Cr	0.0812	0.0827	0.0327	0.0309	
Fe	0.3612	0.3927	0.4796	0.5174	
Mn	0.0218	0.0234	0.0194	0.0219	
Mg	2.0165	2.0598	1.9693	2.0104	
Ca	0.7225	0.5931	0.6229	0.5170	
Na	0.0941	0.0648	0.0998	0.0653	
K	0.0000	0.0000	0.0000	0.0000	
Totals	8.0465	8.0157	8.0162	8.0151	

Recognition of these ultradeep xenoliths have implications for understanding upper mantle dynamics and the genesis of diamonds, kimberlites and eclogites. The compositions of the ultradeep samples indicate that the xenoliths are clearly not primitive melts, obvious restites, or cumulates. Such compositions may have arisen during early fractionation of the upper and lower mantle, or may have resulted from the mixing of deeply penetrating oceanic crustal slabs and primitive mantle. In either case, Anderson's model (*6*) for an eclogite layer at the 400-km seismic discontinuity is seemingly verified by these xenoliths. The samples must have been transported from 300 to 400 km into stable cratonic lithosphere at ~180 km where equilibration took place. A mantle plume may have been responsible. Some of the associated eclogitic diamonds are also of ultrahigh-pressure origin, but others appear to have nucleated at lower pressures (*17*). Formation from carbon gas species at the head of the plume is a possibility. The contrast in ages between ultramafic [3.2 to 3.3 billion years ago (Ga)] and eclogitic (~1.5 Ga) diamonds (*36*) from these kimberlites may reflect the age of the plume event. Both suites of diamonds, however, along with other xenoliths were only transmitted to the surface during kimberlite eruptions at ~90 to 120 million years ago. The kimberlites may have been generated by later plume events, but whether some of the melt is from the transitional zone is unknown. Other ultradeep xenoliths should have been sampled by kimberlites elsewhere, and majorite and β-Mg_2SiO_4 should be present as diamond inclusions if our estimate of 400 km is correct.

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Increase in the Stratospheric Background Sulfuric Acid Aerosol Mass in the Past 10 Years

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Data obtained from measurements of the stratospheric aerosol at Laramie, Wyoming (41°N), indicate that the background or nonvolcanic stratospheric sulfuric acid aerosol mass at northern mid-latitudes has increased by about 5 ± 2 percent per year during the past 10 years. Whether this increase is natural or anthropogenic could not be determined at this time because of inadequate information on sulfur sources, in particular, carbonyl sulfide, which is thought to be the dominant nonvolcanic source of stratospheric sulfuric acid vapor. An increase in stratospheric sulfate levels has important climatic implications as well as heterogeneous chemical effects that may alter the concentration of stratospheric ozone.

THE DOMINANT SOURCE OF SULFURIC acid (H_2SO_4) aerosol in the stratosphere is major volcanic eruptions that impulsively inject sulfur dioxide (SO_2) to altitudes of 20 to 25 km; this SO_2 subsequently forms H_2SO_4 vapor, which is followed by aerosol nucleation and growth. The physical state of the stratospheric aerosol is an aqueous spherical droplet composed of 60 to 80% sulfuric acid for temperatures from −80° to −45°C, respectively (*1*). In 1959, Junge *et al.* (*2*) showed by direct observations through particle impactor measurements that a stable layer of sulfur-containing aerosol particles persists in the stratosphere, albeit at a low level, even during periods without major, tropopause-penetrating volcanic eruptions. Ambient levels of SO_2 in the upper troposphere and stratosphere are low because of its reactivity and water solubility and are not believed capable of producing this natural background. Crutzen (*3*) suggested that a sulfur-bearing compound that is chemically inert and water-insoluble, such as carbonyl sulfide (OCS), may instead be responsible. In this model, OCS diffuses into the stratosphere, where it is dissociated by solar ultraviolet radiation and eventually forms sulfuric acid. Measurements of stratospheric OCS concentrations (*4, 5*) and results of detailed chemical and dynamical modeling studies (*6, 7*) are in general agreement with this dissociation hypothesis. Carbon disulfide (CS_2), which is probably converted to OCS in the troposphere, may also be important. Because it is estimated that up to 25% of the atmospheric burden of these sulfur compounds are by-products of biomass burning, fossil-fuel burning, petroleum refining, and other industrial processes, their atmospheric levels should be increasing. Although there have not been any long-term studies of OCS concentrations in the stratosphere, this gas appears to have been present at the 500 pptv (parts per trillion by volume) level since at least 1976 (*8*).

Problems associated with an increasing sulfuric acid layer in the stratosphere are numerous. In addition to climate considerations, heterogeneous chemical conversion of inactive forms of chlorine by aerosols containing sulfuric acid and water is now thought to be important in stratospheric ozone depletion after major volcanic eruptions (*9*). Increased scattered solar radiation will alter photochemistry and may even accelerate the conversion of OCS to H_2SO_4. Because the aerosol uses up water both in the conversion of OCS and in aerosol formation, it is a sink for H_2O and may play a role in dehydration of the stratosphere, although this effect is expected to be small because of the relative mixing ratios involved.

Balloon soundings over Laramie, Wyoming (41°N), where the vertical distribution of atmospheric aerosols is measured approximately monthly with optical particle counters (*10*), were analyzed for the period

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