

## A new tetragonal silicate mineral occurring as inclusions in lower-mantle diamonds

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Aluminium is one of a small group of elements—Si, Mg, Fe, Al, Ca and O—that form the bulk of the Earth's mantle. In the upper mantle, Al is largely contained in minerals with a garnet structure. But the mineral transformations associated with the breakdown of garnet structures in the uppermost lower mantle have been a matter of uncertainty<sup>1–9</sup>. Here we report the discovery of a new aluminous mineral, present as inclusions in diamonds of lower-mantle origin found at São Luiz, Brazil<sup>10</sup>. This phase has a stoichiometric garnet composition similar to pyrope–almandine but has a distinct tetragonal structure (space group  $I\bar{4}2d$ ), and is here referred to by the acronym TAPP (tetragonal almandine–pyrope phase). Although TAPP has not been recognized in experimental studies, we suggest that it is nevertheless a primary rather than retrogressive phase and has a limited stability field in relatively aluminous bulk compositions in the uppermost lower mantle. TAPP, like garnet, would lead to relatively low densities for basic rocks compared with peridotites (assumed to be the dominant mantle rocks), and we suggest therefore that it may play an important role in determining density differences and the dynamics of segregation between ultrabasic and basic compositions in the mantle<sup>7,11,12</sup>.

Diamonds from São Luiz have been reported<sup>10</sup> to contain inclusions of silicate minerals with the compositions of (Mg,Fe)SiO<sub>3</sub> and CaSiO<sub>3</sub>, together with inclusions of the oxide (Mg,Fe)O. These compositions indicate an assemblage of the minerals (Mg,Fe)-perovskite, Ca-perovskite and ferropericlae, which has been predicted<sup>13</sup> and shown by experiments<sup>6,9,14</sup> to be stable for expected mantle bulk compositions only below depths of the upper-to-lower mantle transition at ~660 km. Such assemblages also yield values of seismic wave velocities consistent with those observed for the lower mantle<sup>14,15</sup>. In addition to the occurrence of the association (Mg,Fe)SiO<sub>3</sub>, CaSiO<sub>3</sub> and (Mg,Fe)O from São Luiz, Mössbauer measurements on Fe oxidation states in the ferropericlae inclusions support a lower-mantle origin<sup>16,17</sup>, while X-ray studies have also shown extremely high confinement pressures on ferropericlae inclusions within São Luiz diamonds<sup>18</sup>.

The new phase, TAPP, has been found to occur in eight diamonds from São Luiz and was first reported<sup>10</sup> as a phase of lower-mantle paragenesis because of its association with (Mg,Fe)SiO<sub>3</sub> and (Mg,Fe)O inclusions. Its chemical composition, as determined by electron microprobe analysis, is closely similar to that of minerals with garnet structure and the mineral was initially described as a garnet<sup>10</sup>. Of the TAPP inclusions identified by chemical analysis, two occurred alone in diamond and five coexisted with separate inclusions of ferropericlae (including one case where TAPP was also in direct contact with a (Mg,Fe)SiO<sub>3</sub> inclusion). In another case, lacking ferropericlae, TAPP was in contact with a Mg, Al, Na silicate. The inclusions of TAPP composition were recovered from

diamonds free of obvious surface-to-inclusion fractures, and in two instances windows were polished on the diamond to confirm the absence of fractures from the inclusion to the diamond surface. Thus, the inclusions are considered to be syngenetic with their diamond hosts and not of extraneous origin. The inclusions were extracted from the diamond by careful crushing of the diamond host.

The TAPP crystals are 30–100 µm in diameter and of apple green colour. They exhibit either a distinct cubo-octahedral morphology, or in one case an elongate and tabular form. Cubo-octahedral morphologies often arise in mineral inclusions in diamonds because the diamond imposes its own morphology on the inclusions during a period of mutual growth<sup>19</sup>.

Representative analyses showing the chemical range in composition of TAPP grains are shown in Table 1. All eight crystals have very similar compositions with the exception of BZ207A, which is Fe–Ti rich but still shows a similar stoichiometry. The TAPP compositions are very similar to pyrope–almandine garnet compositions, although the ratio of Mg/(Mg + Fe) cations (~0.93) would be unusually high for naturally occurring garnets. The TAPP compositions notably show normal garnet Si : Al ratios without evidence of a majorite type of substitution that affects some mantle garnets. Compared with other aspects of mantle garnet compositions, the new phase also shows unusually low CaO in combination with low Cr<sub>2</sub>O<sub>3</sub>. Thus, despite having garnet stoichiometry, TAPP belongs to a different compositional field to mantle garnets. The Fe<sup>3+</sup> content of TAPP is high as seen on the basis of both calculation from electron probe data and from Mössbauer analyses by McCammon *et al.*<sup>17</sup>, who obtained Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) = 0.778 and 0.648 for samples BZ238A and BZ243A respectively. Finally, the results of ion probe analyses show very low concentrations ((0.01–1) × chondrite) of large-ion lithophile, rare-earth and high-field-strength elements<sup>20</sup> in the new phase.

Sample BZ244B was examined using a diffractometer (equipped with a fast area scanning television detector system, FAST TV) with Mo K $\alpha$  radiation, and sufficient single-crystal data were recorded to achieve a full structural determination. Crystallographic data and methods are given in Table 2. The structure determination has shown the tetragonal nature of TAPP with space group  $I\bar{4}2d$ . It contains three independent oxygen sites in general positions, two distinct tetrahedral 'silicon' sites, both with two-fold symmetry, and three other cation sites; M1 has four-fold symmetry and a 'capped' tetrahedral environment, with four short and four long M1–O bonds, whilst M2 and M3 have two-fold symmetry, with octahedral coordination. The Si tetrahedra are not linked together, so that TAPP is an orthosilicate. On the basis of independent sites, it can be described by the formula: (M1)<sub>1</sub>(M2)<sub>2</sub>(M3)<sub>2</sub>(Si1)<sub>1</sub>(Si2)<sub>2</sub>(O1)<sub>4</sub>(O2)<sub>4</sub>(O3)<sub>4</sub> which can be simplified to (M1)(M2)<sub>2</sub>(M3)<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>.

Using the chemical data for major elements (Table 1), coupled with known crystallochemical behaviour, and the results of many least-squares refinement trials and bond-valence calculations, cation assignments were made as follows. (1) The two types of Si sites were modelled to achieve full occupancy by mixing in ~4.5% Al. Ferric iron was considered as a possibility for balancing the Si deficiency in the Si sites but was not consistent with the observed bond lengths. (2) Six crystallochemically controlled model configurations were considered for the siting of the remaining Al<sup>3+</sup>, the Mg<sup>2+</sup> and the transition-metal elements. The best refinement placed Al<sup>3+</sup>, Cr<sup>3+</sup> and Mn<sup>2+</sup> in the smaller octahedral site M2; Fe<sup>2+</sup> into M3; Mg<sup>2+</sup> distributed between predominantly the octahedral M3 site and the 'capped' tetrahedral M1 site; and Fe<sup>3+</sup> solely in the 'capped' tetrahedral site M1. This assignment is supported by values for isomer shift and quadrupole splitting for Fe<sup>2+</sup> and Fe<sup>3+</sup> calculated on the basis of the Mössbauer analyses<sup>17</sup>.

The full site allocations are given in Table 2, but the broad result of this refinement using principal cations gives a formula of

(Mg, Fe<sup>3+</sup>)[Al, Cr, Mn]<sub>2</sub>{Mg, Fe<sup>2+</sup>}<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> where ( ), [ ] and { } indicate M1, M2 and M3 sites respectively.

The chosen model leaves small deficiencies at all M sites, and so some minor switching of cations could be possible. The refinement results, however, can be judged to be quite satisfactory according to all normal criteria (such as *R* values and thermal parameters). In view of such good fit and of the constraints we have been able to

apply (in terms of analytical results and cation charge sums), our proposed model must be close to the actual structure. Some of the bond lengths are relatively long, but it is quite possible that expansion of the crystal structure has occurred following the release of the specimen from its diamond enclosure, and any extraneous bond elongation could be expected to be taken up by TAPP under its natural conditions of high pressure and temperature. Observations

**Table 1 Electron microprobe analyses for three representative grains of TAPP**

Sample	206B	207A	244B	206B	207A	244B	
Analysis	5	4	2	Cations			
Wt%			Cations				
SiO <sub>2</sub>	42.43	39.56	42.12	Si	2.92	2.81	2.91
TiO <sub>2</sub>	0.01	4.20	0.06	Ti	0.00	0.22	0.00
Al <sub>2</sub> O <sub>3</sub>	23.48	20.16	23.83	Al	1.90	1.69	1.94
Cr <sub>2</sub> O <sub>3</sub>	2.22	1.39	2.80	Cr	0.12	0.07	0.15
FeO	4.64	9.41	4.60	Fe <sup>2+</sup>	0.08	0.16	0.08
				Fe <sup>3+</sup>	0.19	0.40	0.19
MnO	0.47	0.25	0.96	Mn	0.03	0.02	0.06
NiO	0.07	0.03	0.01	Ni	0.00	0.00	0.00
NaO	0.15	0.03	0.09	Na	0.02	0.00	0.01
MgO	26.66	24.85	25.63	Mg	2.73	2.63	2.64
CaO	0.12	0.03	0.09	Ca	0.01	0.00	0.01
K <sub>2</sub> O		0.00	0.00	K	0.00	0.00	0.00
Total	100.24	99.91	100.20	Total	8.00	8.00	8.00

Major-element compositions were determined on a Cameca Camebax electron microprobe at the University of Edinburgh, Dept of Geology and Geophysics. The probe was operated at 20 kV with a beam current of 20 nA. Fe<sup>3+</sup> values were calculated on the basis of Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>) = 0.714, averaged from Mössbauer data.

**Table 2 Crystallographic data for TAPP**

*Positions and thermal parameters\**

Atom†	Site	x	y	z
M(1)	4a	0	0	0
M(2)	8d	0.2600(4)	0.2500	0.1250
M(3)	8c	0	0.5000	-0.0227(1)
Si(1)	4b	0.5000	0.5000	0
Si(2)	8d	-0.1508(4)	0.2500	0.1250
O(1)	16e	0.0186(7)	0.2794(7)	0.0573(2)
O(2)	16e	-0.2621(8)	0.0374(6)	0.1011(2)
O(3)	16e	0.4370(7)	0.2954(7)	0.0460(2)

  

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
M(1)	3(1)	3(1)	10(1)	0	0	0
M(2)	9(1)	7(1)	4(2)	0	0	0(1)
M(3)	5(2)	5(2)	6(1)	-2(2)	0	0
Si(1)	8(2)	8(2)	6(2)	0	0	0
Si(2)	8(2)	7(2)	10(2)	0	0	1(1)
O(1)	7(3)	8(3)	9(2)	-3(3)	-2(2)	2(2)
O(2)	13(3)	10(2)	10(2)	6(3)	-2(2)	4(2)
O(3)	8(3)	16(4)	6(2)	6(2)	1(2)	-2(2)

  

*Interatomic distances (Å) and angles (°)*

M(1)-O(1)	2.109(5)	(×4)	M(1)...O(2)	2.521(5)	(×4)
M(2)-O(1)	2.004(5)	(×2)	M(2)-O(2)	1.925(4)	(×2)
M(2)-O(3)	1.866(5)	(×2)	M(3)-O(1)	2.052(5)	(×2)
M(3)-O(2)	2.124(5)	(×2)	M(3)-O(3)	2.014(5)	(×2)
Si(1)-O(3)	1.630(5)	(×4)	Si(2)-O(1)	1.664(5)	(×2)
Si(2)-O(2)	1.625(5)	(×2)			

  

O-M(1)-O	104.3(1), 120.4(2)	O...M(1)...O	86.48(1), 122.05(2)
O-M(2)-O <sup>cis</sup>	103.7(3), 90.8(2), 88.7(2), 89.9(2), 87.9(2), 92.8(2), 76.5(3)	O-M(2)-O <sup>trans</sup>	179.2(4), 166.3(2)
O-M(3)-O <sup>cis</sup>	93.7(2), 103.6(2), 89.4(3), 79.6(2), 84.1(2), 87.7(2), 95.4(3)	O-M(3)-O <sup>trans</sup>	155.7(3), 175.8(2)
O-Si(1)-O	118.3(3), 105.2(1)	O-Si(2)-O	126.8(4), 101.7(2), 113.2(2), 96.4(3)

Tetragonal; space group  $\sqrt{4}d$  (no. 122);  $a = 6.526(4)$  Å,  $c = 18.182(9)$  Å. Crystal dimensions,  $0.06 \times 0.04 \times 0.04$  mm; formula weight 417.36; calculated density,  $3.580$  Mg m<sup>-3</sup>, Delft Instruments Fast, 293(2) K, Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å), graphite monochromator;  $\mu = 1.854$  mm<sup>-1</sup>; 1,581 reflections (322 independent,  $I > 4\sigma$ ); data/parameters = 6.8;  $R = 0.039$ ,  $R_w = 0.071$ . The structure was determined via direct methods (SHELX-86<sup>†</sup>) and refined by the least-squares program SHELX-93<sup>‡</sup>.

\* All atoms refined with anisotropic thermal parameters. The anisotropic displacement factor exponent takes the form;  $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$ , where  $a^*$  and  $b^*$  are reciprocal lattice parameters.

† M(1) = Mg<sup>2+</sup> 0.19025, Fe<sup>3+</sup> 0.0465; M(2) = Al<sup>3+</sup> 0.44000, Cr<sup>3+</sup> 0.0380, Mn<sup>2+</sup> 0.01425; M(3) = Mg<sup>2+</sup> 0.46975, Fe<sup>2+</sup> 0.02025; Si<sup>4+</sup> 0.4787, Al<sup>3+</sup> 0.02125.

of expansion on release from diamond have been made for ferro-periclase inclusions<sup>18</sup>.

The evidence that São Luiz inclusions involving the combination of (Mg,Fe)O, (Mg,Fe)SiO<sub>3</sub> and CaSiO<sub>3</sub> phases are of lower-mantle origin is compelling, but this still leaves open the important question as to whether TAPP is a primary phase in this lower-mantle association or is a retrogressive relict formed under decompression from an origin lower-mantle mineral.

Lower-mantle minerals and high-pressure phases are characteristically of a high density, containing cation sites with large coordination numbers<sup>9</sup>. The calculated density of TAPP at atmospheric pressure is 3.580 g cm<sup>-3</sup> and marginally less than that of a garnet-structured phase of similar composition with 3.634 g cm<sup>-3</sup>. Coordination in the new phase—three four-fold, four six-fold and one distorted eight-fold ('capped' tetrahedron) sites per formula unit—suggests a relatively open structure compared to normal garnet which has three distorted eight-fold, two six-fold and three four-fold sites. But in the absence of any values of bulk modulus or compressibility for TAPP, it is uncertain how its density will compare with garnet at depth in the Earth. If TAPP has a relatively high compressibility, then its density might become greater than that of garnet at high pressure. We also note that the garnet structure is extremely widespread across the range of upper-mantle and crustal pressure-temperature conditions and compositions. Thus if retrogression of a separate very high pressure phase of pyrope-almandine composition occurred, it seems most likely that it would have given rise to the garnet rather than the TAPP structure. The virtual absence of Ca in TAPP is a reflection of it not having a suitable site for Ca or any other large ion; this is because the 'capped' tetrahedral M1 site has a significantly smaller volume than the [8] site in garnet. The absence of such a site in a mineral from the lower-mantle association is appropriate given the stability of a specific Ca-bearing phase in the form of Ca-perovskite.

If we accept TAPP to represent a primary lower-mantle phase distinct from garnet, we must consider its possible phase relations in more detail and why no evidence of it has been found in experimental studies so far. High-pressure experiments show that, in the lower part of the upper mantle, Al is essentially located in a majoritic garnet (relatively low in Al compared with normal garnet), and with passage from upper mantle to lower mantle and the stabilization of (Mg,Fe)- and Ca-perovskites, this garnet becomes less abundant. With increasing depth in the uppermost region of the lower mantle, much recent experimental work<sup>1-3,5,6</sup> shows evidence of increasing substitution of Al into (Mg,Fe)-perovskite. As a consequence, bulk rock compositions which are low in Al, such as common mantle peridotites, are expected to gradually become garnet-free in the uppermost 60 km (from 660 to 720 km depth) of the lower mantle<sup>1,6</sup>.

For bulk compositions containing more Al, such as basic rock compositions close to pyrope-almandine garnet itself, the situation is less clear-cut. Several experimental studies<sup>4,7,9,21-23</sup> have found evidence of an aluminous phase distinct from garnet, but these new phases have not been fully characterized and we note that none of them have X-ray diffraction or chemical compositional features that correspond well to TAPP. In general the broadest consensus of evidence<sup>1-3,5</sup> supports increasing substitution of Al into (Mg,Fe)-perovskite with depth, and it seems likely that normal (Mg,Fe)-garnet compositions become essentially represented by perovskite somewhere in the depth range 800–1,350 km (refs 1–3). At these and greater depths, strongly aluminous compositions may contain corundum<sup>1,2,5</sup>.

The reasons why TAPP has not so far been identified in experimental work possibly include the following. (1) Its stability field may only span a small range of pressures (and temperatures). (2) Over the span of pressure-temperature conditions concerned, TAPP may only occur in a restricted range of bulk compositions, which may not coincide with those of common peridotitic bulk

compositions and might depend on other particular features (for example, the Fe:Mg or ferrous:ferric ratios). (3) Many of the experimental runs which have been carried out on obviously appropriate bulk compositions, such as those on the same compositions as pyrope-almandine garnet, have been done using an actual garnet as starting material<sup>1-5</sup>, and under the short run times of these difficult experiments, metastable persistence of the garnet may have hindered the nucleation and growth of TAPP. (4) The characterization of phases in very fine-grained run products can be very difficult.

With such considerations in mind, and the strong experimental evidence in favour of extensive Al substitution into (Mg,Fe)-perovskite with depth in the lower mantle, it seems most likely that TAPP stability occurs in the uppermost part of the lower mantle. If its stability field overlaps with the high-pressure part of the stability field for garnet with majorite substitution, or with the field in which aluminous (Mg,Fe)-perovskite forms the aluminous phase in peridotite, TAPP may well be restricted to more aluminous basic compositions. Under such circumstances TAPP, like garnet<sup>7</sup>, may be expected to lead to relatively low densities for basic rocks compared with peridotites. In terms of mantle dynamics<sup>7,11,12,14</sup>, therefore, TAPP may play an important part in the development of density differences between subducted basic compositions and peridotitic compositions, which will affect their relative segregation and circulation in the mantle. □

Received 26 September 1996; accepted 8 April 1997.

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**Acknowledgements.** We thank the Diamond Trading Company (London) and Sopemi Ltd (Brazil) for making the samples available; P. Hill and S. Kearns for electron-probe support; A. Livingstone and the Royal Museum of Scotland for supplying the Gandolfi camera used in an initial survey; and A. Blake, D. Parsons and R. O. Gould of the University of Edinburgh for X-ray support. M.T.H. was supported by an NERC research studentship. This work was also supported by NERC at Edinburgh (B.H.) and EPSRC (Cardiff Crystallography Services) at the University of Wales Cardiff.

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