

Diamond- and coesite-bearing chromitites from the Luobusa ophiolite, Tibet

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ABSTRACT

Diamonds and other ultrahigh pressure (UHP) minerals have been reported previously from the Luobusa ophiolite of Tibet, but these minerals have thus far been found only as individual grains. Here we report the occurrence of diamond as an inclusion in OsIr alloy and coesite as part of a silicate assemblage rimming a grain of FeTi alloy, both of which were recovered from chromitite. These occurrences confirm the presence of UHP minerals in the Luobusa chromitite requiring minimum pressures of ~2.8–4 GPa. Individual coesite “crystals” have external form similar to that of stishovite and are polycrystalline, suggesting pseudomorphic replacement and implying a pressure >9 GPa. We propose that the UHP minerals were incorporated into the chromitites in the deep upper mantle or that they have an impact origin; the preponderance of evidence favors the former.

Keywords: diamond, coesite, stishovite, chromitite, ophiolite

INTRODUCTION

The Luobusa ophiolite lies within the Yarlung-Zangbo suture zone, the geological boundary between Asia and India. The ophiolite was emplaced during closure of the Neo-Tethyan ocean in the Early Tertiary (ca. 65 Ma) (Aitchison et al., 2002). It consists chiefly of harzburgite, dunite, and sparse lower-crustal cumulates accompanied by minor basaltic pillow lavas and cherts (Zhou et al., 1996). The ophiolite has been interpreted as a fragment of oceanic lithosphere formed at a mid-ocean ridge (MOR), and later modified in a mantle wedge above a subduction zone (Malpas et al., 2003).

Previous reports of diamonds and other UHP minerals from the Luobusa chromitites (IGCAGS, 1981; Yang et al., 2003; Robinson et al., 2004), were controversial because they were not found in situ and because ophiolites are currently believed to form at shallow levels above oceanic spreading centers. Here we report new findings of diamond and coesite extracted from the Luobusa chromitite; the diamond makes up part of an inclusion within a grain of OsIr alloy, and coesite is the major constituent of a kyanite-bearing silicate assemblage rimming a grain of FeTi alloy. The minimum pressures

required for coesite and diamond crystallization are 2.8 and 4 GPa, respectively. These new finds provide unequivocal evidence of UHP phases in the Luobusa chromitites and shed new light on the origin of these enigmatic deposits.

RESULTS

The microdiamond (6 μm across), intergrown with an unidentified silicate phase of composition $(\text{Mg}_{1.8}\text{Al}_{0.2})(\text{Al}_{0.4}\text{Si}_{1.6})\text{O}_6$, occurs as a syngenetic inclusion in a grain of OsIr alloy (wt%: Os 51.1; Ir 48.7; Ru 0.2) (Figs. 1A and 1B). Similar OsIr alloys without diamonds are recognized in thin sections within chromite grains (Bai et al. 2000). The diamond is identified by a Raman peak at 1332.2 cm^{-1} (Fig. 1C) and its composition (100% carbon) revealed with energy-dispersive X-ray spectroscopy (EDS). The silicate has pyroxene stoichiometry (with slight charge imbalance) but the composition is odd; it could be a highly aluminous enstatite (unknown to us) or any of the high-pressure polymorphs of enstatite.

The abundant coesite (~45 modal%) and kyanite (~15 modal%), intergrown with other phases of unusual composition (~40 modal%), rim an irregular grain of FeTi alloy (labeled 3 in Fig. 2A) that displays a “patchwork quilt” texture formed by symplectic intergrowths intermixed with larger homogeneous domains (Fig. 2B). The contact between the FeTi alloy and silicate assemblage contains a narrow zone of almost pure Ti (#3-17, 3-18, Table 1), which passes outward into a very narrow band of TiSi alloy (#14, 15,

Table 1; Fig. 2B). (Fig. 2A). The compositions of these intergrown Fe/Ti phases in the metallic portion of the specimen (#3-22, 3-9, Table 1) are incompatible with the 1-atmosphere phase diagram of the system and therefore will be investigated in the future with high-pressure experiments.

The silicate assemblage consists predominantly of three phases: (1) long, faceted prisms of coesite (gray in Fig. 2C); (2) an inhomogeneous, apparently amorphous, high-silica phase (up to 63 wt% SiO_2) (pink in Fig. 2C), and (3) crosscutting crystals of Ti-bearing kyanite (blue in Fig. 2C). These phases are accompanied by minute Ti-Si-O and Ti-Si-Al-O-bearing grains (white grains in Figs. 2B and 2C) that are scattered throughout the silicate zone. These mineral grains are too small to analyze quantitatively and their measured compositions (Table 1) are probably affected by neighboring coesite and kyanite.

More than 100 spot analyses of the coesite grains show Raman peaks at 519.7–522.9, 346.06–358.81, 271.19–272.78, and 175.61–178.79 (cm^{-1}) (Fig. 3A, Table DR1 in the GSA Data Repository¹), which are consistent with the standard coesite peaks (521, 355, 271, and 176 (cm^{-1})). The prism-like habit of this coesite is unique. Like quartz, coesite usually forms foam textures when polycrystalline or accepts whatever shape is imposed upon it by its environment. The very-high-pressure polymorph of SiO_2 , stishovite, grows as greatly elongated prisms (Fig. 2D), very similar to the coesite domains of this rock. However, some experiments have shown that coesite may crystallize from a melt as tablets parallel to (010) (Renner et al., 2001); thus the greatly elongated coesite crystals reported here could be tablets if all of them have their platy surfaces approximately

¹GSA Data Repository item 2007220, Appendix (sampling and methods) and Table DR1 (Raman bands values occurred in spectra collected from kyanite and coesite), is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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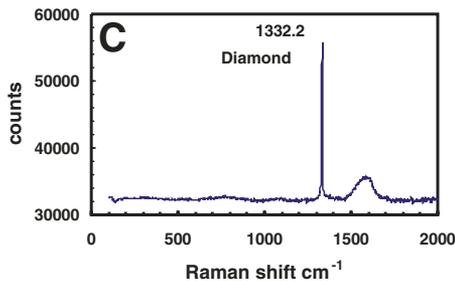
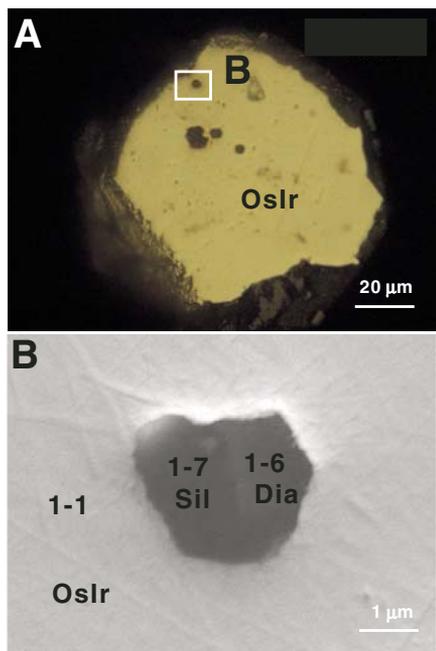


Figure 1. Diamond included in OsIr alloy. **A:** Optical image of entire alloy grain. **B:** SEM secondary-electron image. Diamond occupies approximately one-third of the surface area of the inclusion; unidentified silicate phase occupies the remaining area. **C:** Raman spectrum showing the characteristic shift for diamond.

normal to the plane of the image. If this is the case, the coesite grains should have their [010] axes approximately in the plane of the specimen surface and normal to the elongation direction. In contrast, if they are pseudomorphs after stishovite, they could have any orientation or even be polycrystalline. To distinguish between these two possibilities, we examined the orientation of several coesite domains using electron backscattered diffraction (EBSD) and established that they are polycrystalline and have the wrong orientations to be igneous tablets (Figs. 4A and 4B). These results strongly suggest that the coesite has replaced a preexisting phase consisting of prismatic crystals. Stishovite is the only reasonable candidate for the original phase, implying a minimum pressure of origin of 9 GPa (Zhang et al., 1996). Interestingly, some of our Raman spectra show small peaks consistent with remnant domains of stishovite. Remarkably, coesite also shows little or no evidence of transformation to quartz, implying a very low

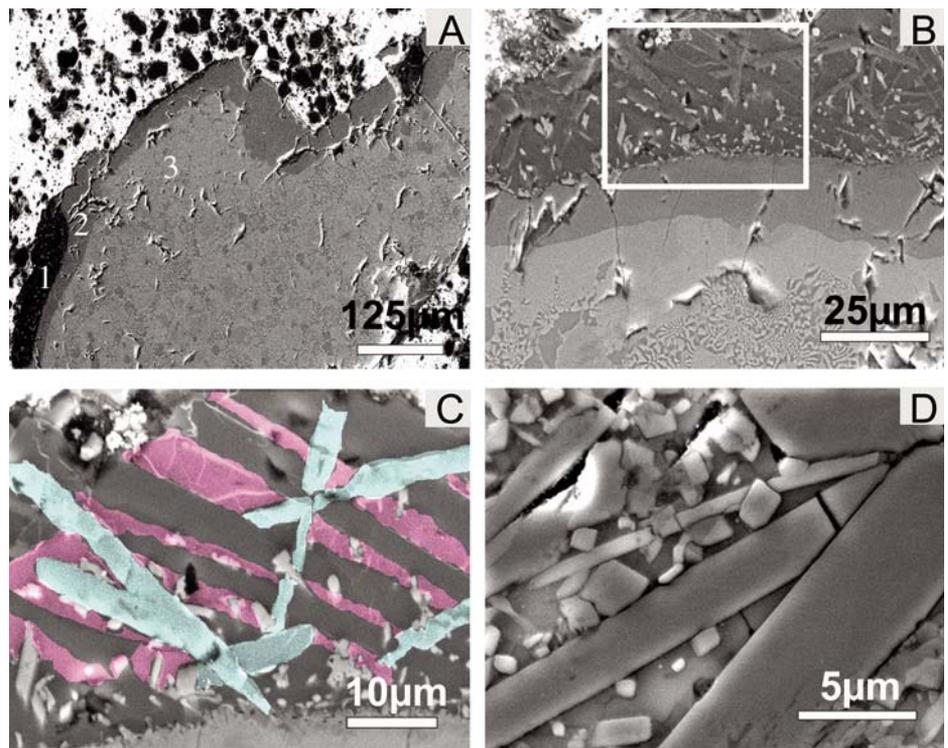


Figure 2. Backscattered electron images of FeTi alloy rimmed by coesite and kyanite. **A:** Light gray zone (labeled 3) consists of FeTi alloy, which is almost completely surrounded by a darker gray zone (labeled 2), composed of nearly pure Ti with a band of TiSi at its outer edge. The black zone on the left side of the grain (labeled 1) consists chiefly of silicate material. **B:** Detail of the three zones showing the symplectic textures of the Fe-Ti alloy, the zone of nearly pure Ti rimmed by TiSi alloy, and the crystal outlines in the silicate zone. **C:** Enlargement of the box in B showing the detailed morphology of the silicate phases. Prismatic crystals of coesite are shown in gray, unknown amorphous material in pink, and crosscutting kyanite crystals in blue. The small, angular, brighter-contrast grains are Ti-Si-O phase. Note that the latter phase is most abundant near the boundary between the silicate material and the metal. **D:** Prisms of stishovite associated with plates of K-hollandite synthesized from SiO₂ and K-feldspar mixture (50:50) at T = 900 °C, P = 10 GPa, time 28 h (run MA-104) in multi-anvil high-pressure apparatus (Dobrzhinetskaya and Green, 2007). Note the similarity to the coesite grains in C.

water fugacity (Mosenfelder et al., 2005), consistent with the apparently low oxygen fugacity.

The kyanite is unusual in that it contains varying amounts (1.98–11.64 wt.%) of Ti (Table 1); to our knowledge, Ti-rich kyanite has not been reported previously. The highly variable Ti contents may suggest the presence of a submicroscopic Ti-rich phase. Raman peaks (cm⁻¹) of the kyanite at 955.01–959.38, 890.88–906.81, and 296.68–301.76 (Fig. 3B, Table DR1) in general fit peaks for standard kyanite (950, 900, and 298 cm⁻¹), although their positions might vary with pressure (Hemley, 1987). The Ti-Si-O and Ti-Si-Al-O grains are too small to obtain Raman spectra and have variable compositions that do not correspond to known phases. Perhaps they, too, could contain submicroscopic inclusions. Future work will address these questions.

The apparently amorphous phase with variable composition yielded no Raman peaks in the entire spectrum from 140 to 4000 cm⁻¹. Its composition does not match any known mineral or natural melt (Table 1). The complete lack of K,

Na, Mg, and Ca in any of the crystalline phases makes us doubt that it is residual melt; we suspect that it was a UHP phase that either became amorphous or melted upon decompression.

DISCUSSION

The diamond and coesite reported here provide unambiguous evidence of UHP minerals as components of the Luobusa chromitite. Anomalous diamonds have been reported from volcanoclastic komatiites of French Guiana (Capdevila et al., 1999), and graphitized diamonds are known in mantle peridotites of the Beni Bousera massif, Morocco (Pearson et al., 1989) and the Ronda massif of Spain (Davies et al., 1993); however, the association of diamond and coesite in podiform chromitites is a new and surprising find. Coesite occurs widely in UHP metamorphic rocks, in meteorite impact craters (e.g., Grieve and Theriault, 2000), as inclusions in diamonds (e.g., Sobolev et al., 2000), and in groszpydite xenoliths from kimberlite pipes (Smyth and Hatton, 1977). Coesite

TABLE 1. REPRESENTATIVES OF PHASE COMPOSITIONS

Spot	Minerals	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	Na ₂ O	Ru	Os	Ir	C
1-1	Os-Ir alloy							0.2	51.1	48.7	
1-6	Diamond in OsIr										100
1-7	Silicate in OsIr	49.1	15.1	0.0	35.3	0.0	0.5				
Spot	Minerals	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	FeO	Na ₂ O	K ₂ O		
2*	coesite	100.61									
4*	coesite	99.72									
6*	kyanite	38.17	61.49	1.98							
7*	kyanite	35.04	54.11	11.64							
26	Si-Ti-oxide	34.5		65.5							
27	Si-Al-Ti-oxide	33.8	0.4	65.8							
29	unknown	62.9	13.7	9.2	0.5	4.7	0.0	4.2	4.9		
0023-2	unknown	52.8	17.1	16.9	0.7	6.6	0.0	3.4	2.5		
Spot	Minerals	Ti	Si	Al	Fe	Cu	Zn				
14	rim zone	2.6	77.5	19.9							
15	rim zone	2.9	78.2	18.9							
3-17*	native Ti	97.43	0.03	0.03	0.59						
3-18*	native Ti	97.64	0.04	0.02	0.5						
3-22	Ti-Fe alloy	52.2	0.7	0.5	45.9	0.6	0.1				
3-9*	Ti-Fe alloy	58.87	2.22	0.01	38.81						

Analyses with (*) are WDS microprobe analyses. Otherwise, EDS analyses with JEOL-ISM-5610LV, 20kV; the total sum of each EDS analysis is 100.

with a prismatic or tabular form has not been previously reported, although topotactically related coesite exsolution lamellae have been described in a thin section of a chromite grain from Luobusa chromitite (Yamamoto et al., 2005). Stishovite has been found in meteorites and impact craters (e.g., Grieve and Theriault, 2000) but no previous evidence for pseudomorphic replacement of stishovite has been reported. Kyanite is common in high-pressure gneisses and eclogites but not with significant TiO₂ concentrations. Associated with these minerals in the Luobusa chromitites is a wide range of other minerals including moissanite, graphite, base-metal and platinum-group-element (PGE) alloys, Fe-silicides, (NiFeCr)C alloys, and numerous native elements (Bai et al., 2000; Yang et al., 2003; Robinson et al., 2004). The presence of diamond requires pressures >4 GPa (depth of >120 km), and the potential former presence of stishovite, replaced now by coesite, would require pressures >9 GPa (depth implied > 280 km). Kyanite inverts to corundum + stishovite above 13–14 GPa (Yong et al., 2006), which would put an upper pressure limit on the UHP assemblage if it were originally kyanite and stishovite.

The depths in Earth implied by these UHP minerals are in stark contrast to those generally accepted for the formation of ophiolites and their included chromitites. The massive, disseminated, layered and nodular ores of the Luobusa chromitites have been interpreted to have formed at depths of <30 km by precipitation from boninitic melt that was reacting with the host peridotites (Zhou et al., 1996). Clearly, however, the UHP minerals reported here are not consistent with this scenario, at least not without modification.

Although this is the first definitive example of UHP phases in an ophiolite, it is not the first

suggestion that some ophiolitic components may have come from great depth. Some workers have argued that FeNi metals and OsIr alloys found in chromitites crystallized in the lower mantle (e.g., Bird et al., 1999). However, those arguments were countered by evidence that FeNi metals can form at shallow levels during serpentinization (e.g., Sleep et al., 2004) and that OsIr alloys show ¹⁸⁷Os/¹⁸⁸Os ratios corresponding to upper mantle values (e.g., Meibom et al., 2002)

A further complication for the rocks under discussion here is that the presence of kyanite is incompatible with peridotite bulk chemistry under all P/T conditions known, and free SiO₂ is compatible with peridotite only in a small P/T window at pressures greater than 14 GPa in the stishovite field. Thus, the occurrence of these minerals in Luobusa requires their isolation from the host rock surrounding the chromitites. Also, the extraordinary preservation of coesite requires extremely low water fugacity (Mosenfelder et al., 2005).

It is clearly difficult to reconcile our new observations with the large body of evidence that demonstrates a shallow origin for ophiolites—Luobusa as well as others. The sum of geological observations and experiments requires that the UHP minerals in the Luobusa chromitites could have originated in only two ways—either from a meteorite impact or from deep-earth sources.

An astrobleme impact, either on land or in the ocean (see Glikson, 1999), would allow the UHP phases to have been overprinted on the pre-existing oceanic lithosphere and therefore no reinterpretation of ophiolite origin is required. Such an origin would also simplify explanation of the perfect preservation of the coesite as a consequence of rapid cooling after shock metamorphism and allow interpretation of the amorphous phase as a quenched impact melt. However,

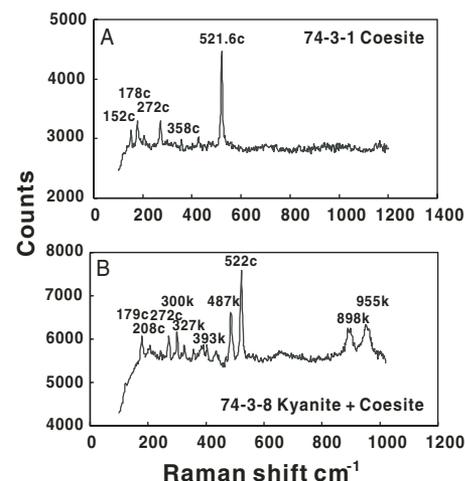


Figure 3. Representative Raman spectra. A: Spectrum of pure coesite (c). B: Spectrum containing signals from both coesite (c) and kyanite (k).

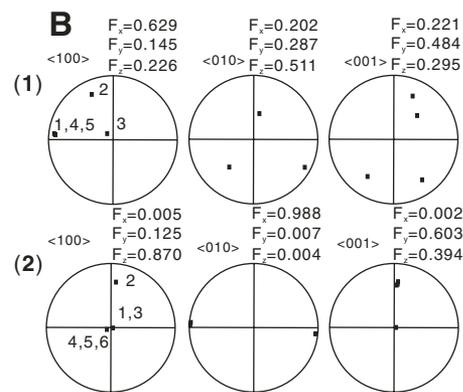
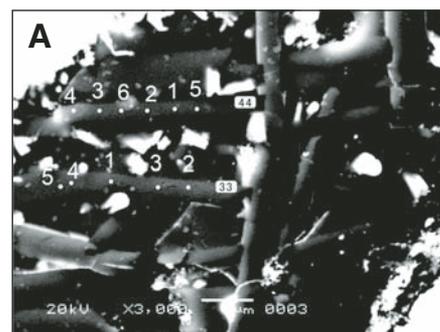


Figure 4. A: SEM secondary-electron images and EBSD analyses of the crystallographic orientation at multiple locations along the lengths of coesite crystals #33 and #44 (A); crystallographic orientations were determined with the aid of the HKL Channel 5 software; equal-area projection, lower hemisphere; (1) crystal #33; (2) crystal #44. Polycrystalline nature and prismatic habit of “crystals” strongly suggest that the coesite is pseudomorphic after stishovite. The rows of gray squares correspond to the locations of the analyses; numbers on the equal-area projections correspond to the numbers of the analyses shown on the images.

there is currently no independent evidence of meteorite impact; the ophiolite consists of normal peridotites, gabbros, and pillow lavas, containing no evidence of shock metamorphism.

Thus, our preferred interpretation is that the UHP minerals originated in the deep mantle at pressures of at least 4 GPa and probably >9 GPa. One explanation could be that the Luobusa ophiolite is a deeply subducted segment of oceanic lithosphere that was returned to the surface by rapid exhumation. However, this scenario is not compatible with the presence of unmetamorphosed gabbros and pillow lavas in the ophiolite and doesn't explain the occurrence of silica-rich minerals in the chromitites. Another possibility would be that the UHP minerals are xenocrysts in the chromitites, but the recent report of exsolution lamellae of coesite in this chromitite (Yamamoto et al., 2005) is incompatible with this hypothesis. Thus, our preferred interpretation is that at least some parts of the massive chromitites within the Luobusa ophiolite crystallized deeper than currently believed. If the coesite is considered primary, origin could be in the moderately deep upper mantle. However, we believe the prismatic shape and polycrystalline nature of coesite domains strongly support a secondary origin of coesite and thus primary stishovite. If that is the case, a deep upper mantle origin is suggested although a lower mantle origin cannot be ruled out because chromitite could be a stable rock type throughout the mantle (Chen et al., 2003; Green, 2004). A deep upper mantle origin has the advantage of perhaps explaining the presence of coesite/stishovite + kyanite as a relic of subducted sediment (Irifune et al., 1994; Dobrzhinetskaya and Green, 2007). To explain the superposition of ophiolitic structures on such chromitites, we envision that the chromitites were components of upwelling mantle beneath a spreading center and that at least parts of them preserved their high-pressure "records." We do not have any additional evidence to offer concerning whether or not subsequent interaction with boninitic magmas is required to explain some aspects of the chromitites in Luobusa.

Clearly, systematic examination of chromitites elsewhere could be instrumental to resolve the conflicting evidence obtained from the Luobusa ophiolite.

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