Revision 3

Discovery of in situ super-reducing, ultrahigh-pressure phases in the Luobusa ophiolitic chromitites, Tibet: New insights into the deep upper mantle and mantle transition zone *

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ABSTRACT

Previous research on super-reducing ultrahigh-pressure (SuR UHP) phases from the Tibetan ophiolitic chromitites were mainly conducted on isolated grains extracted from extremely large samples. This approach has been questioned because of possible contamination. To elucidate the occurrence and origin of these SuR UHP minerals, we studied 33 thin sections and rock chips of three ophiolitic chromitites from the Yarlung

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Zangbo suture zone. Here we report and analyze unambiguously in situ SuR UHP assemblages from the ophiolitic chromitites by electron probe micro-analyzer, scanning microscope and Laser Raman spectrooscope. The SuR UHP and associated phases include: (1) blue moissanite as inclusions in olivine (Fo$_{96-98}$), and in olivine domains between disseminated chromite grains; (2) multiple inclusions of moissanite $+$ wüstite $+$ native Fe in olivine; (3) FeNi and FeCr alloys in olivine and chromite; and (4) native Fe and Si in chromite. Crustal asphaltum and h-BN also occur as inclusions in chromite. Our documented in situ SuR UHP phases, combined with the previously inferred existence of ringwoodite $+$ stishovite, all indicate that these assemblages formed under a highly reducing environment (oxygen fugacities several orders of magnitude lower than that of the iron-wüstite buffer) in the mantle transition zone (MTZ) and in the deep upper mantle. Diamond $+$ moissanite with distinct $^{13}$C-depleted compositions from chromitites have a metasedimentary carbon source. Associations with existing crustal minerals in chromitites demonstrate that carbon-bearing metasedimentary rocks were recycled into the mantle through subduction, and locally modified its composition. Finally we propose a 3-stage model to explain the formation of SuR UHP phase-bearing chromitite. Discoveries of SuR UHP phases in Luobusa and other ophiolitic podiform chromitites from the polar Ural Mountains and from Myanmar imply existence of a new type of ophiolitic chromitite. Such occurrences provide an additional window to explore the physical-chemical conditions of the MTZ, mantle dynamics, and the profound recycling of crustal materials.

**Keywords:** ophiolitic chromitite, in situ, super-reducing UHP phases, deep upper mantle, mantle transition zone, Tibet, moissanite, wüstite
INTRODUCTION

Ophiolites are traditionally considered as the remnants of ancient oceanic crust and upper mantle that formed in low-pressure rift settings, and subsequently were emplaced onto active continental margins (Dilek and Furnes 2014). Podiform chromitites spatially associated with ophiolites are thought to have formed at shallow depths by mantle melt or rock-melt reactions (e.g., Coleman 1977; Zhou et al. 1996). However, documented occurrences of diamonds and other UHP minerals in ophiolitic podiform chromitites and associated peridotites along the Yarlung Zangbo suture zone, Tibet, as well as in the Polar Urals, and in Myanmar (Yang et al. 2014, 2015) suggest a deep-seated stage in the formation of ophiolitic podiform chromitites.

The Luobusa ophiolite crops out along the eastern segment of the Yarlung Zangbo suture between the Indian plate and the Lhasa block (Fig. 1a); it is a fault-bounded slab lying between Tertiary molasse deposits of the Luobusa Formation and the Gangdese batholith to the north, and Triassic flysch deposits to the south (Robinson et al. 2004) (Fig. 1b). The ophiolite evidently formed at a mid-ocean ridge (Zhou et al. 1996) at 162.9 ± 2.8 Ma, as indicated by U-Pb SHRIMP analyses of zircon from comagmatic diabase dikes (Zhong et al. 2006). Podiform chromitites within upper mantle harzburgites probably formed later by rock-melt reaction in a suprasubduction zone at ~126-120 Ma (Malpas et al. 2003; Yamamoto et al. 2013; Zhou et al. 2005, 2014). This ultramafic complex then sank to the mantle transition zone (MTZ), and later ascended to uppermost mantle depths by convection (Arai 2013).

Over the past 25 years, many unusual minerals have been separated and identified from large samples (500 to > 2000 kg) of the Luobusa podiform chromitite and its harzburgite wall rock (Bai et al. 1993, 2000, 2003; Robinson et al. 2004; Xu et al. 2009; Yang et al. 2014).
Minerals include: (1) quartz, feldspars, andalusite, alumina and zircon (Robinson et al. 2015; Xu et al. 2015; Yamamoto et al. 2013). Zircon xenocrysts (U-Pb age range: 100-2700 Ma) also contain low-P mineral inclusions such as feldspar, quartz, rutile, ilmenite, muscovite and andalusite; the zircon xenocrysts are chiefly older than the formation ages of both chromitite and ophiolite, and have a continental crust origin. Three younger ages of ~100 Ma probably result from Pb loss (Yamamoto et al. 2013). (2) SuR UHP minerals, especially diamond and moissanite. (3) Super-reducing native Fe, Ti, Si Mn, and a wide range of alloys (e.g., Ni-Fe-Cr-C, Fe-Ni-Si, Cr-Fe, Ni-Mg-Co and W-Ta) are present in some chromite pods (see review by Liou et al. 2014 and appendix Table A1). Moreover, Robinson et al. (2004) inferred the former existence of ringwoodite ($P$$\geq$18 GPa) attached to a chromite grain, based on Mg-Fe silicates that display octahedral morphology and a spinel structure. Similarly, the presence of stishovite ($P$$>$$9$ GPa at 1000 °C) was inferred based on intergrowths of elongate coesite prisms and an unknown amorphous phase crosscut by later kyanite (Yang et al. 2007); these silicate aggregates decorate the rims of a rounded FeTi alloy bleb. Some chromite crystals contain coesite and clinopyroxene exsolution lamellae. The latter probably had a precursor possessing the CaFeO₄ (CF) structure and formed at 12.5 GPa (Yamamoto et al. 2009). Recent high $P$-$T$ experiments on the MgCr₂O₄ transition indicated that the chromite formed at <12-15 GPa, based on absence of the assemblage (Mg,Fe)₂Cr₂O₅ + Cr₂O₃ (corundum-type) in Luobusa chromitites (Ishii et al. 2015). Thus, the coesite-bearing chromite undoubtedly formed under UHP conditions.

Our identification of SuR UHP assemblages in the Luobusa chromitites challenges traditional hypotheses about the origin of podiform chromitites associated with ophiolites, and raises provocative questions. What was the source region of the SuR UHP minerals? More
perplexing, how did these SuR UHP phases become associated with clearly crustal materials in the Luobusa chromitite? What was the origin of the SuR UHP mineral-bearing chromitites?

Except for the diamond inclusions (Yang et al. 2014) and coesite lamellae in chromite (Yamamoto et al. 2009) recently demonstrated to be in situ, all earlier research on UHP minerals and SuR UHP phases were conducted on grains separated from ophiolitic chromitites, not on in situ inclusions within the chromite and olivine themselves. Occurrences of separated minerals are enigmatic, because possible contamination of the separates is a major concern. In this study (1) we first document the unambiguous occurrence of inclusions of these SuR UHP and associated phases in chromite and olivine from the basal portion of the Luobusa chromitite and a few rare crustal minerals. (2) Then we discuss the inferred ultimate source regions of the SuR UHP and associated phases and their redox conditions. Formation and stabilization of the in situ SuR phases require oxygen fugacities below the iron-wüstithe buffer in the deep upper mantle and the mantle transition zone. Studies of SuR UHP assemblage-bearing ophiolitic chromitites have thus opened a new window on the deep upper mantle and the mantle transition zone (MTZ), as well as documenting the profound recycling of crustal materials.

SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

Nine polished thin sections and 24 discs of polished rock chips were made of 9 chromitite specimens from three ore deposits (Kanjinla, Xiangkashan and Luobusa; Fig. 1b) in the Luobusa area (hereafter termed the Luobusa ophiolitic chromitites). One thin section (YK15), and 2-4 discs of thin rock chips (YK15A, B, C, D) were made from each sample by conventional methods. For the discs of polished rock chips, the selected specimen was sliced (~1 mm thick) employing a micro-diamond saw. Cleaned samples were cold-mounted at room...
temperature and cured for eight hours in epoxy resin (Epofix: Struers Co) with a 1-inch diameter mold. Mounted samples were ground with silicon carbide (gray to colorless) papers from #400 to #2000 (or P-4000), then polished with alumina compounds (particle size from 3µm and 1µm) on a rotation disk made of PVC (thermoplastic resins), not metal. The final 2-4 day polish was made employing a vibration polisher with 0.3µm alumina compounds. During sample preparation, no native Fe, Si, FeO and BN compounds were used. Techniques for our diamond search were similar to the procedure described above, but the selected specimen was sliced ~1 cm thick.

First we investigated the thin sections and discs employing petrographic and binocular microscopes, and marked suitable target areas. The micro-textures of target areas were studied using a field emission scanning electron microscope (FE-SEM: JEOL JSM-7100F at the Institute of Earth Sciences, Academia Sinica, Taipei); identifications of minerals were made by an energy dispersive spectrometer (EDS: Oxford Instruments Ltd., INCA-350) equipped with an FE-SEM, under beam conditions of 15 kV, and 0.1 nA acceleration voltage, and current, respectively. The Raman spectra of moissanite, asphaltum and h-BN were determined by Laser Raman spectroscope (RM1000) in the State Key Laboratory of Continental Tectonic and Dynamics, Institute of Geology, Chinese Academy of Geological Sciences (CAGS). Spectral resolution is 1 cm\(^{-1}\) and the excitation line of the laser is 514 nm. The compositions of olivine, chromite, FeNi alloys and other phases were analyzed at the Institute of Earth Sciences, Taiwan using a field emission electron probe micro-analyzer (FE-EPMA: JEOL JXA-8500F) equipped with five wavelength-dispersive spectrometers. Methods of the EMP analysis were previously described (Zhang et al. 2012). In addition, we studied > 400 thin sections of the ophiolite complex recovered from a pilot-hole at Luobusa. In order to search for diamond, in
cases where it was not present on the surface by binocular and petrographic microscopes, the mounts were polished and re-polished repeated several times for each sample employing a Buehler Phoenix Beta Twin plate/Polisher (Yang et al. 2015). Where in situ diamond seemed to be present, microprobe, SEM and Laser Raman spectroscope studies were carried out to confirm its presence. Yang’s CAGS group checked ~40 disc samples. In all, the group found four in situ diamond inclusions in chromite from the Luobusa chromitite. During this procedure, the mounts did not come in contact with a diamond saw or any other diamond-bearing materials, thus, excluding the possibility of contamination.

LUOBUSA OPHIOLITE AND CHROMITITE

Luobusa ophiolite

The lithological profile of the pilot-hole (LSD-1, 1478.8 m) indicates that the Luobusa ophiolite consists of three overturned units: mantle tectonite, mantle-crust transition zone, and crustal cumulate (authors’ unpublished research). The tectonite unit (0-1207 m) is chiefly harzburgite with numerous layers and lenses 2-20 m thick of lherzolite and dunite. The transition zone (1207-1412 m) between tectonite and cumulate consists of fresh dunite 194 m thick with or without minor clinopyroxenite and diabase. The cumulate (1412-1478.8 m) unit consists exclusively of gabbro; comagmatic pillow lava and a capping layer of chert crop out on the surface.

Harzburgitic and lherzolitic tectonites consist of variable amounts of coarse-grained olivine (Fo89~90), enstatite (En90), Cr-bearing diopside (Cr2O3: 0.61-0.92 wt%) and spinel ± rare pentlandite and FeNi alloys; these phase assemblages exhibit granular or porphyroclastic textures. All coarse-grained enstatite crystals in the peridotites contain abundant clinoenstatite
and diopside lamellae. With a few exceptions, spinel grains in lherzolite and harzburgite have variable Mg# (Mg/Mg+Fe) of 0.57-0.78, Cr# (Cr/Cr+Al) of 0.17-0.39, and very low TiO₂ (< 0.2 wt%). Dunite of the tectonite unit consists of olivine (> 90 vol%, Fo₉₁₋₉₂) and chromite (< 5 vol%) ± enstatite, and shows granular to porphyroclastic textures. Olivine is coarse-grained, from 2 mm to > 5 cm and displays kink bands. Chromite grains have lower Mg-# (0.39-0.63) and higher Cr-# (0.65-0.89) than chromite in the mantle peridotites.

Podiform chromitites

Podiform chromitites occur as lenses 20-250 m long and 0.5-5 m thick, as massive layers 0.5-3 m thick, irregular masses up to 20 m thick, and as veins within harzburgites. The ore district is 6.5 km long and 2.3 km wide. Most podiform chromitites display a dunite envelope several centimeters to several meters thick surrounded by harzburgite. Podiform chromitites are mainly magnesiochromite (Mg-Chr), associated with forsterite ± diopside, and exhibit massive (Fig. 2a), nodular (Fig. 2b), disseminated (Fig. 2c), and brecciated textures. These textures lack sharp boundaries (Fig. 2d). Olivine, near-end-member forsterite (Fo₉₆₋₉₈), contains elevated NiO (0.42-1.31 wt.%) and variable Cr₂O₃ (up to 1.07 wt.%). Most Mg-Chr grains are chemically homogenous and have high Cr/(Cr+Al) and Mg/(Fe+Mg) ratios of 0.77-0.84 and 0.70-0.76, respectively. Average Fe³⁺/ΣFe ratios of the chromite range from 0.22 to 0.32, based on charge balance, for 9 EPMA samples. Some grains exhibit a thin chromite rim with extremely high Cr# 0.90-0.97 and low Mg# 0.60-0.69 that formed at shallow depths. In addition to diamond (Fig. 2e), the chromite contains inclusions of olivine, diopside, metal alloys, native elements, brucite and FeNi sulfides. Some possible non-UHP phases, such as Cr-Na-bearing pargasite, an unidentified Al-rich mineral, and hydrous phases with variable Si-Cr-
Fe-Mg compositions are also present as inclusions in chromite. Most olivine inclusions in chromite are partially replaced by lizardite/antigorite, Cr-bearing chlorite and tiny blebs of secondary FeNi alloys. Based on the contrasting inclusion assemblages, associated UHP polymorphs, and chromite textures, the chromites may have formed at different mantle depths. Olivine contains inclusions of moissanite, chromite, wüstite, native Fe and FeNi alloys (see following section).

**IN SITU MATERIAL IDENTIFICATION**

We now describe newly recognized *in situ* SuR UHP phases, native elements, and metal alloys in disseminated chromitites (Fig. 2c).

### Moissanite (i.e., natural SiC)

Moissanite crystals differ from silicon carbide in the polishing papers in both color and size, which rules out contamination due to sample preparation. Many moissanite crystals in chromitite sample YK15A are blue, granular or prismatic grains tens to ~200 µm in diameter (Fig. 3a). They occur as inclusions in olivine or as an interstitial phase in olivine domains (Fig. 3b). The distinct Raman bands at 788 and 969 cm⁻¹ are consistent with those of the moissanite standard (Fig. 3c).

### Native (i.e., metallic) Si and Fe, and wüstite

Native Si and Fe occur together in a composite inclusion pocket in chromite from a disseminated chromitite (YX18B); native Fe is present in olivine from sample 13YK15A. Native Si is also reported as inclusions in moissanite recovered from chromitites (Robinson et
Native Si on the surface is rounded or leaf-like with variable dimensions (2-8µm) (Fig. 4a), and shows a strong Si peak in the energy dispersive X-ray (EDX) spectrum (Fig. 4b). Native Fe is rounded or flake-like, 2-3 µm in diameter (Fig 4a). It has a strong Feα peak in its EDX spectrum (Fig. 4c). The native Fe is nearly pure iron, but contains minor Si at its margin (see Fig. A1 element maps); it appears that a Fe-Si phase locally replaced the native Fe along its margin.

We recognized wüstite by EDX spectra and X-ray element mapping (Fig. 5). It is euhedral, ~ 2 µm across, and is associated with an unknown W-Ca-Si-O phase, native Fe, moissanite and an FeNi alloy in a 40 x 60 micrometer domain within olivine in sample YK15A (Fig. 3b).

**FeNi alloys**

Primary FeNi alloys occur in the Luobusa chromitites as interstitial crystals between chromite grains, and as inclusions in chromite and olivine (Figs. 6a, b, c). The FeNi alloys exhibit plate-like or rounded shapes, and range in size from several to > 100 µm. Their main component is Ni (Cr0-2-Fe7-20Ni78-93, Table 1). In addition, secondary FeNi alloys together with hydrous phases are common as tiny grains in serpentine after olivine, or as relatively coarser fracture fillings. Rare FeCr alloy inclusions in chromite (Figs. 6d, e) and olivine contain very minor Mn; a TiC alloy is rarely present at the olivine margins (see Fig. 3d).

**Minerals of crustal origin**

Asphaltum and hexagonal boron nitride (h-BN) occur as minute inclusions in a chromite crystal from sample YK15B. Their Raman spectra are compatible with standards: asphaltum...
shows two broad peaks at 1350 and 1590 cm\(^{-1}\) (Fig. 7a); h-BN has a strong peak at 1364 cm\(^{-1}\) (Fig. 7b).

DISCUSSION

Moissanite formation

Moissanite (SiC) is a rare super-reducing mineral that has been reported in meteorites, in close spatial association with diamond in kimberlites and eclogites, in ophiolitic podiform chromitites and in peridotites (for review, see Hazen et al. 2013). In our study, moissanite in the diamond-bearing Luobusa chromitite is associated with or occurs as inclusions in olivine; the olivine also contains inclusions of wüstite + native Fe (Fig. 3b). Reactions producing moissanite may be expressed by the following:

\[
\text{SiC} + \text{O}_2 = \text{C} + \text{SiO}_2 \quad (1)
\]

\[
\text{SiC} + \text{Mg}_2\text{SiO}_4 + \text{O}_2 = \text{C} + 2\text{MgSiO}_3 \quad (2)
\]

Woermann and Rosenhauer (1985) calculated the log fO\(_2\)–T redox stability of SiC for reaction (2) with \(\log fO_2 = 8.307 - 44635/T + 0.2841\log T + 0.0062P/T\) (\(P\) in bars, \(T\) in K, and assuming constant \(\Delta V\)(solid)). Reaction (2) is compatible with a moissanite-bearing assemblage for the Luobusa chromitite. Experiments at 1.5 and 9.0 GPa and 1300-1500 °C by Ulmer et al. (1998) indicated that the formation of moissanite - olivine was only observed in run U1062 at 9.0 GPa and 1300 °C using a starting assemblage of VO/ZrO\(_2)/(\text{Opx} + \text{C})\) with very low oxygen fugacity (Log fO\(_2\) = -15.9 bar). Similarly, Dobrzhinetskaya and Green (2007) produced moissanite in their diamond synthesis experiments at 1450-1500 °C, 8.5 GPa. These experiments suggested
that formation of moissanite requires a pressure of at least 8.5 - 9 GPa in diamond-bearing rocks.

The occurrence of moissanite and associated SuR assemblages suggests that crystallization occurs under extremely reducing conditions. Moissanite stability requires oxygen fugacities several orders of magnitude lower than that of the IW buffer (Essene and Fisher 1986; Frost and McCammon 2008; Mathez et al. 1995; Schmidt et al. 2014; Ulmer et al. 1998; Woodland and Koch 2003). Accordingly, deep-origin hypotheses have been proposed, such as moissanite being a remnant from a primordial ultra-reduced mantle or from the core-mantle boundary (Mathez et al. 1995), having a possible lower mantle origin for those from Luobusa ophiolitic chromitite (Trumbull et al. 2009), being stable in the \( P-T \) fields of diamond and molten Si from kimberlite (Shiryaev et al. 2011), and representing one of the deepest mantle minerals known to have reached the surface (Hazen et al. 2013). In contrast, Schmidt et al. (2014) considered that formation near the core-mantle boundary or the lower mantle should be ruled out on the basis of temperature, because moissanite cannot survive at very high temperature.

Redox conditions in the mantle may not be homogeneous (Ulmer et al. 1998; McCammon 2005). Rocks in the deep upper mantle are likely to be reduced relative to the fayalite-magnetite-quartz (FMQ) buffer (e.g., Ballhaus 1995; Woodland and Koch 2003). Ulmer et al. (1998) also hypothesized that low fO\(_2\) conditions must exist somewhere in the upper mantle, which would permit moissanite to crystallize and survive. Moreover, oxygen fugacities more reducing than IW in the deep upper mantle have been suggested to account for platinum-group element fractionation between a partial melt and its mantle residue (Ballhaus 1995). In summary, the ultimate source of moissanite in ophiolitic chromitites is not definitely known, but the mantle transition zone, and/or possible deep upper mantle origin is a distinct possibility.
Native Fe formation and redox conditions of SuR assemblages

As described above, in situ super-reducing phases in the Luobusa chromitites include diamond, moissanite, wüsite, native Fe and Si, as well as FeNi alloys. Except for diamond, these phases chiefly occur in meteorites, but are rare in terrestrial rocks. Previous studies indicated that oxygen fugacity is relatively high (near the fayalite-magnetite-quartz buffer) at the top of the upper mantle due to the concentration of Fe$^{3+}$ in modally minor phases; however fO$_2$ decreases significantly with depth. At the 410 km discontinuity, redox conditions lie below the iron-wüstite buffer (Woodland and Koch 2003). Thus, fO$_2$ is near iron metal equilibrium in the MTZ and in the lower mantle (McCrummon 2005). The relatively high oxygen fugacities of the upper mantle would destabilize the SuR phases (Hirsch 1991; Mathez et al. 1995). The formation of native Fe in the Luobusa chromitites may be related to the existence of high Fe$^{3+}$ content in chromite and equilibrium of moissanite and olivine. Average Fe$^{3+}$/∑Fe ratios of chromites are 0.22-0.32 for Luobusa chromitite samples, and the Fe$^{3+}$ contents are generally though to be underestimated in comparison with those measured directly by Mössbauer spectroscopy (Quintiliani et al. 2006; Ruskov et al. 2010). High concentration of Fe$^{3+}$ occurs even under highly reducing conditions, and charge balance at low fO$_2$ occurs through disproportionation (3Fe$^{2+}$ = Fe$^{0}$ + 2Fe$^{3+}$), where iron metal is formed in discrete blebs (Frost et al. 2004; Lauterbach et al. 2000). Moissanite is a SuR phase formed under oxygen fugacities significantly below fO$_2$ values defined by the IW buffer (Frost and McCrummon 2008, Ulmer et al. 1998). At such low oxygen fugacities, most Fe$^{2+}$ should be reduced to metal. Ni-rich FeNi alloys probably are also formed in such reducing conditions. Thus coexisting mantle phases such as olivine and orthopyroxene should have unusually high X$_{Mg}$ values (Schmidt et al. 1998).
This is consistent with observations in the Luobusa chromitite where moissanite and native Fe are present as inclusions in high X_Mg olivine (Fo$_{96-98}$), or are intimately associated with the olivine.

### SuR UHP assemblages from the Luobusa chromitites: A window on the deep upper mantle and MTZ

Diamond is well known in kimberlites/lamproites, peridotites, mantle eclogites, and UHP metamorphic rocks. Most diamond crystals formed at high $T$ and $P$ at minimum depths of 130-250 km (Cartigny 2005; Sobolev and Shatsky 1990; Zhang et al. 1997). Exceptional cases evoke the possibility of crystallization in the MTZ or lower mantle based on studies of mineral inclusions in kimberlitic diamonds (Cartigny 2005; Stachel et al. 2005). Occurrences include documented or inferred inclusions of majorite, ferropericlase, stishovite, TAPP (a tetragonal almandine-pyrope phase), MgSi- and CaSi-perovskite (Stachel et al. 2000, 2005), wüstite, native Fe (Wirth et al. 2009) in diamond, and in ultradepth xenoliths (Haggerty and Sautter 1990). Except for a few reports, UHP minerals from the deepest upper mantle, MTZ and the lower mantle are extremely rare, presumably because of widespread back reaction on decompression.

In addition to diamond (~200 µm in Fig. 2e, as well as separated grains 200-500 µm in size described by Yang et al. 2014) and moissanite in the Luobusa chromitites, wüstite and FeNi alloys also occur in the Luobusa chromitites. An iron-rich FeNi alloy is the main component in the Earth’s core (Birch 1952; McDonough and Sun 1995), and also occurs as inclusions in Kimberlitic diamond. Wüstite and primary FeNi alloys are thought to be stable in the lower...
mantle (Birch 1952; McCammon 2005). Similarly, diamond associated with inferred stishovite probably also was derived from the MTZ. Mineralogical/chemical characteristics of the chromitite suggest that diamond, moissanite and associated highly reduced assemblages formed under the low fO$_2$ environment of the MTZ and possible in the adjacent upper mantle; this conclusion is supported by the co-existence of associated wüstite and inferred ringwoodite. *In situ* identification of SuR UHP assemblages in the Luobusa chromitites demonstrates that these phase associations do not reflect contamination. Thus, diamond-bearing chromitites in ophiolitic suture zones provide new constraints on the multistage formation of ophiolitic podiform chromitites, and on the $P$-$T$ compositional evolution and redox environment of the deep upper mantle and MTZ.

**Recycling of crustal materials**

Asphaltum is of clear crustal origin, and occurs in porous sediments or as inclusions in minerals of the sedimentary strata. Natural cubic boron nitride (c-BN) was first found in a ball-like aggregate recovered from a Luobusa chromitite, and occurs as inclusions in TiN, and in coesite (Dobrzhinetskaya et al. 2009) that was inferred to have replaced stishovite (Yang et al. 2007). Qinsongite (i.e., c-BN) apparently formed through reaction of crustal boron, originally stored in mica or clay in a deeply subducted pelitic rock, with mantle nitrogen, then was exhumed by entrainment in chromitite (Dobrzhinetskaya et al. 2014). The natural hexagonal form of boron nitride (h-BN) has the same chemical origin as c-BN, but crystallized under lower $P$-$T$ conditions. The presence of asphaltum and h-BN along with previous reported crustal minerals, especially ancient zircon grains of continental origin, suggests derivation from
crustal materials including metasedimentary rocks that were recycled into the mantle through subduction. Some grains may have been included in the chromite by precipitation from rising asthenospheric and suprasubduction-zone magmas (Robinson et al. 2015), and are metastably preserved.

Both diamond and moissanite separates from the Luobusa chromitites have distinct 13C-depleted isotopic compositions (δ13C from -18 to -35‰ for diamond, -22 to -32‰ for moissanite), which is much lighter than the dominant mantle carbon reservoir (δ13C = -5‰; Trumbull et al. 2009). The distinctive low δ13C values of associated diamond + moissanite likely reflect a metasedimentary carbon source derived from mixtures of organic matter and carbonate. This metasedimentary carbon undoubtedly returned to the mantle via subduction (Cartigny 2009). Trumbull et al. (2009) proposed a similar origin. There authors indicated that isotopic fractionation from the mantle carbon reservoir with a δ13C value of -5‰, with or without Rayleigh distillation cannot explain the 13C-depleted range of moissanite. Subduction of biogenic carbonaceous material, however, does satisfy both the unusual isotopic and redox constraints on moissanite formation. The initial carbon source of the low δ13C values of diamond (including kimberlitic diamond) and moissanite remains under debate, but many studies support the hypothesis that extremely light carbon isotopic compositions of these phases reflect deep mantle recycling of crust materials (e.g., Cartigny, 2009; Trumbull et al. 2009; Walter et al. 2011; Wirth et al. 2009). Another possibility is that the low δ13C values of diamond and moissanite reflect derivation from reduced fluids originating from metamorphosed organic carbon (Schmidt et al. 2014). Low δ13C values of diamond and moissanite combined with the existence of c-BN in an inferred stishovite suggest the insertion of crustal materials into the deep Earth, including the MTZ. The suboceanic mantle thus may
be more heterogeneous than previously thought. This is consistent with seismic tomographic studies demonstrating that lithospheric slabs can be subducted to the MTZ or deeper, and possibly accumulate at the mantle-core boundary (Fukao 2001).

**IMPLICATIONS**

Early identification of SuR UHP minerals was obtained on grains separated from very large samples of chromitite. The true nature of the separated minerals in chromitite is problematic due to possible contamination during sample preparation. Newly identified *in situ* SuR UHP and associated SuR phases occur as inclusions in chromite and olivine in Luobusa ophiolitic podiform chromitites, proving that these SuR phases are not exotic contaminants. These findings require that the SuR UHP assemblage of diamond, moissanite, wüstite, primary FeNi alloys, and associated native Fe and Si initially formed under a highly reducing environment likely in the mantle transition zone. Diamond and moissanite with distinct, low $^{13}$C-depleted isotopic compositions probably reflect a metasedimentary carbon source; low-$P$ crustal minerals as xenocrysts metastably persist in the chromitites, demonstrating that these materials including carbon-bearing metasedimentary rocks were recycled into the mantle.

Four models have recently been proposed to explain the origin of diamond-bearing chromitites: (1) deep recycling (Arai 2013); (2) deep subduction (MaGowan et al. 2015); (3) deep-seated mantle plumes (Yang et al. 2015); and (4) shallow origin-hydrous mafic magma models (Zhou et al. 2014). Based on petrological and mineralogical characterizations and available geochronological data of chromitites and host mantle harzburgites, we propose an alternative 3-stage model.
(1) Stage I: Shallow-crustal formation of the Luobusa ophiolite occurred. Mineralogical and chemical characteristics of the harzburgite indicate that it is a remnant of oceanic lithosphere subjected to a moderate degree of partial melting and melt expulsion. The ophiolite evidently formed at a mid-ocean ridge at 162.9±2.8 Ma, as indicated by U-Pb SHRIMP dating of zircon from comagmatic diabase dikes (Zhong et al. 2006).

(2) Stage II: Chromitite formation attended intra-oceanic lithospheric slab subduction to profound mantle depths. The production of a slab window at ca. 120-160 km occurred due to breakoff of the downgoing oceanic lithosphere, allowing upwelling and decompression melting of the underlying asthenosphere. The resultant magmas formed in the MTZ (and deep upper mantle) under a highly reducing environment, and contained ringwoodite, SuR UHP minerals such as diamond, moissanite, wüstit, various metal alloys, and UHP chromite with inferred CF structure. During crystallization of the Cr-rich magma, chromite formed and encapsulated these SuR UHP materials.

(3) Stage III: UHP chromite-bearing melt then rose through the mantle wedge and reacted with uppermost mantle peridotites, subsequently precipitating additional chromitite at about 120 ± 10 Ma (Yamamoto et al., 2013) in a suprasubduction zone environment. In summary, discoveries of diamond and other SuR UHP phases in ophiolitic podiform chromitites in the Yarlung Zangbo suture zone, Tibet, as well as in the Polar Urals, and in Myanmar imply the existence of a new type of chromitite. Such mineral assemblages provide an additional way to explore the physical-chemical conditions of the deep upper mantle and MTZ, mantle dynamics, as well as the profound recycling of crustal materials.

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**Figure captions**

**FIGURE 1.** Distribution of ophiolites along the Yarlung-Zangbo suture zone, and Luobusa podiform chromitites, Tibet. a) Regional location of the Luobusa ophiolite. b) Simplified geological map of the Luobusa area showing three chromitite deposits (Kanjinla, Xiangkashan, and Luobusa).

**FIGURE 2.** Photographs and characteristic X-ray images showing occurrences and textures of chromitite, as well as a diamond inclusion in chromite. a) Banded, massive chromitite in harzburgite from Xiong et al. (2015). b) Nodular chromitite: dark chromite
nODULES IN OLIVINE MATRIX. c) SCAN OF A POLISHED THIN SECTION OF CHROMITITE (YK15) SHOWING INTENSELY DISSEMINATED TEXTURE. d) MASSIVE AND DISSEMINATED TEXTURES ARE GRADATIONAL. e) Cr AND C MAPPING OF A DIAMOND INCLUSION IN CHROMITE FROM A LUOBUSA CHROMITITE (YANG ET AL. 2014 REPORTED, BUT DID NOT ILLUSTRATE THIS OCCURRENCE). AMOR C, AMORPHOUS CARBON. MINERAL ABBREVIATION AFTER WHITNEY AND EVANS (2010). Chr, chromite; Dia, diamond; Ol, olivine.

FIGURE 3. Occurrences and Raman spectrum of moissanite. a) Photograph of part of polished rock chip, taken under binocular microscope. Blue moissanite grains occur as inclusions in olivine, and as an interstitial phase between olivine grains. In the image, most moissanite grains are under the surface, but the margins of a few grains are exposed. Reflected light (YK15A, discs of a polished rock chip from sample YK15). b) Backscattered electron image shows a multiple inclusion domain in olivine, and a large moissanite crystal; most parts of which lie beneath the surface, with only its margins exposed. c) Raman spectrum of moissanite (Moi) shown in (b). d) Enlarged view of the multiple inclusions in olivine, containing inclusions of wüstite, native Fe, FeNi alloys, and an unknown phase (for details, see figure. 5).

FIGURE 4. Backscattered electron (BSE) image of inclusions in chromite. a) Mutiple inclusions of native Si, Fe and olivine in chromite. b, c) Energy dispersive X-ray (EDX) spectra of native Si and Fe; weak peaks of Mg, Si and Cr are from nearby chromite and olivine.

FIGURE 5. SEM-BSE image and X-ray maps of Fe, O, Si, Ca and W of wüstite (Wus) and an associated unknown phase (outlined in red), consisting chiefly of W, Ca, Si and minor O.
FIGURE 6. Occurrences of metal alloys in chromitites. a, b, c) BSE images of FeNi alloy in chromite and olivine. d) FeCr alloy in chromite. d) EDX spectrum of the FeCr alloy with very minor Mn. Mineral abbreviation: Srp, serpentine.

FIGURE 7. Inclusions of asphaltum and hexagonal boron nitride (h-BN) in a chromite crystal from sample YK15B. a, b) BSE images and Raman spectra of asphaltum and h-BN.

FIGURE Al. Backscattered electron image and X-ray maps of Fe, O, Si, Mg and Cr of native Fe. Central part of the native Fe is pure Fe, but its margin partially contains minor Si. Small circles in the native Fe show same position in each map.

APPENDIX

Previously separated and identified minerals, native metals and alloys from large samples (500 to > 2000 kg) of the Luobusa podiform chromitite and its wall rock harzburgite (Bai et al. 1993, 2000, 2003; Robinson et al. 2004; Xu et al. 2009, 2015; Yang et al. 2014) are summarized in Table A1.

The native Fe is near pure iron indicated by EDX spectrum and X-ray element maps that are shown Fig. A1.
Table 1  Electron microprobe analyses of FeNi alloys*

<table>
<thead>
<tr>
<th>Sample</th>
<th>YK15</th>
<th>YK51</th>
<th>YX15</th>
<th>YX15</th>
<th>YX15</th>
<th>YX15</th>
<th>YX 22</th>
</tr>
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<tbody>
<tr>
<td>Note</td>
<td>in/OI</td>
<td>in/OI</td>
<td>in/Chr</td>
<td>in/Chr</td>
<td>in/Chr</td>
<td>in/Chr</td>
<td>in/Chr</td>
</tr>
<tr>
<td>Cr</td>
<td>0.9</td>
<td>0.5</td>
<td>1.7</td>
<td>1.9</td>
<td>0.5</td>
<td>0.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Fe</td>
<td>13.9</td>
<td>7.0</td>
<td>20.1</td>
<td>15.3</td>
<td>14.2</td>
<td>14.9</td>
<td>20.9</td>
</tr>
<tr>
<td>Ni</td>
<td>85.3</td>
<td>92.4</td>
<td>78.1</td>
<td>82.8</td>
<td>85.2</td>
<td>84.4</td>
<td>76.2</td>
</tr>
<tr>
<td>Fe/(Fe+Ni)</td>
<td>0.14</td>
<td>0.07</td>
<td>0.21</td>
<td>0.16</td>
<td>0.14</td>
<td>0.15</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* Normalized as element. in/Ol, inclusion in olivine; in/Chr, inclusion in chromite.
Table A1  SuR UHP and associated minerals from Luobusa chromitites, Tibet  
(In previous reports)*

| Native elements: C (diamond), Si, Ti, Fe, Cr, Al, Mn |
| Silicon carbide: moissanite (SiC) |
| Metal alloys: Ni-Fe-Cr-C, Fe-Ti-Si, Cr-Fe, Ni-Mg-Co, W-Ta and Ni-Mn-Co, Cr-C |
| PGE and other alloys: Os-Ir, Os-Ir-Ru, Pt-Fe, Ir-Fe and Si-Al |
| Nitrides: osbornite (TiN) and qinsongite (c-BN) |
| Oxides: wüstite, Si-rich rutile, type-II TiO$_2$, coesite, corundum |
| Fe-silicates with variable amounts of Fe and Si |
| Crustal xenocrysts: zircon, feldspar, rutile, quartz, kyanite |

* Data source: see text. SuR-UHP: super-reducing ultra-high pressure.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5

Backscattered electron image

YK15A

Wus

Unknown phase (CaWSiO)

2.5μm

O Kα1

Wus

2.5μm

Si Kα1

2.5μm

Fe Kα1

Wus

2.5μm

Ca Kα1

2.5μm

W Mα1

2.5μm

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Fig. 6
Fig. 7
Fig. A1