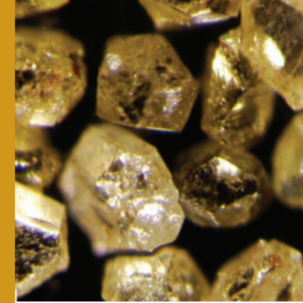

Diamonds in Ophiolites

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Ophiolites are a newly documented host of diamonds on Earth. Abundant diamonds have indeed been separated from peridotites and chromitites of ophiolites in China, Myanmar, and Russia. In addition, diamond grains have recently been discovered in chromite from the Cretaceous Luobusa ophiolite (Tibet) and the early Paleozoic Ray-Iz ophiolite (polar Urals, Russia). These diamonds are accompanied by a wide range of highly reduced minerals, such as Ni–Mn–Co alloys, Fe–Si and Fe–C phases, and moissanite (SiC); these have been found as either mineral separates or inclusions in diamonds and indicate growth under superreducing conditions. The diamond-bearing chromite grains likely formed near the mantle transition zone and were then brought to shallow levels in the upper mantle to form podiform chromitites in oceanic lithosphere. Because these diamond grains occur widely in peridotites and chromitites of many ophiolites, we refer to them as ophiolite-hosted diamonds. It is possible that such diamonds may be common in the upper oceanic mantle.

Keywords: diamond-bearing chromitites, UHP minerals, podiform chromitites, mantle transition zone, highly reduced minerals

DIAMONDS ON EARTH

Natural diamonds occur in a variety of crustal and mantle rocks, mainly in kimberlites from subcontinental lithosphere, in ultrahigh-pressure (UHP) metamorphic rocks formed by subduction of continental crust, and in meteorites and rocks associated with impact structures. The best-known diamonds and the ones of most commercial importance are from kimberlites and lamproites (Gurney et al. 2010). They are formed mainly where pressure conditions are appropriate for carbon to crystallize as diamond, and they are brought to the surface mainly through the eruption of alkaline magmas that commonly form kimberlites and lamproites. Most such diamonds are of Archean age and many are peridotitic in character. However, the protoliths of younger Proterozoic diamonds were eclogitic, websteritic, or lherzolitic in composition (e.g. Field et al. 2008; Gurney et al. 2010). Most kimberlitic diamonds formed from melts or fluids in the upper mantle at depths of <200 km (e.g. Boyd and Gurney 1986; Liu et al. 2009). However, a few of these diamonds have mineral inclusions suggesting derivation from much greater depths (400–670 km) (Tappert et al. 2005; Walter et al. 2011; Kaminsky 2012).

Less common are microdiamonds in UHP metamorphic rocks formed by deep subduction of crustal material at convergent plate margins (e.g. Sobolev and Shatsky 1990; Xu et al. 1992; Ogasawara 2005). UHP metamorphic diamonds were initially recognized about 20 years ago during detailed study of major orogenic belts. These diamonds commonly occur as very small (0.01 to 0.1 mm) inclusions within metamorphic minerals such as garnet, diopside, phengite, and zircon, or at the mineral grain boundaries (Shertl and Sobolev 2013). The discovery of such microdiamonds suggests that continental slabs can be subducted to depths of 120–150 km or more and returned to the surface by tectonic exhumation (e.g. Liou and Tsujimori 2013).

Meteorites and terrestrial impact craters also contain microdiamonds (Koeberl et al. 1997; Karczemska et al. 2009). The largest-known deposit of impact diamond is the Popigai crater in Siberia. Most of the UHP metamorphic and impact diamonds have little commercial value because they are small and skeletal and generally occur in low concentrations.

DIAMONDS IN OPHIOLITIC PERIDOTITES AND CHROMITITES

Over the last 30 years there have been a number of reports of diamonds in ophiolitic peridotites (e.g. Bai et al. 1993), but these findings have generally been dismissed as the result of natural or anthropogenic contamination. Our studies of ophiolites in China, Russia, and Myanmar have confirmed the common presence of microdiamonds in both ophiolitic peridotites and podiform chromitites. These occurrences raise many questions regarding the source of carbon, the processes by which the diamonds are formed and incorporated into ophiolitic chromitites, and the petrogenesis of oceanic mantle. Ophiolites are fragments of ancient oceanic lithosphere emplaced onto continental margins, accretionary prisms, or island arcs during plate collisions (Dilek and Furnes 2011). Mantle peridotites in many ophiolites host small bodies of chromite (podiform chromitites), which likely formed from subduction-influenced melts migrating through the mantle above subducting slabs (Zhou et al. 1996; Rollinson and Adetunji 2013).

The Tethyan ophiolites in southern Tibet occur within the ~2000 km long Yarlung–Zangbo suture zone, which marks the plate boundary between India and Eurasia. They include, from east to west, the Luobusa, Zedang, Xigaze, Dangqiong, Purang, and Dongbo massifs (Fig. 1). These massifs, some of which are very large (Xigaze covers ~700 km^2, Purang ~600 km^2, and Dongbo ~400 km^2), consist mainly of harzburgite,

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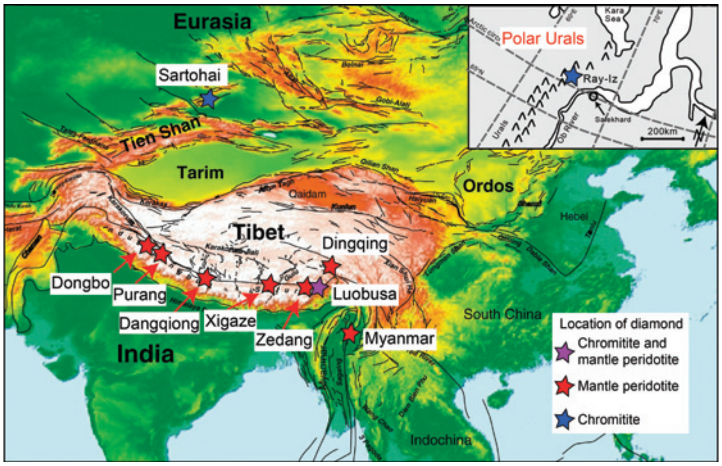

Figure 1 Locations of ophiolite-type diamonds discovered on Earth. Six locations, including Dongbo, Purang, Dangqiong, Xigaze, Zedang, and Luobusa, are situated along the 2000 km long Yarlung–Zangbo suture; one location is at Dingqing, in the Bangong–Nujjiang suture, Tibet, one in Myanmar, one in Sartohai, in Xinjiang Province, China, and one (see inset map) in the polar Urals, Russia.

lherzolite, and dunite, with minor crustal gabbro, dikes, and basalt. Only the Luobusa ophiolite hosts significant quantities of podiform chromitite within the harzburgite, where it forms lenticular masses of high-chrome magnesiochromite commonly enveloped by dunite (Zhou et al. 1996). These upper mantle peridotites originally experienced partial melting and depletion in a mid-ocean ridge tectonic environment at around 175 Ma. They were then further depleted (due to repeated partial melting episodes) and metasomatized around 125 Ma by slab-derived fluids, enriched in large-ion-lithophile elements (LILEs, i.e. Cs, K, Rb, Sr, and Ba) and in light rare earth elements (LREEs, e.g. La and Ce) in a suprasubduction zone setting (Hébert et al. 2012). Slabs of oceanic lithosphere formed at mid-ocean ridges can be trapped in the upper plates of intraoceanic subduction zones following subduction initiation, and their mantle units can then be metasomatized by fluids derived from the subducted slabs (Dilek and Thy 2009; Dilek and Furnes 2014 this issue).

The suprasubduction zone–generated Ray-Iz ophiolite in the polar Urals of Russia (Fig. 1) consists mainly of depleted mantle harzburgite and dunite, and it contains more than 200 podiform chromitite bodies that are similar to those in the Luobusa ophiolite (Pervozhikov et al. 1990). It was emplaced westward onto the Laurasian continental margin in the late Cambrian to early Ordovician during arc–continent collision (Savelieva et al. 2007; Pervozhikov et al. 1990).

We have separated several thousand grains of diamond from the peridotites and chromitites of the Luobusa and Ray-Iz ophiolites and have confirmed the presence of six in situ grains of diamond in the chromitites (Fig. 2a). The in situ diamonds occur as subhedral to euhedral crystals, ~0.2–0.5 mm in diameter, contained in small patches of carbon hosted in magnesiochromite (Fig. 2b, c, d). These patches are generally 0.5–1 mm across and circular to irregular in shape; they consist mainly of amorphous carbon, as deduced from the absence of any Raman pattern and from element mapping by electron microprobe (Fig. 2c). The amorphous carbon is a solid glass and very hard, and commonly contains small fragments of chromite (Fig. 2d).

Several tens of grains of diamond have also been separated from individual samples ranging from 300 to 600 kg in weight from other ophiolitic massifs along the Yarlung–Zangbo suture zone (Yang et al. 2013). These diamonds are yellowish green in color, are about 0.2–0.5 mm in size, and have octahedral and cone-like forms. They are similar to those found in the Luobusa massif, and they commonly contain inclusions of Ni–Mn–Co alloy, a feature that distinguishes them from kimberlitic and metamorphic diamonds. We have also discovered diamonds in podiform chromitites of the Devonian Sartohai ophiolite in western China and in peridotites of the Jurassic Myitkyina ophiolite (Myanmar), which occurs in the southeastern extension of the Bangong–Nujiang suture of central Tibet (Fig. 1).

The chromitites and peridotites of all the ophiolites also contain a wide range of native elements (e.g. Fe, Ni, Ti, Si, Cr, Al), base metal and platinum group element alloys (e.g. FeSi, FeTi, Ni–Mn–Co, OsIr), and numerous other minerals such as coesite, kyanite, corundum, zircon, rutile, almandine garnet, olivine, amphibole, chlorite, and sulfides (Table 1 and Appendix I as supplementary online material; Bai et al. 2000; Robinson et al. 2004; Yang et al. 2007; Yamamoto et al. 2013). The occurrence of Ni–Mn–Co alloys, Fe–Si and Fe–C phases, and moissanite (SiC) along with these diamonds is significant because it indicates superreducing conditions at extremely low oxygen fugacity in the mantle, where the diamonds crystallized.

PERSPECTIVES

The diamonds from ophiolites of various regions (China, Russia, Myanmar) and ages (early Paleozoic to Cretaceous) show many similarities in their morphology, carbon isotopes ($\delta^{13}C$ = –18 to –28‰), trace elements, and mineral inclusions, but they are different in these respects from most diamonds occurring in kimberlites, UHP metamorphic belts, and impact craters (Griffin et al. 2013). The newly confirmed in situ diamonds, highly reduced phases, and crustal minerals in chromitites and peridotites of ophiolites require a reevaluation of the petrogenesis of oceanic mantle lithosphere and the formation of diamonds in the lower mantle. The in situ diamonds reported here likely formed at depths of 150–300 km or even deeper (Yang et al. 2007; Yamamato et al. 2009, 2013). These depths are far greater than the depths where the melts of suprasubduction zone ophiolites evolve (Dilek and Furnes 2011).

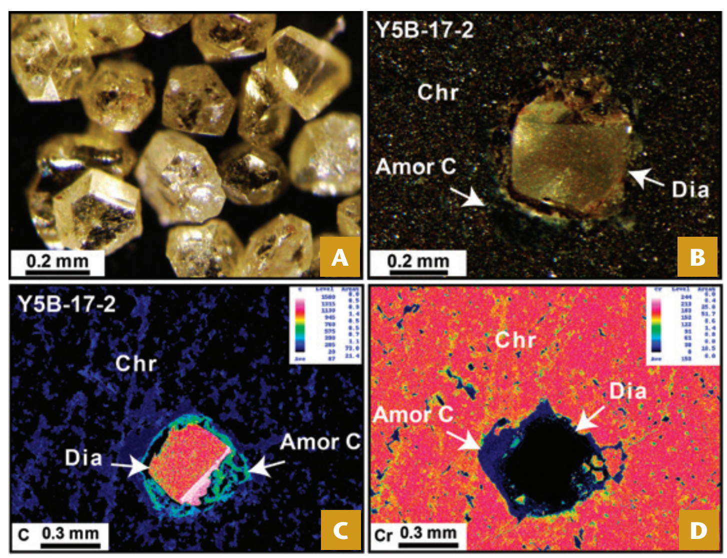

Figure 2 A photograph, a photomicrograph, and element maps of diamonds from the Ray-Iz ophiolite of the polar Urals, Russia. (**A**) Diamond grains separated from chromitite of the Ray-Iz ophiolite. (**B**) In situ diamond occurring as an inclusion in chromite (sample Y5B-17-2). (**C**) Carbon element map showing a diamond grain (reddish orange) in a subcircular patch of amorphous carbon (light green) hosted in chromite (dark blue). (**D**) Chromium element map showing small chromite grains in the amorphous carbon patch shown in (C). Chr = chromite, Amor C = amorphous carbon, Dia = diamond.

The chromite grains and perhaps some small chromitites carrying diamonds appear to have formed at or near the top of the mantle transition zone. The presence of many silicate minerals, such as zircon, corundum, kyanite, and rutile in ophiolitic chromitites and peridotites (Robinson et al. 2011; Yamamoto et al. 2013), suggests recycling of continental crust via subduction into the mantle transition zone. Water, CO_2, and other fluids released from subducted rocks become mixed with highly reduced fluids from greater depths, producing numerous native elements, such as diamonds, Si, Al, and Ti (Robinson et al. 2011). The melts and fluids then rise through the mantle to the top of, or above, the transition zone (>300 km depth), where UHP chromite (with dissolved Si) begins to crystallize, encapsulating diamond, moissanite, and other highly reduced phases. With continued upwelling, coesite exsolution lamellae form in the chromite grains and stishovite is replaced by coesite, but the diamonds are preserved as inclusions in chromite grains. All these processes require depths around 300 km or more in the mantle (Fig. 3).

Following their formation, diamond-bearing chromitites had to be transported upward and incorporated into the rising asthenosphere beneath a spreading center and eventually into suprasubduction zone mantle wedges. One effective way to transport these diamond-bearing peridotites and chromitites to shallow mantle depths is by plumes or superplumes (Fig. 3). Then, the diamond-bearing peridotites and chromitites are distributed, as a result of convection, throughout the upper mantle.

Most of the diamond-bearing peridotites and chromitites are subducted back into the lower mantle, but some of them become trapped in suprasubduction zone environments, where they can be modified by hydrous melts and slab-derived fluids and then incorporated into newly formed suprasubduction zone oceanic lithosphere. There is no evidence that the ophiolites themselves were ever subducted; many of the ophiolites described in this study contain unmetamorphosed or weakly metamorphosed gabbros, lavas, and dikes, as well as moderately to extensively serpentinized peridotites. Thus, the continental crust material must have been introduced into the lower mantle by subduction, long before formation of ophiolitic magmas at shallow depths in the upper mantle (cf. Yamamoto et al. 2013). One very important aspect of this model is that podiform chromitites in ophiolites may not always originate at shallow depths in the uppermost mantle, as widely thought. The chromitite formation may initially begin within or near the mantle transition zone.

The spherical shape of most carbon patches in which the in situ diamond grains occur suggests that a C-rich fluid was present during, or shortly after, chromite crystallization. The diamonds appear to have grown from these C-rich fluids (Fig. 3), but the absence of inclusions of magnesiochromite or Mg-olivine in the diamonds and the fact that not all carbon patches contain UHP minerals suggest that the diamonds crystallized in the fluids before they were encapsulated in the chromitites. The common presence of Ni–Mn–Co alloys in the diamonds suggests that these highly reduced phases were present in the C-rich fluids and may have acted as seeds or catalysts for crystallization of the diamonds. Diamonds and other unusual minerals were preserved in ophiolitic peridotites because they were encapsulated within chromitite grains.

It is unlikely that the carbon patches formed by transformation of diamond to graphite during decompression because this process should have produced pseudomorphs of the diamond grains, as documented in the Beni Bousera and Ronda peridotite massifs of Morocco and Spain (Davies et al. 1993), rather than subcircular patches of amorphous carbon. Also, some of the in situ diamond grains in these carbon patches are euhedral, which argues against formation of the amorphous carbon by alteration. The in situ and separated diamonds are much larger (mostly 0.2–0.5 mm) than those used to grind and polish the samples (<0.04 mm). Thus, it is highly unlikely that the diamonds or amorphous carbon were introduced during preparation of the samples (cf Dobrzhinetskaya et al. 2013).

The common presence of diamonds and associated UHP minerals in ophiolites suggests that the oceanic mantle is compositionally and isotopically more heterogeneous than previously thought, and it raises many questions regarding mantle processes and the formation of ophiolitic melts.

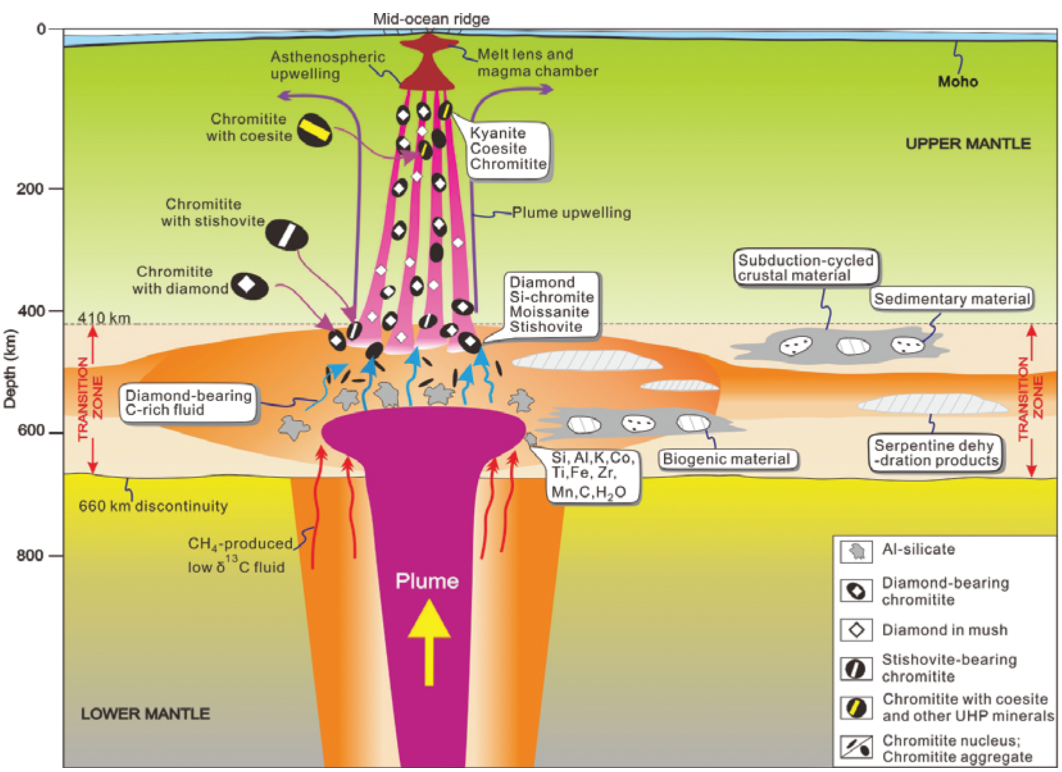

Figure 3 A conceptual model for the formation and occurrence of diamonds and associated ultrahigh-pressure minerals in the oceanic mantle. See text for discussion.

Exactly where and when are the diamonds formed, and how are they introduced into the mantle peridotites and chromitites now exposed in ophiolites? How are diamonds and highly reduced, crustal-type minerals preserved in oceanic mantle peridotites and chromitites? Most podiform chromitites contain evidence of formation at shallow mantle depths in suprasubduction zone environments, making it difficult to understand how UHP and highly reduced phases can be introduced into these enigmatic bodies. Can podiform chromitites and the diamonds they contain be formed in a single tectonomagmatic cycle, or do the peridotites and their chromitites in oceanic lithosphere go through repeated cycles of formation and reformation at various mantle depths prior to their incorporation into ophiolites? We expect that answers to these and other questions will be provided by future interdisciplinary investigations now that diamonds, UHP minerals and associated crustal minerals have been confirmed as integral features of peridotites in many ophiolites. Clearly, ophiolites still have much to tell us about the nature and evolution of oceanic mantle.

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SUPPLEMENTARY ONLINE MATERIAL

Table 1 and Appendix 1 available as supplementary online material at www.elementsmagazine.org/supplements/.

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