

# THE FATE OF SUBDUCTED CONTINENTAL CRUST: EVIDENCE FROM RECYCLED UHP–UHT MINERALS

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**Newly recognized occurrences of ultrahigh-pressure minerals in ultrahigh-temperature felsic granulites and in chromitite associated with ophiolite complexes lead to speculation about the recycling of supracrustal materials through deep subduction, mantle upwelling, and return to the Earth's surface. This idea is supported by possible "organic" light carbon isotopes observed in diamond and moissanite in kimberlite xenoliths and chromitite. These findings presage another renaissance in the study of UHP granulite facies lower-crustal basement and ophiolites and in our understanding of the geodynamics of continental subduction and mantle cycling.**

## UHP MINERALS IN NEW TECTONIC ENVIRONMENTS

The discovery of minerals and microstructures indicative of ultrahigh-pressure (UHP) metamorphism in a variety of new tectonic environments is providing insight into the fate of subducted crust. Two of the most recent findings of UHP minerals in ultrahigh temperature (UHT) granulites and in chromitites associated with ophiolite complexes are highlighted below. Also presented is a schematic cross section of the outer shells of the Earth, showing the recycling of crustal materials in various tectonic regimes (Fig. 1). These findings, together with many other well-documented occurrences of global UHP orogens, reveal that microdiamond, coesite, and other UHP phases are more common than previously thought in both Alpine- and Pacific-type orogens.

Occurrences of microdiamond (+ coesite) as inclusions in kyanite, garnet, and zircon from felsic granulites in the northern Bohemian massif (e.g. Kotková et al. 2011) together with earlier findings of microdiamond, coesite, and nano-size  $\alpha$ -PbO<sub>2</sub>-structured TiO<sub>2</sub> polymorph in pelitic gneisses of the central Erzgebirge suggest that a large part of the Bohemian massif crustal basement has been exhumed from mantle depths of >150 km and subjected to mid-crustal high-temperature (HT) to UHT granulite facies recrystallization. Moreover, the occurrence of diamond and coesite inclusions in garnet and kyanite of UHT felsic granulites from northwestern Africa are unusual as these rocks document much higher *P*–*T* conditions (*P* > 4.3 GPa, *T* > 1100°C), exhibit topotaxial overgrowths of diamond and coesite, lack palisade quartz around relict coesite, and have intergrowths of coesite and phengite possibly after K-cymrite (Ruiz-Cruz and Sanz de Galdeano 2012, 2013). The close association of mantle-derived garnet peridotites with such UHP–UHT granulites suggests that these peridotite bodies became interdigitated with deeply subducted continental crust under UHP conditions rather than being tectonically emplaced at shallow crustal levels.

More startling is the fact that UHP minerals have been discovered in podiform chromitites in ophiolite. For example, diamond, moissanite, possible coesite pseudomorphs after stishovite, Fe–Ti alloys, osbornite, cubic boron nitride, TiO<sub>2</sub> II, and zaponite occur as nano- to micro-scale inclusions in podiform chromitite from the Luobusa ophiolite, Tibet (Yang et al. 2007; Li et al. 2009; Dobrzhinetskaya et al. 2009). In situ microdiamond ( $\pm$  moissanite) inclusions in chromite grains also

have been recognized in several ophiolitic massifs along the 1400 km long Yarlung–Zangbo suture between India and Asia, and in the Polar Urals (Yang and Robinson 2011). These UHP minerals and chromite containing exsolution lamellae of coesite + diopside (Yamamoto et al. 2009) suggest that the chromitites formed at *P* > 9–10 GPa and at depths of >250–300 km. Thin lamellae of pyroxene in chromite, similar to those from Tibet, have been documented in chromitites in the northern Oman ophiolite (Miura et al. 2012). The precursor phase most likely had a Ca-ferrite or Ca-titanite structure; both are high-pressure (HP) polymorphs of Cr-spinel at *P* > 12.5 and 20 GPa (at 2000°C), respectively (Chen et al. 2003). Apparently, these UHP-mineral-bearing chromitites had a deep-seated evolution prior to extensional mantle upwelling and partial melting at shallow depths to form the overlying ophiolite complexes.

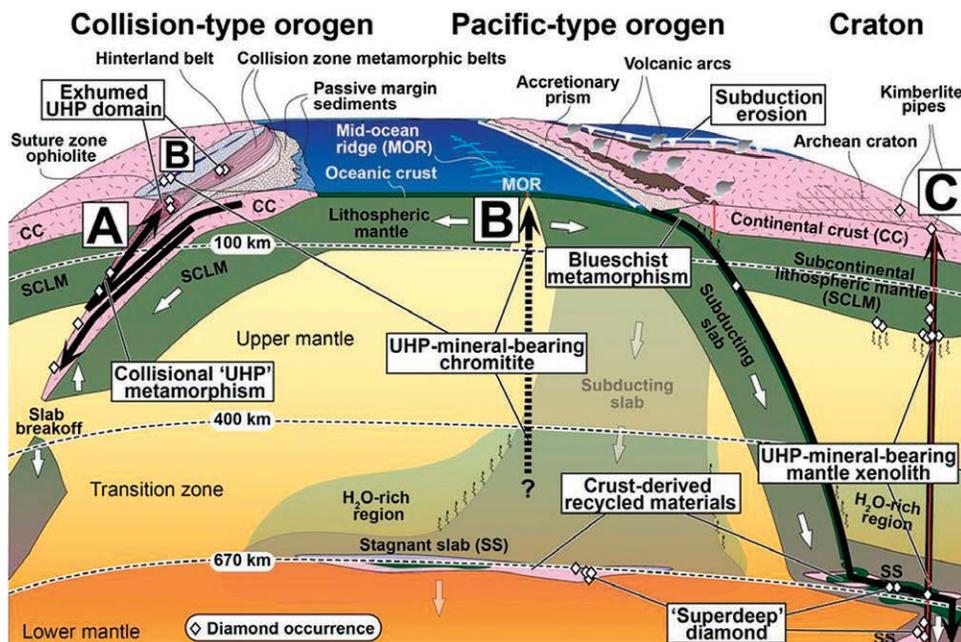
Just where diamond in chromitites formed and whether or not diamond is involved in the recycling of oceanic/continental lithosphere rich in C and volatiles are open questions. The tectonic setting of these ophiolites reflects mantle upwelling and recycling of subducted oceanic/continental materials. The formation of diamond in the subcontinental lithospheric mantle is likely related to the oxidation of asthenosphere-derived, methane-rich fluids (Malkovets et al. 2007). The preservation of diamond is also controlled by the oxygen fugacity of the Earth's mantle (Stagno et al. 2013). Some Brazilian diamonds have "organic" light carbon isotope values ( $\delta^{13}\text{C} = -25\text{‰}$  to  $-14\text{‰}$ ) and contain micro-to nano-inclusions of "superdeep" mineral associations (Wirth et al. 2007, 2009; Walter et al. 2011). These inclusions include phase egg [AlSi<sub>3</sub>(OH)] + stishovite, spinel + nepheline–kalsilite, wüstite + ferropericase, native iron + magnesite,  $\alpha$ -PbO<sub>2</sub>-structured TiO<sub>2</sub>, wollastonite-II, cuspidine, tetragonal almandine–pyrope, and various halides derived from precursor phases stable at depths of >700 km. Walter et al. (2011) also identified two new minerals (NAL, an aluminum silicate phase, and CF, a calcium ferrite phase) previously known only from experiments. Majorite-bearing diamonds from South African kimberlites also record "superdeep" mantle environments (Griffin 2008). Eclogite-associated kimberlitic diamonds frequently have light  $\delta^{13}\text{C}$  values ( $-22\text{‰}$  to  $-6\text{‰}$ ) and contain coesite and garnet inclusions with high  $\delta^{18}\text{O}$  values ( $+6\text{‰}$  to  $+16\text{‰}$ ); the anticorrelation between C and O isotope ratios suggests a recycling origin (Schulze et al. 2003, 2013).

## PERSPECTIVES

These new findings should certainly renew interest in the exploration of UHP minerals and rocks in ophiolite and granulite terranes. The isotopic and inclusion characteristics of kimberlitic diamonds provide compelling evidence for deep subduction of oceanic lithosphere, recycling of surface "organic" carbon into the lower mantle, and exhumation to the Earth's surface, probably via a deep-mantle plume. Diamond and moissanite from chromitites associated with ophiolites in southern Tibet and the Polar Urals have extremely light  $\delta^{13}\text{C}$  values,  $-29\text{‰}$  to  $-18\text{‰}$  (Yang and Robinson 2011), much lighter than most peridotite-associated kimberlitic diamonds ( $-8\text{‰}$  to  $-2\text{‰}$ ). Although the origin of such light isotopic compositions in diamonds is the subject of debate, numerous studies of carbon isotope compositions of superdeep kimberlitic diamonds from Brazil and Siberia suggest that they were derived from deep-mantle cycling of oceanic crust (e.g. Taylor and Anand 2004; Bulanova et al. 2010; Walter et al. 2011). Composite mineral inclusions in Brazilian diamonds indicate crystallization at lower-mantle conditions; for example, inclusions of tetragonal almandine–pyrope were suggested to be a retrograde phase of Mg-perovskite stable at *P* > 30 GPa (Armstrong and Walter 2012).

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**FIGURE 1** A schematic cross section of the Earth's outer shells showing recycling of crustal materials in different tectonic regimes. The bold black arrows represent global pathways (to the mantle–core boundary and to the Earth's surface) of continental materials. Label A is a general trajectory of subduction/exhumation of UHP metamorphic rocks in a collision-type orogen. Label B represents UHP-mineral-bearing chromitites associated with ophiolite complexes; unusual chromitites with UHP minerals and/or crustal-derived minerals might have formed from recycled materials. Subduction erosion in Pacific-type orogens allows subduction of a significant volume of continental material into the transition zone (Maruyama et al. 2010). Label C is a kimberlite pipe in which diamondiferous material from the subcontinental lithospheric mantle as well as superdeep mantle material can be transported.

Over the last decade, global mantle seismic tomography has been used to image slab stagnation; geochemical evidence of recycled material in the peridotitic mantle and the entire subduction / mantle plume cycle has been also documented. High-pressure experiments have revealed that reidite (a high-pressure polymorph of zircon) in a subducting slab is stable at  $P < 20.5$  GPa and  $1500^\circ\text{C}$  (Tange and Takahashi 2004). In fact, crust-derived, quartz-bearing zircons in garnet peridotite xenoliths from the Trans–North China orogenic belt (Liu et al. 2010, xenocrystic zircons in mantle xenoliths in Namibia and China (Liati et al. 2004; Zheng et al. 2006), and abundant, crust-derived, recycled zircons in orogenic peridotites from the Urals (Bea et al. 2001) have been described. Podiform chromitites associated with the ophiolites of Tibet, the Polar Urals, and Oman, mentioned above, contain rare supracrustal zircon, corundum, feldspar, garnet, kyanite, sillimanite, quartz, and rutile, and have much older U–Pb zircon ages than the formation ages of ophiolites (Robinson et al. 2012; Yamamoto et al. 2013). Paleozoic and Proterozoic zircons have been found in gabbroic rocks in the axial zone of the Mid-Atlantic ridge (Pilot et al. 1998; Skolotnev et al. 2010). This direct evidence of crustal recycling into the mantle should lead to another research renaissance, which will integrate the efforts of geophysicists, geochemists, mineral physicists, and geologists.

The identification of rare UHP minerals (e.g. moissanite, K-cymrite, K-wadeite) requires state-of-the-art analytical tools. Systematic data for the ages of subduction, UHP metamorphism, and granulite facies overprinting, together with accurate  $P$ – $T$  estimates, are essential for delineating the tectonic evolution of crustal basement and lithospheric chromitite. Raman identification of submicron-size inclusions in domains of zircon from all lithologies, secondary ion mass spectrometry (SIMS) analyses of in situ stable isotopes (O, C, and N), together with O isotope data from minerals formed at different stages are necessary to determine the amount of recycled supracrustal materials, the source of fluids, and the extent of fluid–rock interactions through subduction, mantle–plume ascent, and exhumation (e.g. Dobrzhinetskaya 2012; Schulze et al. 2013).

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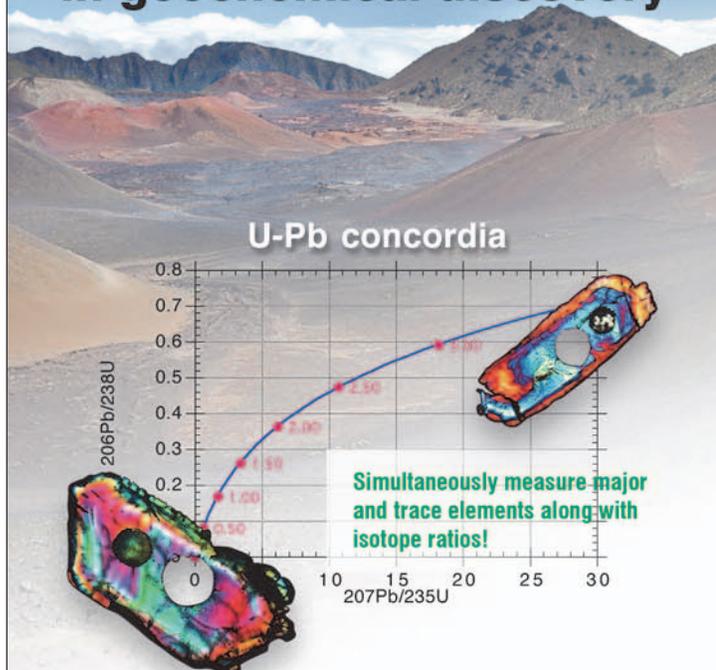
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