

Going up or going down? Diamonds and Super-Reducing UHP assemblages in ophiolitic mantle

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Diamonds have been reported from the mantle parts of ophiolites for ≥ 30 years, but have been widely dismissed as contaminants, because their morphology (octahedral + planar cubic faces) and isotopically light C ($\delta^{13}\text{C}$ to -27) are unlike kimberlitic diamonds. However, diamonds have now been found *in situ* in the chromitites and peridotites of many ophiolites in Tibet (Yarlung-Zangbo suture) and the Polar Urals [1]. LA-ICPMS analyses of the diamonds show LREE-enriched trace-element patterns parallel to those of kimberlitic fibrous diamonds. The patterns are distinct from those of synthetic diamonds, and the ophiolitic diamonds thus appear to be natural. However, there are also striking differences from cratonic diamonds: strong negative anomalies in Sr, Sm, Eu and Yb; extremely low Fe; high Ta and Mn-Ni-Co (present as alloy microinclusions). The diamonds are accompanied by a range of alloys, native metals, carbides and silicides; these and the low Sm-Eu imply very low $f\text{O}_2$. High-Si rutile and coesite pseudomorphs after stishovite suggest pressures ≥ 10 GPa. Finally, some peridotites yield whole-rock Re-Os T_{RD} ages back to 3.4 Ga [2]. The presence of these super-reducing ultrahigh pressure (SuR-UHP) assemblages in large ultramafic massifs raises important questions: Are the SuR-UHP rocks widespread at depth, and brought up along sutures, or are they related to the subduction process? Do the old T_{RD} ages indicate an origin as subducted SCLM, or does such ancient depleted material exist in the "convecting mantle"? How did the massifs come up rapidly enough to avoid graphitizing the diamonds? These SuR-UHP massifs carry unique information on the tectonics of collision zones, mantle convection processes, and the physical and chemical makeup of the deep mantle.

[1] Yang *et al.* (2013) *Science (subm.)*. [2] Shi *et al.* (2012) *Geol. Rev.* **58**, 649-652.

Micro-scale carbonation of single facets of Portlandite

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The carbonation of portlandite to calcite is considered a key adhesive process in almost all historic mortars, right up until the beginning of the 20th century. Even in the present day, so-called "high-calcium cements", which rely on this reaction, are still widely used for cosmetic and conservation purposes. While the precursor hydroxide and the consequent carbonate have previously been extensively characterized, a subject of much current interest is the physical manifestation of the conversion between the two, i.e. by what mechanism does the reaction get from crystalline portlandite to crystalline calcite?

To study this reaction *in-situ* and at very early stages, it is necessary to generate pristine calcium hydroxide surfaces on which to perform subsequent reactions; crystalline facets of portlandite as a reactive substrate is key to isolating the reaction path of carbonation and any intermediates that may occur. To provide these facets, artificial specimens of portlandite were generated by precipitation from aqueous solution by way of a novel nitrogen-drying cell. Following exposures to pure CO_2 lasting from 1 to 48 hours, a new phase was seen growing on the portlandite surfaces, characterized using scanning electron microscopy. This was subsequently identified as highly voluminous calcium carbonate "nodules" using transmission electron microscopy, small angle electron diffraction and Raman spectroscopy. While the carbonate Raman spectra ultimately tended towards calcite, spectra taken with the first one to three hours were closer to that of an amorphous phase of calcium carbonate. In addition to its low crystallinity, this new phase was seen, using TEM, to be highly expansive; generating large volumes of carbonate with the consumption of relatively little hydroxide. This is believed to be a consequence of the sequestration of water within the rapidly formed nodules, which would then gradually stabilize to calcite with time or heating.