

Diamond formation through isochemical cooling of CHO fluids vs redox buffering: examples from Marange peridotitic and Zimmi eclogitic diamonds

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Traditional models for diamond formation within the lithospheric mantle invoke either carbonate reduction or methane oxidation. Both these mechanisms require some oxygen exchange with the surrounding wall-rock at the site of diamond precipitation. However, peridotite does not have sufficient buffering capacity to allow for diamond formation via these traditional models and instead peridotitic diamonds may form through isochemical cooling of H₂O-rich CHO fluids [1].

Marange mixed-habit diamonds from eastern Zimbabwe provide the first natural confirmation of this new diamond growth model [2]. Although Marange diamonds do not contain any silicate or sulphide inclusions, they contain Ni-N-vacancy complexes detected through photoluminescence (PL) spectroscopy that suggest the source fluids equilibrated in the Ni-rich depleted peridotitic lithosphere. Cuboid sectors also contain abundant micro-inclusions of CH₄, the first direct observation of reduced CH₄-rich fluids that are thought to percolate through the lithospheric mantle [2].

In fluid inclusion-free diamonds, core-to-rim trends in $\delta^{13}\text{C}$ and N content are used to infer the speciation of the diamond-forming fluid. Core to rim trends of increasing $\delta^{13}\text{C}$ with decreasing N content are interpreted as diamond growth from oxidized CO₂- or carbonate-bearing fluids. Diamond growth from reduced species should show the opposite trends - decreasing $\delta^{13}\text{C}$ from core to rim with decreasing N content. Within the CH₄-bearing growth sectors of Marange diamonds, however, such a 'reduced' trend is not observed. Rather, $\delta^{13}\text{C}$ increases from core to rim within a homogeneously grown zone [2]. These contradictory observations can be explained through either mixing between CH₄- and CO₂-rich end-members of hydrous fluids [2] or through closed system precipitation from an already mixed CH₄-CO₂ H₂O-maximum fluid with XCO₂ (CO₂/[CO₂+CH₄]) between 0.3 and 0.7 [3].

These results demonstrate that Marange diamonds precipitated from cooling CH₄-CO₂-bearing hydrous fluids rather than through redox buffering. As this growth mechanism applies to both the fluid-rich cuboid and gem-like octahedral sectors of Marange diamonds, a non-redox model for diamond formation from mixed CH₄-CO₂ fluids is indicated for a wider range of gem-quality peridotitic diamonds. Indeed, at the redox conditions of global diamond-bearing lithospheric mantle (FMQ -2 to -4; [4]), CHO fluids are strongly water-dominated and contain both CH₄ and CO₂ as dominant carbon species [5].

By contrast diamond formation in eclogitic assemblages, through either redox buffering or cooling of carbon-bearing fluids, is not as well constrained. Zimmi diamonds from the West African craton have eclogitic sulphide inclusions (with low Ni and high Re/Os) and formed at 650 Ma, overlapping with the timing of subduction [6]. In one Zimmi diamond, a core to rim trend of decreasing $\delta^{13}\text{C}$ (-23.4 to -24.5 ‰) and N content is indicative of formation from reduced C₂H₆/CH₄-rich fluids, likely derived from oceanic crust recycled during Neoproterozoic subduction. Unlike mixed CH₄-CO₂ fluids near the water maximum, isochemical cooling or ascent of such reduced CHO fluids is not efficient at diamond precipitation. Furthermore, measurable carbon isotopic variations in diamond are not predicted in this model and therefore cannot be reconciled with the ~1 ‰ internal variation seen. Consequently, this Zimmi eclogitic diamond likely formed through redox buffering of reduced subduction-related fluids, infiltrating into sulphide-bearing eclogite.

References 1. Luth and Stachel, 2014. *CMP*, 168, 1083 2. Smit et al., 2016. *Lithos*, 265, 68-81 3. Stachel et al., in review 4. Stagno et al., 2013. *Nature*, 493, 84–88 5. Zhang and Duan, 2009. *GCA* 73, 2089–2102 6. Smit et al., 2016. *Precamb Res*, 286, 152-166