

Fluid-rich microinclusions in diamonds open windows to large mantle processes.

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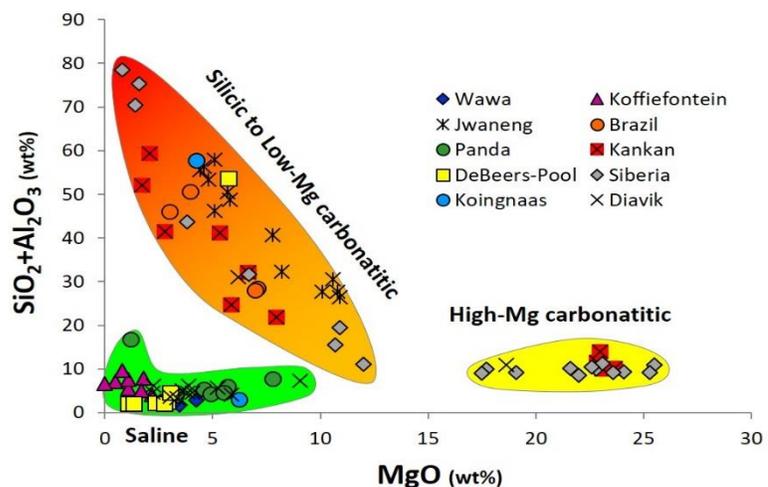
Introduction

Diamond formation in the Earth's mantle is induced by circulating carbon- and water-rich (C-O-H) mantle fluids and melts. This broadly accepted concept is based on (1) the concentric growth patterns of diamonds, as revealed by cathodoluminescence images indicating that they grew undisturbed into surrounding fluids/melts; (2) their association with veins and alteration zones in xenoliths; and (3) evidence that mineral inclusions in diamonds show enrichments in incompatible trace elements from the fluids that also deposited their host diamond. Deep C-O-H mantle fluids are often encapsulated as μm -scale high-density fluid (HDF) inclusions in fast-growing diamonds (i.e. 'hailstone boart', 'sugary', 'fibrous', 'cloudy'). Due to the physical strength and chemically inert nature of their diamond hosts, these inclusions remain pristine for billions of years even when brought to Earth's surface, and represent our only direct samples of deep Earth C-O-H fluids.

The compositions of HDF micro-inclusions in individual diamonds are homogenous. To date, out of ~250 diamonds analyzed by electron microprobe (EMPA) for their individual micro-inclusion major element compositions, HDFs show significant radial (core-to-rim) changes in only 4 diamonds. Thus ~98% of known fluid-rich diamonds are homogenous, and the individual micro-inclusions in a single diamond spans a limited range of compositions from core-to-rim (typically <10-20% 1σ for the major oxides). HDFs in diamonds from 4 continents and 8 cratons vary in major-element compositions between four major types (Fig. 1): a hydrous-silicic end-member rich in Si, Al, K and water; a hydrous-saline fluid end-member rich in Cl, K, Na and varying water and carbonate; and high- and low-Mg carbonatitic end-members rich in Ca, Mg, Fe, K and carbonate (Navon et al., 1988; Weiss et al., 2009 and references therein). Similar HDF compositions appear in diamonds from different lithospheric provenances and ages, and it is common to find more than one HDF type in a suite of diamonds from the same locality and/or kimberlite. The HDF end-members can be distinguished by their variation in MgO vs. $\text{SiO}_2+\text{Al}_2\text{O}_3$ (in wt.%; Figure 1), or by their relative abundances of water-carbonate-silicate-apatite (Extended Abstract No. 11IKC-004457).

Figure 1: $\text{SiO}_2+\text{Al}_2\text{O}_3$ vs. MgO in HDFs (wt% on a water- and carbonate-free basis). The high-Mg carbonatitic compositions are close to experimental near-solidus melts of carbonate-peridotite, while the low-Mg carbonatitic to silicic HDFs form an array close in composition to experimentally produced fluids/melts in the eclogite+carbonate \pm water system (Weiss et al., 2009). Datapoints include HDF compositions from the published literature.

HDFs of different end-member compositions display two main trace-element patterns, one with high field strength element (HFSE) depletions and large ion lithophile element (LILE) enrichments similar to calcalkaline magmas and continental rocks, the other with lower LILE abundances and 'smoother' overall



trace-element patterns similar to oceanic basalts. Radiogenic isotope data from HDFs are very scarce, nevertheless, available data show $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.703-0.723 (Akagi and Masuda, 1988; Klein-BenDavid et al., 2014; Smith et al., 2012), indicating sources ranging from ‘depleted’ oceanic mantle to old continental crust. Thus, HDFs record a large range of compositions and sources for deep C-O-H diamond-forming fluid agents. Their study permits a glimpse back in time to the active role C-O-H fluids play in the global material circulation, deep Earth processes, and their impacts on the sub-continental lithospheric mantle (SCLM).

Deep C-O-H mantle fluids, diamond formation and regional tectonics and volcanism

A strong connection has been established between high-Mg carbonatitic HDFs and carbonated peridotite sources, either lithospheric or asthenospheric in origin, while silicic and low-Mg carbonatitic HDFs have been related to hydrous eclogite (plus or minus carbonate). Recently, Weiss et al. (2015) reported the first conclusive trace-element and Sr isotope evidence for seawater-altered subducting slabs as the source of deep C-O-H-bearing mantle fluids having saline compositions, and that these fluids are parental to carbonatitic and silicic melts in the lithosphere. These authors suggested that the whole spectrum of deep C-O-H fluids observed in diamonds (from saline-to-carbonatitic-to-silicic) is linked to saline fluids derived from seawater-altered subducted oceanic lithospheric slabs, and that carbonatitic and silicic melts develop through fluid-rock interaction of parental saline fluids with peridotitic or eclogitic lithologies in the lithospheric mantle (Fig. 2). Moreover, they linked the chemistry of the parental saline fluids and the timing of host diamond formation to Mesozoic plate subduction under western North America as the source for the saline fluids. These results imply a strong association between subduction, deep C-O-H mantle fluids, metasomatism and fluid-rich diamond formation, emphasizing the importance of subduction-derived fluids in affecting the composition of the deep SCLM.

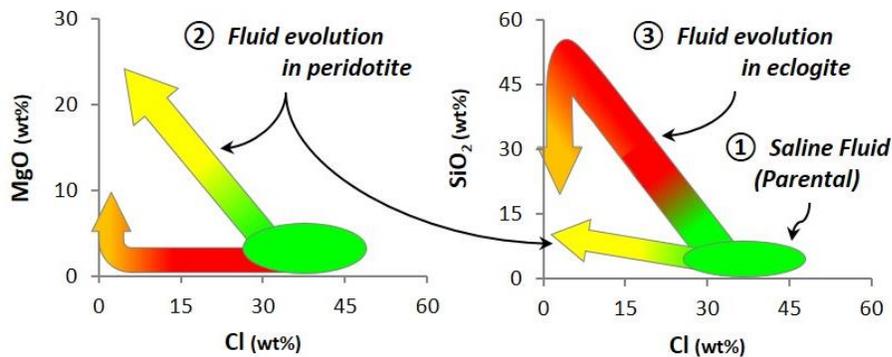


Figure 2: HDF compositional evolution depicted in the inset MgO-Cl and SiO₂-Cl trends. When the parental saline fluids (1) enter the lithosphere they react with local lithology. The melt-depleted nature of cratonic lithospheric peridotite prevents notable melting unless the saline fluids traverse either carbonated-peridotite or

eclogite lenses, leading to *in situ* formation of high-Mg carbonatitic (2) and silicic melts (3), respectively. The presence of carbonate in eclogite may lead to formation of low-Mg carbonatite fluids with increasing melting. Rapid diamond formation occurs during fluid-rock interaction due to the oxidation gradient between the evolving fluids and local lithosphere.

Another example for a connection between deep C-O-H mantle fluids and regional tectonics comes from HDFs encapsulated in a suite of diamonds from the DeBeers-Pool and Finsch kimberlites in the Kaapvaal craton, South Africa (Extended Abstract No. 11IKC-004461 and Weiss et al. unpublished data). New U, Th and He compositional data in these diamonds reveal 3 episodes of chemical changes in the Kaapvaal craton SCLM during the last ~1 Gyr, each by a different metasomatic agent. The youngest episodes indicate direct relationships between highly-saline fluid metasomatism, fluid-rich diamond formation and late-Mesozoic kimberlite eruptions, while the older silicic and carbonatitic metasomatic events may be related to the Namaqua-Natal Orogeny (~1 Gyr), Damara Orogeny (~500 Myr), or Karoo magmatism (~200 Myr) (Extended Abstract No. 11IKC-004460).

The fingerprints of old C-O-H fluid metasomatism in young mantle plumes

HIMU basalts stand out hotspots with the highest Pb isotope ratios, high Os isotope ratios, low Sr isotope ratios slightly higher than depleted MORB, and Nd-Sr isotopes plotting ‘below’ the ‘Nd-Sr mantle array’. Its mantle source is generally considered to be recycled basaltic oceanic crust. However, recent high-precision analyses of olivine phenocrysts in HIMU lavas indicate derivation from peridotite partial melting, rather than pyroxenitic remnants of recycled basalt, and show exceptionally high Ca/Al ratios that are far outside the range previously reported for olivines from MORB and OIB (Weiss et al., 2016). The high Ca/Al ratios indicate a metasomatic enrichment process involving carbonatitic fluid. A key piece to the HIMU puzzle is similarities in trace-element patterns between high-Mg carbonatitic HDFs in diamond, Group I kimberlites, and HIMU lavas, indicating that the mantle sources experienced similar histories of trace-element enrichment and depletion. This “HIMU–diamond-forming fluids connection” indicates that deep C-O-H fluids plays a major role in forming the HIMU OIBs, and provides new support for the involvement of C-O-H-fluid metasomatised SCLM in mantle plumes (Fig. 3).

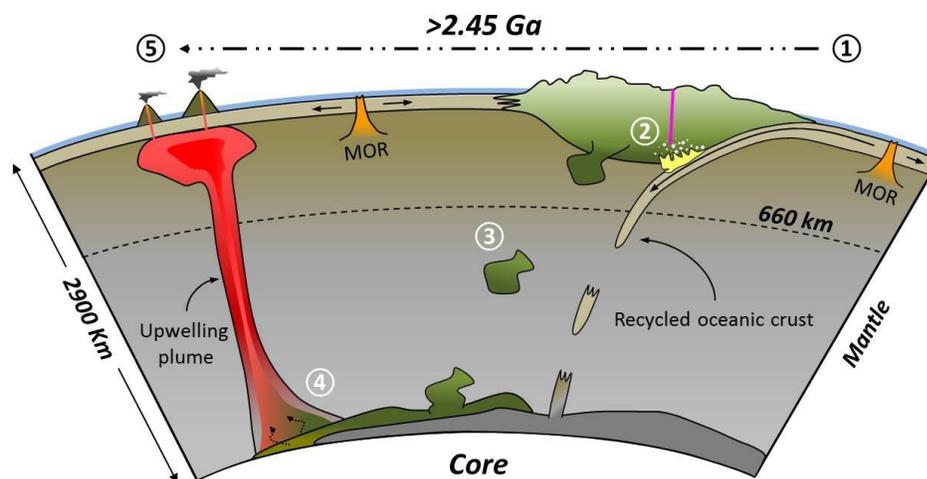


Figure 3: Conceptual model for the formation of the HIMU mantle source: (1) Subduction during the Archean or early Proterozoic. (2) Metasomatism of the melt-depleted SCLM by carbonatite-rich fluids-melts released by the subducting slabs (which can also produce diamonds); the metasomatism SCLM develops high Pb and Os isotopes over time. (3) The SCLM

delaminates and is transported to a mantle boundary layer, likely the core–mantle boundary. (4) Entrainment of recycled SCLM into an upwelling plume. (5) The upwelling plume generates the HIMU OIB.

References

- Akagi T, Masuda A (1988) Isotopic and elemental evidence for a relationship between kimberlite and Zaire cubic diamonds. *Nature* 336:665-667
- Klein BenDavid O, Pearson DG, Nowell GM, Ottley CJ, McNeill JCR, Logvinova A, Sobolev NV (2014) The source and time-integrated evolution of diamond-forming fluids – trace element and Sr isotopic evidence. *Geochimica et Cosmochimica Acta* 125:146–169.
- Navon O, Hutcheon ID, Rossman GR, Wasserburg GJ (1988) Mantle-derived fluids in diamond microinclusions. *Nature* 355:784-789.
- Smith EM, Kopylova MG, Nowell GM, Pearson DG, Ryder J (2012) Archean mantle fluids preserved in fibrous diamonds from Wawa, Superior craton. *Geology* 40:1071-1074
- Weiss Y, Kessel R, Griffin WL, Kiflawi I, Klein-BenDavid O, Bell DR, Harris JW, Navon O (2009) A new model for the evolution of diamond-forming fluids; evidence from microinclusion-bearing diamonds from Kankan, Guinea. *Lithos* 112:660-674.
- Weiss Y, McNeill J, Pearson DG, Nowell GM, Ottley CJ (2015) Highly saline fluids from a subducting slab as the source for fluid-rich diamonds. *Nature* 524:339-342.
- Weiss Y, Class C, Goldstein S, Hanyu T (2016) Key new pieces to the HIMU puzzle from olivines and diamond inclusions. *Nature*, 537:666–670.