

Sulphide inclusions in sub-lithospheric diamonds

Lotta I.M. Kempainen¹, Emilie Thomassot², Simon C. Kohn¹, Galina P. Bulanova¹, Ian J. Parkinson¹ and Chris B. Smith¹

¹ University of Bristol, United Kingdom, lk15127@bristol.ac.uk, simon.kohn@bristol.ac.uk, galina_bulanova@hotmail.com, ian.parkinson@bristol.ac.uk, chris_b_smith@btopenworld.com
² Centre de Recherches Pétrographique et Géochimiques (CRPG-CNRS) et Université de Lorraine, Vandoeuvre-Les-Nancy, France, emilie@crpg.cnrs-nancy.fr

Overview

Sulphide inclusions hosted in sublithospheric (“superdeep”) diamonds from the Juina-5 and Collier-4 kimberlites (Brazil) are being studied by a variety of techniques. Protected from any reequilibration by their host diamond, these samples offer a unique opportunity to investigate the deep sulphur cycle, potentially adding new constraints on recycling of surface material at depths.

Background

Inclusions in diamonds provide a direct insight into the chemistry of diamond-forming domains of the Earth’s mantle, allowing for an understanding of the recycling of volatiles through the Earth’s interior. Diamond formation is often interpreted as the result of redox reactions; diamonds may grow by the interaction of a reduced fluid with oxidised mantle (Thomassot et al., 2007), or by the infiltration of oxidised fluids into reduced ambient mantle (Stachel and Harris 2009; Palot et al. 2014). Sulphide inclusions are abundant in lithospheric diamonds relative to normal mantle sulphur contents (~200 ppm), but their involvement in diamond formation requires further investigation.

The majority of known diamonds have formed in the Earth’s lithospheric upper mantle (<300km) in peridotite (“normal” mantle) or eclogite (of mafic lithology). The major and trace element chemistries of the sulphide inclusions they host are well documented in literature; for example, peridotitic sulphide inclusions are generally characterised by higher Cr and Ni contents compared to eclogitic diamonds, reflecting on the higher degrees of partial melting having affected their source region (Fig. 1A).

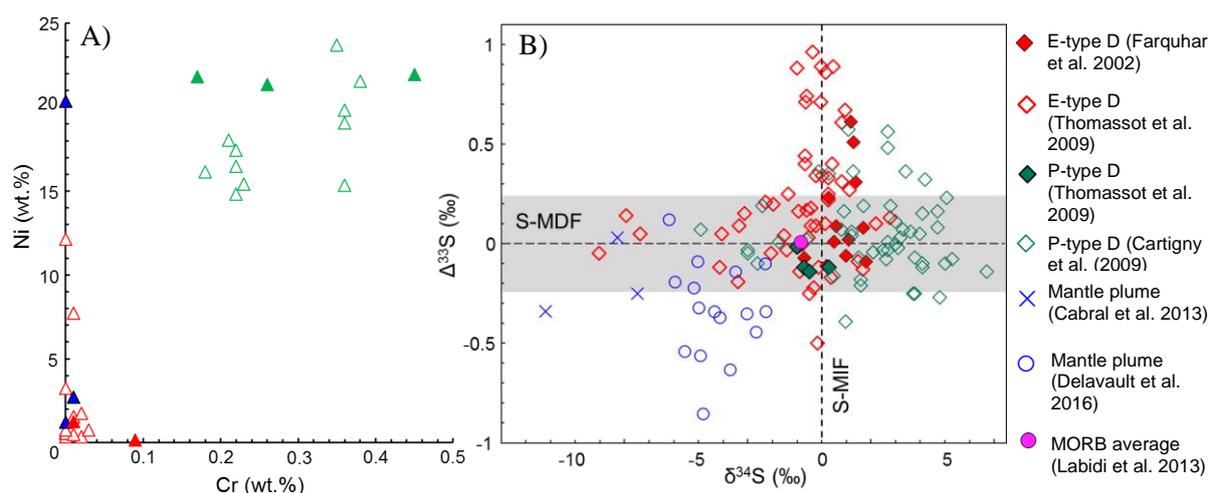


Figure 1: A) Ni versus Cr plot with compositions of eclogitic (red) and peridotitic (green) diamond inclusions from Jwaneng (open symbols from Thomassot et al. 2009) and Mwadui (closed symbols from Stachel et al. 1998) and three inclusions from Machado River (blue symbols from Burnham et al. 2016). B) $\delta^{34}\text{S}$ (mass-dependent fractionation, S-MDF) versus $\Delta^{33}\text{S}$ (mass-independent fractionation, S-MIF) plot showing the compositions of sulphides included in E-type and P-type diamonds, plume material and MORB.

Less is known about the sulphides hosted in sublithospheric diamonds, which make up only a small (<5%) proportion of diamonds studied worldwide, but can sample trapped mantle material at depths >410km (Stachel et al. 2000; Walter et al. 2011). Previous work has shown that superdeep diamonds from Juina-5 and Collier-4 grew by interaction of oxidised oceanic slab-derived carbonate melts with a reduced ambient mantle (Burnham et al. 2015; Thomson et al. 2016). Therefore, one source of sulphur for sulphide inclusions in these diamonds could be a surface-derived sulphate component (e.g. precipitated from a C–O–S–H-rich fluid). Alternatively, sulphide may have been trapped in reduced form, as sulphide included in a subducting slab, or originating from the mantle.

P-type sulphides can preserve mantle-like sulphur isotope signatures, while E-type inclusions can exhibit more scatter in $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ compositions due to the heterogeneity of their crustal protoliths (Farquhar et al. 2002; Cartigny et al. 2009; Thomassot et al. 2009) (Fig. 1B). Sulphur mass-independent fractionation (S-MIF, $\Delta^{33}\text{S} \neq 0$) is a signal observed in rocks and diamonds preserving sedimentary material of Archaean age (>2.45 Ga), when photolysis of volcanic SO_2 released into an oxygen-poor atmosphere allowed the formation of sulphates (with negative $\Delta^{33}\text{S}$ anomalies) and elemental sulphur (with positive $\Delta^{33}\text{S}$ signatures) (Farquhar et al. 2000). The latter are preserved in few lithospheric diamonds (Farquhar et al. 2002; Thomassot et al. 2009). Negative $\Delta^{33}\text{S}$ values have been measured in material sampled by mantle plumes (Cabral et al. 2013; Delavault et al. 2016), and the apparent deficit of negative anomalies at the surface could suggest the presence of a negative $\Delta^{33}\text{S}$ reservoir in the lower mantle (Farquhar et al. 2002; Cabral et al. 2013).

Samples, results and discussion

The chemical composition of sulphide inclusions hosted in diamonds from Collier-4 and from Juina-5 is being investigated. The diamonds are 0.5-3 mm in size and octahedral or macle-shaped, often being highly resorbed or broken fragments of originally larger crystals (Fig. 2A and 2B). The inclusions are 5-40 μm in size and consist mainly of iron sulphide ($\text{Fe}_{(1-x)}\text{S}$), although minor exsolutions of chalcopyrite (CuFeS_2) and pentlandite ($(\text{Fe,Ni})_9\text{S}_8$) may also occur. According to electron-microprobe analyses (Thomson et al. 2014) and synchrotron-based x-ray microtomography (SXRTM), sulphides coexist at the edges of inclusions with non-sulphide phases, perhaps suggesting exsolution from a former S-bearing melt (Fig. 2C). The phases coexisting with sulphide have an eclogitic affinity and include Ca-perovskite, Ca-walstromite, spinel, clinopyroxene and coesite (Thomson et al. 2014).



Figure 2: A) Collier-4 diamond polished on two surface contains large polyphase inclusions. B) a resorbed sulphide-bearing diamond from Juina-5. C) Back-scattered electron image of an unmixed Ca-perovskite inclusion in a Juina-5 diamond where sulphide (sul) occurs (Thomson et al. 2014).

The sulphur isotope compositions of superdeep sulphide inclusions will be analysed by secondary ion mass spectrometry (SIMS) using CRPG national facility (Cameca 1280), providing a unique opportunity to investigate the ability of sulphur to preserve recycled signatures during transfer to the Earth's lower mantle. Sulphide inclusions of recycled origin can have mantle-like S isotope compositions, but analysing solely mantle-like $\delta^{34}\text{S}$ values could reflect on the interaction of deep-sourced sulphur, or fluid-hosted SO_4^{2-} with the diamond-forming medium. The S isotope signature can be diluted with mantle-derived sulphur ($\Delta^{33}\text{S} = \sim 0$), especially through interaction with fluids/melts.

However, observing a S-MIF signal would suggest the presence of relatively undisturbed recycled, ancient sediment in the lower mantle diamond-forming region.

Although they can be obscured by mantle mixing and assimilation processes, the compositions and sulphur isotopic signature of sulphide minerals can be used to investigate the nature of the sulphur-bearing phase interacting with the diamond-forming medium. Observing differences in the geochemical or isotopic compositions of sulphides trapped as single phase Fe-sulphide and ones inside polyphase inclusions could suggest different provenances of sulphur in the lower mantle.

References

- Burnham AD, Thomson AR, Bulanova GP, Kohn SC, Smith CB and Walter MJ (2015) Stable isotope evidence for crustal recycling as recorded by superdeep diamonds. *Earth Planet Sci Lett* 432:374-380
- Burnham AD, Bulanova GP, Smith CB, Whitehead SC, Kohn SC, Gobbo L and Walter MJ (2016) Diamonds from the Machado River alluvial deposit, Rondônia, Brazil, derived from both lithospheric and sublithospheric mantle. *Lithos* 265:199-213.
- Cabral RA, Jackson MG, Rose-Koga EF, Koga KT, Whitehouse MJ, Antonelli MA, Farquhar J, Day JM and Hauri EH (2013) Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of Archaean crust. *Nature* 496(7446):490-493
- Cartigny P, Farquhar J, Thomassot E, Harris JW, Wing B, Masterson A, McKeegan K and Stachel T (2009) A mantle origin for Paleoarchean peridotitic diamonds from the Panda kimberlite, Slave Craton: evidence from 13 C-, 15 N- and 33, 34 S-stable isotope systematics. *Lithos* 112:852-864
- Cartigny P, Palot M, Thomassot E and Harris JW (2014) Diamond formation: a stable isotope perspective. *Annu Rev Earth Planet Sci* 42:699-732
- Delavault H, Chauvel C, Thomassot E, Devey C and Dazas B (2016) Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume. *Proc Natl Acad Sci* 113(46):12952-12956
- Farquhar J, Wing BA, McKeegan KD, Harris JW, Cartigny P and Thiemens MH (2002) Mass-independent sulfur of inclusions in diamond and sulfur recycling on early Earth. *Science* 298(5602):2369-2372
- Labidi J, Cartigny P and Moreira M (2013) Non-chondritic sulphur isotope composition of the terrestrial mantle. *Nature* 501(7466):208-211
- Stachel T, Harris JW and Brey GP (1998) Rare and unusual mineral inclusions in diamonds from Mwadui, Tanzania. *Contrib Mineral Petrol* 132(1):34-47.
- Stachel T, Harris JW, Brey GP and Joswig W (2000) Kankan diamonds (Guinea) II: lower mantle inclusion parageneses. *Contrib Mineral Petrol* 140(1):16-27.
- Stachel T and Harris JW (2009) Formation of diamond in the Earth's mantle. *J Phys: Condens Matter* 21(36):364206
- Thomassot E, Cartigny P, Harris JW and Viljoen KF (2007) Methane-related diamond crystallization in the Earth's mantle: stable isotope evidences from a single diamond-bearing xenolith. *Earth Planet Sci Lett* 257(3):362-371
- Thomassot E, Cartigny P, Harris JW, Lorand JP, Rollion-Bard C and Chaussidon M (2009) Metasomatic diamond growth: A multi-isotope study (13 C, 15 N, 33 S, 34 S) of sulphide inclusions and their host diamonds from Jwaneng (Botswana). *Earth Planet Sci Lett* 282(1):79-90
- Thomson AR, Kohn SC, Bulanova GP, Smith CB, Araujo D and Walter MJ (2014) Origin of sub-lithospheric diamonds from the Juina-5 kimberlite (Brazil): constraints from carbon isotopes and inclusion compositions. *Contrib Mineral Petrol* 168(6):1081
- Thomson AR, Walter MJ, Kohn SC and Brooker RA (2016) Slab melting as a barrier to deep carbon subduction. *Nature* 529(7584):76-79
- Walter MJ, Kohn SC, Araujo D, Bulanova GP, Smith CB, Gaillou E, Wang J, Steele A and Shirey SB (2011) Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions. *Science* 334(6052):54-57