Abiotic and biotic control of the δ^{65}Cu and δ^{66}Zn composition of seawater

S.H. LITTLE*, D. VANCE AND D.M. SHERMAN

Bristol Isotope Group, School of Earth Sciences, University of Bristol, Bristol BS8 1RJ UK
(*correspondence: s.little@bristol.ac.uk)

Dissolved copper in seawater is isotopically heavy (1.1‰) relative to both rocks (0‰) and the riverine input (0.7‰). Particulate Cu in the oceans is adsorbed to ferromanganese crusts and is isotopically lighter than seawater, at 0.1-0.4‰. EXAFS and μ-XRF indicate that Cu in the crusts is predominantly associated with the Mn-oxide, δ-MnO_2. Consistent with these observations, the experimental $\Delta^{65}Cu_{solid\text{-}soln}$ on inorganic sorption of Cu to δ-MnO_2 is -0.5‰. Thus, abiotic fractionation of Cu in large part explains the heavy isotopic composition of seawater.

The additional control can be sought in the dissolved Cu fraction, the speciation of which is dominated by complexation to siderophore-like ligands, likely exuded by phytoplankton. We have cultured cyanobacteria, and show that there is indeed a small positive $\Delta^{65}Cu_{ligand\text{-}soln}$ associated with this complexation. Similarly, Cu sorbs to deprotonated surfaces of dissolved organic matter with an isotopic fractionation of +0.27‰ [1], and several species of bacteria preferentially take up ^{63}Cu [2]. All of the above provide mechanisms to enrich the dissolved fraction in heavy ^{65}Cu.

δ^{65}Cu in the oceans is hence a balance of both inorganic and organic complexation, and our observations contribute to an internally consistent picture. This is not yet the case for zinc, however. Lab experiments [3] and our synchrotron-based study indicate that Zn behaves similarly to Cu in terms of its crystal chemistry and abiotic fractionation. Unlike Cu, however, Zn in ferromanganese crusts is isotopically heavier than the δ^{66}Zn of seawater. Further work is required to understand this discrepancy.

[1] Bigalke *et al.* (2010) *Env. Sci. Tech* **44**, 5496–5502 [2] Navarrete *et al.* (2011) *GCA* **75**, 784–799 [3] Pokrovsky *et al.* (2005) *J. Colloid Interf. Sci.* **291**, 192–200.

Origin and evolution of carbonatite magma parental for diamond and syngenetic inclusions

YU.A. LITVIN

Institute of Experimental Mineralogy, Russian Acad. Sci., Chernogolovka, Moscow Dstr. 142432, Russia
(litvin@iem.ac.ru)

Introductory remarks

Mantle-carbonatite model of diamond genesis [1], genetic classification of primary inclusions in mantle-derived diamond [2] and generalized composition diagram for multi-component heterogeneous parental medium for diamond and syngenetic inclusions [3] are the key findings based on integration of mineralogical and experimental data.

Origin of diamond-parent carbonatite magma

In the making stationary chamber of diamond-parent carbonatite magma, two episodes are of a significant part: (1) Mg-Ca-carbonatite primary melts can result from mantle peridotite in response to chemical attack of high-temperature “metasomatic agents” rich in CO_2, K-Na-alkaline carbonates and silicates, minor incompatible and REE elements;

(2) primary carbonatite melts dissolve peridotite minerals, solid and dispersed carbon, minor soluble phases and involve xenogenetic ones. Diamond-forming activity of mantle carbonatite chamber begins when diamond solubility concentration in the magma is attained. During cooling, carbon oversaturation in respect to diamond is reached producing nucleation and growth of diamond.

Evolution of diamond-parent carbonatite magma

In compositional evolution of the fractionated parental magma during cooling, two physicochemical mechanisms which control magmatic ultrabasic-to-basic and peridotite-to-eclogite paragenetic transitions have a dominant role: (1) carbonatization of olivine and orthopyroxene; (2) garnetization of olivine due to reaction between olivine and jadeite components [4]. The both reaction mechanisms control continuous transition from formation of peridotite mineral paragenesis to the eclogite one in diamond-parent carbonatite magma.

Syngenesis diagrams for diamond, paragenetic and xenogenetic inclusions

Syngenesis melting relations of the eclogite-carbonatite-sulfide-diamond system are studied at 7 GPa. Syngenesis diagrams offer a clearer view of how diamond and paragenetic phases have formed. These reveal physicochemical mechanism of origin of natural diamond, PT-conditions of formation of paragenetic silicate and carbonate minerals and their coexistence with xenogenetic minerals and melts. Thus physicochemical conditions of primary caption of paragenetic and xenogenetic phases by growing diamond are revealed. Support: RFBR 1105/00401.

[1] Litvin (2007) *Geol Soc Amer Spec Pap* **421**, 83-103 [2] Litvin (2009) *Rus Geol Geoph* **50**, 1188-1200 [3] Litvin (2010) *Proceed XI Rus Min Soc General Meeting*, 77-78 [4] Gasparik, Litvin (1997) *Eur J Mineral* **9**, 311-326.