

## Calculation of mass (im-)balance in the oceanic cycling of Cu and Zn isotopes

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The stable isotope systems of the transition metals are increasingly being developed as tracers for the paleoenvironment. However, as yet, controls on their modern cycling in the oceans are little known. In particular, constraints on their modern oceanic mass balance are sparse [1].

We present best estimates for the fluxes and isotopic composition of Cu and Zn for the known oceanic inputs (rivers, aeolian dust) and outputs to sediments (in normal marine and anoxic settings), the latter based on estimates for Mo, with Cu/Mo or Zn/Mo ratios of different types of marine sediments [2, 3]. For both Cu and Zn, the sum of the known input fluxes is greater than that of the output fluxes, i.e. the cycles are out of balance. This imbalance is also observed in the isotope ratios of sources and sinks. For  $\delta^{65}\text{Cu}$ , we find flux-weighted outputs that are isotopically light (at  $\sim 0.3\text{‰}$ ) compared to the inputs (at  $\sim 0.6\text{‰}$ ). For  $\delta^{66}\text{Zn}$  we observe the reverse, with a sink for Zn that is isotopically heavy (at  $\sim 0.7\text{‰}$ ) compared to the input, the latter indistinguishable from detrital sediments (at  $\sim 0.3\text{‰}$ ).

Taken at face value, these calculations require that the Cu and Zn cycles include an unidentified additional sink to achieve flux and isotopic mass balance. For Cu, this sink should be isotopically heavy (at ca.  $+2\text{‰}$ ) while for Zn, a missing sink for light isotopes (at ca.  $-1\text{‰}$ ) is implied. However, we consider these projected missing sink isotopic compositions to be implausible. Instead, we discuss the possibility of (an) additional source(s) of Cu and Zn, the presence of which would reduce the isotopic extremity of each missing sink. We suggest that one such source may be solubilisation of a portion of the large riverine particulate flux at the river-sea interface.

[1] Little, Vance, Landing & Walker Brown (submitted), *GCA*. [2] Morford and Emerson (1999), *GCA* **63**, 1735–1750. [3] McManus, Berelson, Severmann, Poulson *et al.* (2006), *GCA* **70**, 4643–4662.

## Differentiation of the mantle ultrabasic-basic magmas and diamond-forming carbonatite melts on experimental evidence

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Generalized melting diagram-complex of upper-mantle peridotite-eclogite system

The diagram-complex consolidates garnet peridotite Ol-Opx-Cpx-Grt and four eclogitic simplexes. Primary komatiitic magma is formed under control of invariant peritectic Ol+Opx+Cpx+Gr+L linked with olivine eclogite simplex by univariant Ol+Cpx+Grt+L curve. Peridotite and silica-saturated eclogite compositions are separated by Opx-Cpx-Grt plane. Peritectic points of peridotite and Coes-eclogites (Coes+Opx+Cpx+Gr+L) are linked by univariant Opx+Cpx+Grt+L curve. While piercing the Opx-Cpx-Grt plane, the curve has temperature maximum known as thermal eclogitic barrier [1]. The barrier represents an insuperable obstacles for ultrabasic-basic magma both equilibrium and fractional differentiation.

“Peridotite-to-eclogite tunnel” mechanism against the thermal eclogitic barrier

Fractional crystallization of primary komatiitic magma is accompanied by increasing concentration of jadeite component at residual melts. This activates mechanism of ultrabasic-basic magma differentiation with formation of continuous peridotite-eclogite series. By experimental data, the differentiation is controlled by reaction of Ol- and Jd-components above 4.5 GPa [2]. As result Ol is disappeared and Grt formed. Liquidus reaction point Ol+Jd-Cpx = Grt+L operates effectively in Ol elimination along the univariant curve Ol+Cpx+Grt+L that brings residual melts compositions into the Cpx-Grt join. The join is a commonplace for all the peridotite and eclogite simplexes. Here “peridotite-to-eclogite tunnel” mechanism is proved and makes the round the thermal eclogitic barrier. As a result, it paves the way for continuous fractional crystallization of ultrabasic-basic magmas and transfer from Ol-bearing peridotite to Coes-bearing eclogite rocks. Differentiation of the carbonatite melts parental for diamonds and primary inclusions.

By experimental evidence, a changeable composition of the carbonatite parental melts for diamond and inclusions is based on peridotite<sub>30</sub>carbonatite<sub>70</sub>-eclogite<sub>35</sub>carbonatite<sub>65</sub>-carbonatite system [3]. Differentiation of parental melts is controlled by “peridotite-to-eclogite tunnel” mechanism associated with carbonatization of peridotitic Mg-components. Fractional differentiation is responsible for formation of diamond-hosted mineral inclusions for peridotite and eclogite parageneses. *Support*: RFBR grant 11-05-00401.

[1] O’Hara (1968) *Earth-Sci. Rev* 4, 69-133. [2] Gasparik & Litvin (1997) *Eur. J. Mineral.* 9, 311-326. [3] Litvin *et al.* (2012) *Geochem. Internat* 9, 726-759.