Fractionation of Cu isotopes during adsorption and metabolic uptake by bacteria

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Here we use Cu isotopes (measured as the ratio of $^{65}Cu/^{63}Cu$ and reported in delta notation relative to the NIST 976 standard) as a tool to investigate Cu-bacteria interactions, including surface adsorption and metabolic uptake. Experiments were conducted with individual Gram-positive (*Bacillus subtilis*) and Gram-negative (*Escherichia coli*) bacterial species and with bacterial consortia from several natural environments. Adsorption experiments were conducted with live or dead cells over the pH range 2.5 to 6 (to prevent precipitation of Cu). Surface adsorption of Cu onto live bacteria cells resulted in separation factors ($\Delta^{65}Cu_{solution\text{-}solid} = \delta^{65}Cu_{solution} - \delta^{65}Cu_{solid}$), of +0.25‰ to +1.3‰ for *B. subtilis* and +1.0‰ to +2.4‰ for *E. coli*. The preference of the lighter Cu isotope in the cells appears to be metabolically-driven, as heat-killed bacterial cells preferentially adsorbed the heavier Cu isotope. Furthermore, the $\delta^{65}Cu_{solution}$ of the live cell adsorption experiments evolved as a function of time, despite the fact that the total amount of adsorbed Cu remained constant. Bacteria in the metabolic uptake experiments (i.e. grown in Cu-citrate-rich media) preferentially incorporated the lighter Cu isotope with a $\Delta^{65}Cu_{solution\text{-}solid}$ of ~ +2.0‰. Our results demonstrate that live bacterial cells preferentially sequester the lighter Cu isotope regardless of the experimental conditions. The mechanisms involved are likely related to the active cellular transport and regulation of Cu. Hence, Cu isotopes may prove to be powerful tools for probing molecular-scale bacteria-Cu interactions. Conversely, Cu isotopes in natural systems may be used distinguish bacterial activity.

Sources of diamond-forming fluids

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Diamond-forming fluids trapped as microinclusions in fibrous diamonds are a unique samples of mantle fluids to which inferred metasomatic fluids can be compared. The major-element composition and volatile content of these high-density fluids (HDFs) span two arrays: (a) between a high-Mg carbonatitic end member and a saline one and (b) between a low-Mg carbonatitic end member and a hydrous-silicic one; and are attributed to melting of carbonated peridotite and carbonated eclogite, respectively [1]. All four end-members are rich in K_2O and in the highly incompatible trace elements (alkalies, LILE, LREE, Nb and Ta).

A closer examination of the trace elements between Cs and La reveals two patterns. One is mostly flat and has moderate decrease of concentrations with decreasing ionic radius ('Bench'); the other ('Table') has elevated Ba, U, Th and LREE, depleted Nb and Ta and in most cases, highly depleted alkalis (K, Rb and Cs). The two can be best distinguished by their U/Rb and La/Nb ratios. Both patterns were found in HDFs of both arrays suggesting decoupling between the major and trace elements.

The smooth 'Bench' pattern can be approximated by very small degree of melting of a PM or OIB source with no need for accessory phases. The more fractionated 'Table' pattern can be produced by melting of a SCLM source with ~1% carbonate and ilmenite and 0.5% phlogopite and rutile. It cannot be produced by melting a PM source.

Looking for a possible relation between the two patterns, we examine the possibility to produce 'Tables' from 'Benches' by fractional crystallization or percolation. The first requires the removal of more than 80% phlogopite, which is not compatible with the major element data. Percolation of a melt with a 'Bench' pattern through SCLM rocks with the above accessory phases also lead to evolution of a 'Table' pattern.

Conclusion: the 'Bench' patterns can be produced by melting an asthenospheric source and the 'Table' by melting of SCLM or by percolation of 'Bench'-like fluids through SCLM rocks. In either case, melt must be collected from a large volume to explain the similarity in patterns and the uniform carbon-isotope composition of fibrous diamonds.

[1] Weiss *et al*. (2009) *Lithos* **112**, 660–674.