No evidence of diffusive homogenisation of carbon isotopes in Yakutian diamonds

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C-N isotopes of diamonds are potentially useful in establishing the source and temporal evolution of C-bearing fluids in the mantle. Complex growth forms revealed by CL images indicate that many diamonds grew under varying conditions. However, using C-N isotopes to probe the evolutionary history recorded in succesive growth bands is only of use if there is no diffusive equilibration at the µm scale. Little information is available about carbon diffusion. Harte *et al*. (1999) suggested that diffusion potentially homogeneises C in diamonds due to their long residence in the mantle. Hauri *et al*. (2002) and Bulanova *et al* (2002), however, argued that diffusion was insuffucient to equilibrate C in Yakutian diamonds at the 50 µm scale .

Here we report SIMS data with high spatial resolution (<30 µm, spot size 20 µm) on traverses across <110> plates of Yakutian diamonds. Most diamonds, of both P- and E- type paragenesis, have $\delta^{13}C$ between -8‰ and -2‰ close to that of ambient asthenospheric mantle. Variation in $\delta^{13}C$ in excess of 1‰ is found between successive growth bands in 5 of the 11 stones studied to date, indicating a punctuated growth history (SIMS reproducibility ±0.2‰). Diamond 1703 from Mir records a remarkable 10‰ difference in $\delta^{13}C$ between the octahedral core and rim. A traverse conducted at a 40° angle to the contact established that there is no resolvable diffusive exchange between the succesive growth bands at 30 µm scale. We therefore conclude that C isotope diffusion is non-existant at the 30 µm scale and that $\delta^{13}C$ variations in succesive growth bands do record information about the composition of the C-bearing fluids that formed diamonds. SIMS N isotope data from the Yakutian samples is underway to characterise the coupled C-N isotope variations of these crystals.

References

Bulanova, G.P. *et al*., 2002. *Chemical Geology*, **188,** 105-123.
Harte, B. *et al*., 1999. *Mineralogical Magazine*, **63,** 829-856.
Hauri, E.H. *et al*., 2002. *Chemical Geology*, **185,** 149-163.

Insights into enzymatic reduction of metal-oxides from single-molecule tunneling studies of multiheme cytochromes

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We have performed recent experiments that aim to elucidate the molecular mechanisms of enzymatic bacterial metal reduction by studying purified multiheme cytochromes (OmcA, MtrC) from *Shewanella oneidensis* MR-1 with single-molecule electron tunneling spectroscopy. Enzyme-mediated direct electron transfer (ET) between metal-reducing bacteria and mineral surfaces is a prominent environmental redox process that directly and indirectly influences subsurface geochemistry. By developing a means to chemically adsorb cytochromes to a solid surface, tunneling spectroscopy showed distinctly different conductance for OmcA and MtrC (Wigginton *et al*, 2007) indicative of two different surface-directed electron tunneling mechanisms for these proteins (Wigginton *et al*, submitted). The data suggest that one or more heme groups in MtrC participate in ET, and therefore MtrC may be tuned to a specific redox potential for biological function. In contrast, OmcA may function as a non-specific multi-pathway reductant of mineral surfaces because the tunneling spectra suggest that superexchange ET is the predominant mechanism. We are further scrutinizing this difference by using a novel configuration for biomolecule scanning tunneling microscopy (STM) to determine if MtrC and OmcA show different distant-dependent tunneling behavior. This configuration uses an insulated Au STM tip functionalized with cytochromes to systematically vary the separation distance between the cytochromes and a hematite surface. These experiments, performed as a function of solution chemistry, are also designed to provide specific information on the effects of pH, ionic strength, and electrolyte compositions on ET efficiency.

References

Wigginton N.S., Rosso K.M., Lower B.H, Shi L., and Hochella M.F. Jr. (2007) *Geochim. Cosmochim. Acta* **71**, 543-555.
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