

Large exchange through the 660km discontinuity: Evidence from C- and N- isotopes in super-deep diamonds

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Diamond provides a unique opportunity to sample parts of the mantle that remain inaccessible by any other means. Some mineral associations in diamond, such as majoritic garnet, calcic and magnesian perovskite and manganoan ilmenite with ferroperricite have been recognised as originated from the transition zone down to the lower mantle (Stachel *et al.* [1]; Kaminsky *et al.* [2]). In addition, nitrogen is potentially a good tracer for mantle geodynamics. Exchanges between an inner reservoir (characterised by negative $\delta^{15}\text{N}$) via degassing at oceanic ridges with an outer reservoir (characterised by positive $\delta^{15}\text{N}$) via recycling at a subduction zones can lead to nitrogen isotopic contrast in a stratified mantle.

Taking advantage of the rather common occurrence super-deep mineral inclusion assemblages in diamonds from Juina (Brazil) and Kankan (Guinea), we carried out a detailed study of C and N-isotopes. There are broadly similar ranges of $\delta^{15}\text{N}$ between upper (UM) and lower (LM) mantle diamonds from +3.8‰ down to -8.8‰ and from +9.6‰ down to -39.4‰ for respectively Juina and Kankan diamonds. Both sets of results suggests extensive material-isotopic exchange through the 660km discontinuity, this contrast with the existence of isolated lower mantle. Most of $\delta^{15}\text{N}$ values are negative and in the present upper mantle range with the exception of 3 Kankan diamond values down to -39.4‰. These very low $\delta^{15}\text{N}$ are compatible with primitive material and provide evidence that mantle has kept heterogeneities.

Three zoned super-deep diamonds demonstrate large $\delta^{13}\text{C}$ variations with parts which are typical of their local transition zone $\delta^{13}\text{C}$ value. Most likely these diamonds have initiated their growth in the LM and following slow uplift in a convective mantle have equilibrated in the TZ, and in doing so show an evolution in carbon isotopic composition.

Therefore the C- and N- independent isotopic tracers provide evidences that a significant amounts of material are exchanged across the 660km discontinuity.

[1] Stachel *et al.*, 2000. *CMP* **140**, 16-27. [2] Kaminsky *et al.*, 2001. *CMP* **140**, 734-753.

Biomarkers for methane cycling: From marine to terrestrial settings

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Lipid biomarkers derived from methanogens (e.g. archaeol and other ether lipids) and methanotrophs (e.g. specific bacteriohopanoids) have shown potential in the investigation of methane biogeochemistry. To develop this approach, we have determined these biomarkers' distribution and isotopic composition in a range of settings, including marine sediments, wetlands and permafrost. Controls on biomarker concentrations are evaluated, and the potential for examining ancient methane cycling is discussed.

Archaeol and hydroxyarchaeol are common in Archaea and are expected to occur in the diverse settings such organisms inhabit. However, both compounds are absent or undetected in most environments, including surface marine sediments, dry and aerated soils, and shallow peat and permafrost. Instead, significant quantities of ether lipids are limited to 'classical' archaeal settings: extreme environments or hotspots of methane cycling. The latter include water-saturated soils and peat, marginal marine sediments below the sulfate-methane transition zone, and even the faecal material of ruminants. This suggests the potential for using archaeal lipids to quantify methanogen biomass and interrogate methane biogeochemistry. Indeed, archaeol concentrations across all settings are apparently dictated by the same environmental controls that govern methanogenesis rates, including for example, water saturation of soils, temperature and the bioavailability of organic matter.

We have explored the potential for applying these compounds as methane-cycling proxies to ancient settings. Archaeol occurs in organic-rich Paleocene sediments and Pliocene sedimentary cycles from the Benguela upwelling system, and in both cases its concentration dramatically increases in response to elevated organic matter contents. Archaeol is also present in thermally immature lignites; intriguingly, its concentration is much higher in Eocene deposits suggesting elevated rates of methanogenesis during past warm intervals. Despite this potential, further work must be underpinned by quantification of intact polar lipids, experimental testing of observation-based inferences and integration with other approaches.