Nature of fluids in the deep mantle (>300km) inferred from a carbon and nitrogen micro-analytical study of a single ultra-deep diamond from Kankan, Guinea

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The nature of the deep mantle, especially the transition-zone, is a topic of very broad interest to solid Earth geochemists and geophysicists. Data on actual samples from this region are extremely scarce. Diamonds are derived from the base of the lithosphere down to the lower mantle (>660km) and provide a unique opportunity to sample this region of critical rheological and chemical changes in the Earth. In order to evaluate the nature of fluids percolating through the transition zone, we present the first carbon and nitrogen isotope micro-analytical study of a deep-diamond (Kankan, Guinea) by Secondary Ion Mass Spectrometry (SIMS). This diamond contains a single $CaSiO_3$-walstromite inclusion, presumed to represent retrogressed former $CaSiO_3$-perovskite and hence indicative of an ultra-deep (lowermost transition zone to lower mantle) paragenesis. The large size of the diamond allows to investigate variability in the diamond growth medium along detailed traverses. Combined C-N isotope and N abundance measurements allow us, for the first time, to place strong constraints on the nature of the parental fluid for an ultra-deep diamond.

Carbon isotopic compositions show a small but systematic decrease of $\delta^{13}C$ values from the core to the rim of the diamond. $\delta^{15}N$ is negatively correlated with $\delta^{13}C$, whereas nitrogen abundances show a positive correlation. These co-variations in $\delta^{13}C$-$\delta^{15}N$-[N] are consistent with open system isotopic fractionation where the isotopic and elemental evolution of the fluid is related to diamond crystallisation. The speciation of carbon and nitrogen of the fluid precursor of this deep diamond may be constrained through modelling of these co-variations. Such modelling indicates diamond growth from a reduced, CH_4-bearing fluid, with nitrogen behaving compatibly. Due to uncertainities in $\delta^{15}N$, we cannot constrain whether nitrogen was present in the fluid phase as N_2 or the NH_4^+. Although the origin of the diamond forming fluid (subducted or mantle material) is still a matter of debate, these results have fundamental implications for the fO_2 in the deep mantle and the deep volatile cycle of the Earth.

A critical evaluation of TEX_{86} derived sea surface temperatures in the Paleogene

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The application of glycerol dialkyl glycerol tetraether (GDGT) based sea surface temperature proxies (e.g. TEX_{86}) has brought about major advances in our understanding of Cenozoic climate. However, TEX_{86} approaches yield very high temperatures at high latitudes during Paleogene hyperthermals, and the resulting low latitudinal temperature gradients challenge our understanding of the physical climate system. Here, we examine existing TEX_{86} data and revisit the modern calibration dataset. A comparison of TEX_{86} SST estimates to those derived from oxygen isotopes or Mg/Ca ratios of well preserved 'glassy' planktonic foraminifera reveals a strong correlation between foraminiferal and GDGT-based approaches, but the latter are 4-6°C warmer. We have also compared TEX_{86} SST estimates from shelf sea settings to associated continental mean air temperatures (MAT) derived from soil bacterial GDGTs (the MBT/CBT index). Again, the two approaches exhibit a strong correlation but with the former yielding 4-6°C warmer temperatures. Intriguingly, SSTs derived from the recently proposed TEX_{86}^L approach are lower and consistent with foraminifera-based approaches and MBT/CBT derived MATs.

We also developed SST records from multiple sites in the SW Pacific, in order to place hyperthermal SST estimates into a longer-term Paleogene context. Our estimates indicate that sea floor and sea surface temperatures increased by 10°C or more from late Paleocene (18 to 23°C) to early Eocene times (30-32°C). MBT/CBT-derived MATs broadly parallel the SST trends, but with 4-6°C lower values throughout the entire sequence. These records suggest that elevated high southern latitude SSTs are reproducible at multiple sites and do document the relative long-term Paleogene climate evolution recorded by benthic foraminifera and inferred from faunal and floral assemblages.

Combined, these two lines of evidence indicate that high latitude EECO temperatures were indeed significantly higher than those of today, but they also suggest that the specific estimates could be as much as 4-6°C too warm. There are multiple explanations for this, but one possibility is an oceanographic and/or ecological control on the GDGT assemblages exported to sediments, an explanation that could also explain the unexpected offset between SSTs derived from TEX_{86}^L compared to other calibrations. Specifically, the offset in both ancient and modern settings is associated with low GDGT-2 to GDGT-3 ratios. In contrast to previous inferences, those low ratios are not limited to cold regions and in fact are associated with shallow water settings and upwelling zones. We propose that this reflects depth-dependant differences in GDGT distributions that are manifested differently in the various TEX_{86} calibrations, with some reflecting primarily shallow water signatures and others reflecting integration over a greater depth range.