3.7 billion year old biogenic remains

T. Hassenkam and M. T. Rosing

Nano-Science Center, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark; Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark

ABSTRACT

3.7 Billion year old inclusions inside garnet crystals contain $^{13}$C depleted carbonaceous material consistent with biogenic origin. Additional evidence in the form of the other elements of life mainly O, N and P were found to be structural bound to this material by using a new technique, AFM-IR. Here we show additional evidence that support our claim. By overlaying maps generated by the AFM-IR we show how the location of 100's of nm sized contiguous domains of nitrile and possibly phosphonate overlap inside the inclusion. This shows that O, N and P are not only co-localized to the same inclusion but they are co-localized to the same patch of carbonaceous material inside the inclusion. They therefore provide spatial characterization for potentially the oldest biogenic remains in Earth’s geological record and corroborates earlier claims for the biogenic origins of carbon in Isua metasediments.

KEYWORDS

AFM-IR; Isua supercrystal belt; nitrile; phosphonate; remains of early life

3.7 billion years old metasedimentary rocks from Isua, West Greenland contain trails of carbonaceous compounds, with isotopic ratios consistent with biogenic origin. The carbonaceous material form trails of contiguous inclusions across Metamorphic garnet crystals inside the host rock. We have recently shown how the other elements of life (mainly oxygen, nitrogen and possibly phosphor) is structurally bound to this carbonaceous material that has been trapped inside these inclusions since their formation 3.7 billion years ago. By in situ infrared absorption with a spatial resolution in nanometer regime within these inclusions we have generated spectra and maps showing the distribution of nitrile and the presence of oxygen in form of anhydride and carboxyl groups and possibly phosphor in the form of phosphonate. These results were found to be consistent with biogenic material isolated for billions of years.

The instrument used for generating the maps and spectra shown here and in the original manuscript was an atomic force microscopy (AFM) equipped with a tuneable IR (infrared) laser (AFM-IR) that is able to record IR absorption information with nanometer resolution on surfaces suitable for AFM.

Figure 1 shows part of an inclusion found inside a garnet crystal (Fig. 1a). The internal surface inside the inclusion was covered with 100–500 nm thick carbonaceous material. In Fig. 1b we have displayed an IR absorption map consistent with nitrile (2230 cm$^{-1}$) (green most intense) combined with IR absorption consistent with phosphonate (960 cm$^{-1}$/1270 cm$^{-1}$) (red/pink most intense). The primary absorptions for phosphonate at 1040 cm$^{-1}$ and 1160 cm$^{-1}$ was for technical reasons too intense for making maps.

The maps suggest that the distribution of the two compounds was heterogeneous inside the inclusion since for most regions of the carbonaceous material inside the inclusion there was either none or only traces of either nitrile or phosphonate. But in some patches, there was a high IR absorption in distinct domains ranging from 100 nm to 1 μm across. These high absorption domains for the two compounds roughly overlapped, so on the map there was roughly three distinct patches approximately 1 μm across where the density of the compounds was increased compared to the background level.

Also, shown in the figure (Fig. 1c) are two spectra recorded where the two types of compounds were co-located. In the plot, we have shown the intensity on a logarithmic scale since the absorption consistent with phosphonate was very intense. The position of the absorption peaks in the spectra consistent with phosphonate bonded to aromatic molecules is around 960, 1040, 1160, 1270 cm$^{-1}$, most of which are present in both
spectra. In spectra S1 there is also an absorption at 1660 which could be caused by C–C bonds. In these two spectra, there was no evidence for anhydride or carboxyl groups at 1824 cm$^{-1}$ and 1720 cm$^{-1}$ respectively, so the oxygen was only found with the phosphonate. Finally, the absorption for nitrile can be found at 2230 cm$^{-1}$.

In the original paper, we concluded that the structural binding of nitrogen, oxygen and phosphorous to the carbonaceous material inside the inclusions was evidence for biogenic origin of the carbonaceous material. The map shown in Fig. 1 not only demonstrate that nitrogen, oxygen and phosphor were structurally bound to the carbonaceous material inside the inclusion but the compounds were in this case co-located in patches approximately 1μm across. This co-localization of the compounds was not just in the same inclusion but in the same patch of carbonaceous material inside the inclusion which therefore lends further support to the biogenic origin of this material.

**Disclosure of potential conflicts of interest**

No potential conflicts of interest were disclosed.

**Funding**

The research was supported by the Danish National Research Foundation (DNRF; fund number DNRF53) to Nordic Center for Earth Evolution. The research was performed by support from the NanoGeoScience group.

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