Carbonaceous inclusions from the oldest sediments on Earth

Magnus Harding[1,2], Austin Jarl Boyd[1], Sandra Siljeström[3], Madina Shamsuyeva[4], Pooyan Aliuos[4], Minik Rosing[1], Tue Hassenkam[1]
[1]Globe Institute, University of Copenhagen, Copenhagen, Denmark, [2]Sino-Danish College (SDC), University of Chinese Academy of Sciences, Beijing, China, [3]RISE Research Institutes of Sweden, Stockholm, Sweden, [4]Institute of Plastics and Circular Economy IKK, Leibniz University Hannover, Hannover, Germany

Background incl. aims:
The Isua Supracrustal Belt in Southwest Greenland contains rocks which are at least 3.7 billion years old, and are among the oldest rocks on Earth. Sediments found here display contiguous horizons of carbonaceous material parallel with sedimentary bedding planes (Rosing 1999). This material, present as graphitic carbon, has been proposed to be some of the oldest remnants of life on Earth, inferred based on its mode of occurrence, carbon isotope ratios, its association with heteroatoms such as nitrogen, oxygen, phosphorous and iron, and from the nanoscale crystal structure (Ohtomo et al. 2014, Hassenkam et al. 2017), evidence which is all compatible and together suggestive of an origin of the graphitic material as biogenic pelagic detritus.

In certain places, the graphite is enclosed in secondary metamorphic minerals such as garnets. This graphite occurring as inclusions has been targeted by previous studies, which also identified certain viscous fluid inclusions. The study presented attempts to characterize the chemistry of these fluid inclusions occurring alongside the graphitic material within garnet porphyroblasts.

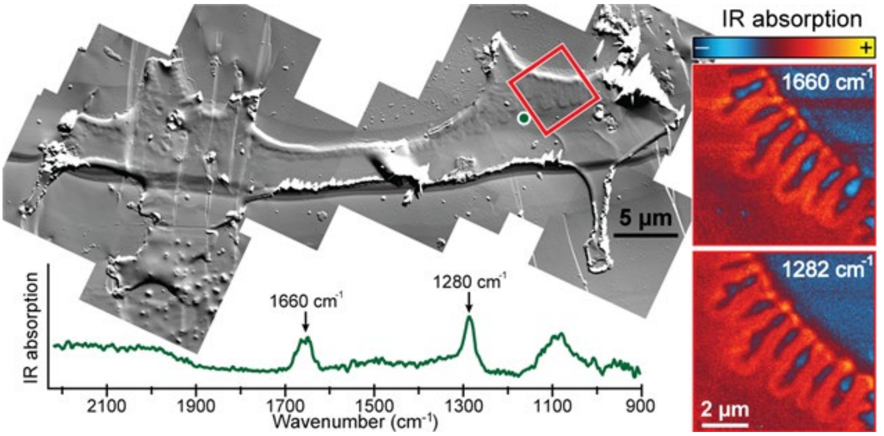
Methods:
In this study, the liquid inclusions are accessed by breaking open the garnets and their residues are subsequently characterized using atomic force microscopy (AFM), as well as infrared spectroscopy coupled to AFM (NanoIR). Optical photothermal infrared spectroscopy (O-PTIR) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are also used to characterize the chemistry of the inclusion residues and to assess their association with the solid graphitic inclusions.

Results:
Using AFM-based infrared spectroscopy, we obtain infrared absorption spectra from just the inclusion at a high spatial resolution. The liquid inclusion residues are ubiquitously characterized by infrared absorption at wavenumbers 1280 cm-1 and 1660 cm-1, interpreted as the C-N and C=O vibrational absorption from amide-like functional groups. Similarly, ToF-SIMS shows secondary species containing C, N and O from the inclusion residues. O-PTIR shows how the amide-like infrared absorption signal can be traced along horizons of graphitic material.

Conclusion:
This study shows how infrared spectroscopical methods coupled to optical and scanning probe microscopy methods can be used to characterize the chemistry of minute domains of ancient carbonaceous material occurring as inclusions in garnet porphyroblasts. The observations from NanoIR were corroborated by ToF-SIMS analyses. Together, these methods indicate that the carbonaceous material consists of C, N, and O-rich material in an amide-like configuration.

The chemistry of the inclusions is consistent with that which would be expected from degraded biogenic matter. Together with previous studies, this is highly suggestive of a biological origin for the carbonaceous material found in the oldest sediments on Earth.

Graphic:



Keywords:

AFM, IR-spectroscopy, ToF-SIMS, early life

Reference:

Rosing, M.T., 1999. 13C-depleted carbon microparticles in ≥3700-Ma sea-floor sedimentary rocks from west Greenland. Science 283, 674–676.
https://doi.org/10.1126/science.283.5402.674
Ohtomo, Y., Kakegawa, T., Ishida, A., Nagase, T., Rosing, M.T., 2014. Evidence for biogenic graphite in early Archaean Isua metasedimentary rocks. Nature Geoscience 7, 25–28.
https://doi.org/10.1038/ngeo2025
Hassenkam, T., Andersen, M.P., Dalby, K.N., Mackenzie, D.M.A., Rosing, M.T., 2017. Elements of Eoarchean life trapped in mineral inclusions. Nature 548, 78–81.
https://doi.org/10.1038/nature23261