3.2.12

Characterization of the organic matter in an Archean chert (Warrawoona, Australia)

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To address the question of the origin of life on Earth, a special attention has been paid to the carbonaceous matter in the oldest Archean rocks. The discovery of microstructures in cherts from the Warrawoona Group, considered as the oldest microfossils on Earth (3.465 Byr) created a considerable interest in the organic matter (OM) contained in this deposit. However, the biogenicity of this OM has been recently challenged, emphasizing the need of reliable biomarkers in such ancient OM. In this study, the OM isolated from a chert of the Towers Formation in the Warrawoona Group was analysed using a combination of microscopic and spectroscopic techniques.

High resolution transmission electron microscopy (HRTEM) reveals a rather low level of organization in the polyaromatic network of this OM. However, the average size of the polyaromatic layers is quite large. Electron paramagnetic resonance (EPR), which aims at studying free radicals, shows, in agreement with HRTEM, that the OM in the Warrawoona chert has not reached the graphite stage. The EPR parameters of this chert can be mimicked by submitting cherts of biogenic origin to a thermal stress. These parameters are similar to those of terrestrial kerogens and indicate a substantial level of heteroelements in the free radicals. The FTIR spectrum of the OM shows an aliphatic absorption. The pattern of this band is similar to what is usually observed in mature terrestrial kerogens and sharply differs from the typical one observed either in the interstellar medium or in meteorites pointing to a lower CH_3/CH_2 ratio. Solid state ^{13}C NMR, performed for the first time on this type of material, reveals that the OM of the Warrawoona chert is highly aromatic and confirms the occurrence of C-O or C-N functions and of aliphatic chains.

The combination of the aforementioned analytical techniques reveal that the OM of this Archean chert has not reached the graphite stage and that its chemical structure is based on a macromolecular network of large polyaromatic units with a substantial contribution of heteroelements and aliphatic chains. Although consistent with a biological origin and different from that of the insoluble OM of meteorites, this chemical structure cannot provide definite evidence for excluding an abiotic origin for this chert OM.

3.2.13

Hydropyrolytic release of hopane and sterane biomarkers from 2.7 Ga kerogens

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The indigeneity of molecular fossils in bitumens from late Archean rocks of the Hamersley Province, Western Australia [1] was tested using high-pressure hydrogen pyrolysis (HyPy) to release biomarkers bound in kerogen. HyPy experiments consisted of three steps: 1) thermal desorption (50-340° C), 2) low-temperature pyrolysis (340-500° C), and 3) high-temperature pyrolysis (500-550° C). Hydrocarbon products were collected in a trap downstream of the flow-through reactor bed. After pyrolysis, additional hydrocarbon products were extracted from the residue in the reactor. All products were analyzed for steranes and hopanes using metastable-reaction monitoring (MRM)-GCMS.

Both the thermally desorbed and the pyrolysis products contained traces of sterane and hopane biomarkers having similar composition to biomarkers in associated bitumen. The stereochemistry of these released biomarkers indicates lower maturity compared to the highly mature biomarkers in bitumens. In particular, 1) $\alpha\alpha\alpha$-20R dominate C_{27-29} steranes, 2) the thermally unstable C_{27-29} $\beta\alpha\alpha$-20R isomers are present, and 3) %$\beta\alpha$-hopanes are elevated compared to bitumens. Kerogen-bound hopanes and steranes released by pyrolysis and chemolysis methods routinely comprise a less mature distrbution than their free counterparts. Thus, the difference in maturity of HyPy products compared to bitumen is consistent with the presence of bound biomarkers in late Archean kerogens. These results are most consistent with a sygenetic relationship between biomarkers and associated kerogens, giving credence to biomarker-inferred presence of cyanobacteria and eukaryotes in late Archean ecosystems [1].

Rearranged hopanes and steranes are also present in the HyPy products, suggesting the presence of residual bitumen in kerogens. Moreover, products of the pyrolysis residue contained 1) 99.5% of an internal standard added to the kerogen before pyrolysis and 2) a high relative abundance of biomarkers. These results indicate that HyPy products released at all stages could be occluded within the pseudo-graphitic matrix as opposed to being covalently bound.

References

[1] Brocks J. J., Logan G. A., Buick R., and Summons R. E. (1999) *Science* **285**, 1033-1036.