EPSC Abstracts
Vol. 8, EPSC2013-115, 2013
European Planetary Science Congress 2013

Biogenicity and syngenicity in archean cherts

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Abstract

This study aims at determining biogenicity and syngenicity markers for Archean cherts. To this end, we studied the kerogens from nine cherts of various ages (Devonian to Archean), localities and metamorphic facies through a combination of microscopic, spectroscopic and pyrolytic methods. All samples were shown to be in the carbonization stage without having reached the graphitization one. The presence of a significant aliphatic component in the kerogen appears as a prerequisite for applying the biogenicity marker previously proposed from pyrolysis [1]. The correlation between the age of Precambrian samples and the shape of their EPR signal previously proposed [2] was further corroborated and shown not to be influenced by metamorphism. Although lineshape analysis alone does not allow contamination detection, this is made possible through cumulative thermal treatment performed in parallel.

1. Introduction

The main two challenges in the study of the organic matter (OM) from the most ancient rocks on Earth (such as the Archean cherts) are to establish their biogenicity and syngenicity. Indeed, ancient geological materials may have been contaminated through geological time. Thus, establishing the syngenicity of the organic matter embedded in a mineral matrix is a crucial step in the study of very ancient rocks. Pyrolysis-GC-MS was recently proposed as an emerging technique for establishing biogenicity of 3.5 Gyr old insoluble organic matter in cherts [1] and the electron paramagnetic resonance (EPR) lineshape of the OM was shown to be related to the age of the chert [2]. In the framework of a larger study aiming at testing the general potential of this approach, we investigated the chemical structure of the OM from a set of nine cherts of various ages (Devonian to Archean), localities and metamorphic facies. Their corresponding kerogens were analyzed by elemental analysis, ^{13}C Nuclear Magnetic Resonance spectroscopy, Raman spectroscopy, EPR spectroscopy, High Resolution Transmission Electron Microscopy and Pyrolysis-Gas Chromatography-Mass Spectrometry.

2. Results

This multi-technique analysis showed that the carbon in all the chert samples fall into the carbonization stage and has not undergone graphitization (Fig. 1). Moreover, for samples of Archean age, the influence of time seems predominant over that of temperature in this kinetically-driven process. Therefore, for the case of well-preserved Archean samples, the notion of geothermometry is no longer suitable. We also showed that determination of biogenicity by pyrolysis-GC-MS requires the presence of a significant aliphatic component, otherwise fatty acid decarboxylation may bias the *n*-alkane distribution. However, in most cases, mature samples such as Archean cherts usually do not have such an aliphatic fraction, thus pointing to the limits of this approach and the need for another biogenicity marker.

A correlation between the age of Precambrian samples and the shape of their EPR signal (from Gaussian to Lorentzian and SupraLorentzian) was established and statistically tested for a large set of cherts having a metamorphic grade no higher than *greenschist* (i.e. before the graphitisation domain), thus making the previously proposed correlation more robust. As thermal treatments impact organic matter maturity, the effect of temperature on this syngenicity proxy was studied. Furthermore, the possible effect of metamorphism on this proxy was ruled out for the chert samples older than 2 Gyr that we analysed, based on the study of Silurian cherts having the same age but various metamorphic grades. We determined that even the most metamorphosed sample did not exhibit the SupraLorentzian lineshape typical for an Archean sample. In the hope of detecting organic contamination in Archean cherts, a "contamination-like" mixture was prepared and studied by EPR. This showed that lineshape analysis alone does not allow contamination detection and that cumulative thermal treatment needs to be performed in parallel. Such treatment was applied to three Archean chert samples, making dating of their carbonaceous matter possible. EPR thus appears as a powerful tool to study primitive organic matter and could be used in further exobiology studies on low-metamorphic grade samples (from Mars for example).

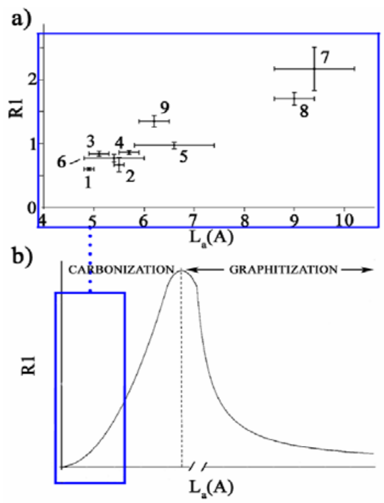

Figure 1: Evolution of Raman R1 ratio [I(D1)/I(G)] vs polyaromatic layer extent La directly imaged by High resolution Transmission Electron Microscopy. The studied Archean samples are gathered in the blue rectangle, indicating they were only carbonized

References

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