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Analysis of single Precambrian oil-bearing fluid inclusions as a way of constraining evolution of eukaryotes

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Organic molecular fossils, such as steranes, which were found in 2.5-2.7 billion-year-old bitumens in Western Australia are the oldest purported evidence for eukaryotes. These steranes together with methylhopanes, which are indicative of cyanobacteria, are also among the oldest evidence for the presence of oxygen on Earth. However, the syngeneity of these organic biomarkers with the host rock has recently been questioned and the biomarkers may in fact be later introductions to the rock.

A type of sample where biomarkers are better constrained in the rock is oil-bearing fluid inclusions, which consist of small amounts, typically picoliters or less, of oil trapped inside a mineral matrix. Hopanes and steranes have been detected in 2.2 billion-year-old oil-bearing fluid inclusions from Elliot Lake, Canada. The analytical approach consisted of crushing the samples (that contained multiple inclusions), followed by solvent extraction of the organic content and gas chromatography mass spectrometry (GC-MS) analysis. However, due to the frequent occurrence of multiple generations of inclusions even in small rock samples, bulk crushing may yield information that is not well constrained with respect to age and organic content. It would, therefore, be more advantageous if single oil-bearing inclusions could be successfully selected and analysed. In addition many Precambrian oil-bearing fluid inclusions are so small (less than 10μm), oil-poor and few that analyzing with conventional techniques is not possible. Here we present an approach employing time-of-flight secondary ion mass spectrometry (ToF-SIMS) to selectively open individual oil-bearing inclusions by C60+ ion etching, and to subsequently analyse their content for steranes and hopanes.

To develop the approach, a number of Ordovician oil-bearing inclusions (15-30μm) from hydrothermal veins in the Siljan impact structure, Sweden, were analysed. The method consists of the following steps: i) localization of a suitable inclusion in a polished thin section using optical microscopy, ii) opening of the inclusion by ion etching with a focused C60+ beam inside the ToF-SIMS instrument while recording in real-time the opening of the inclusion and, iii) mass spectrometric analysis of the exposed inclusion contents with ToF-SIMS. ToF-SIMS spectra from the analysed inclusions showed a large number of organic peaks that are characteristic for crude oils, including all major diagnostic peaks for several hopanes and steranes.

The developed approach has now been applied on Precambrian samples. Four different oil-bearing fluid inclusions trapped in a 1.43 Ga sandstone from the Roper Superbasin in Northern Australia were opened and analysed with ToF-SIMS. The ToF-SIMS spectra of the oil in the different inclusions were very similar to each other, indicating that the same oil was trapped in all inclusions. The spectra were characterized by high portion of peaks indicating aromatic moieties. In addition the ToF-SIMS spectra also contained peaks that could be assigned to alkanes, cycloalkanes, steranes and hopanes. This is similar to the result obtained when crushing the same sample except for the detection of steranes. The detection of steranes is significant as steranes indicate presence of eukaryotes and presence of pockets of oxygen during a time when the ocean was likely dominated by anoxia. If applied to other Precambrain sample this approach could help to answer questions regarding early evolution of life on Earth, including the first appearance of the eukaryotes on Earth.