A NEW METHOD FOR STUDYING EVOLUTION OF EUKARYOTES – TOF-SIMS ANALYSIS OF STERANES AND HOPANES IN SINGLE OIL-BEARING FLUID INCLUSIONS. S. Siljeström1,2, J. Lausmaa2, P. Sjövall3, C. Broman1, V. Thiel1 and T. Hode4, 1Department of Geology and Geochemistry, Stockholm University, Stockholm, Sweden (sandra.siljestrom@geo.su.se), 2Department of Chemistry and Materials Technology, SP Technical Research Institute of Sweden, Borås, Sweden, 3Geobiology Group, Geoscience Center, University of Göttingen, Göttingen, Germany, 4Department of Geology, Portland State University, Portland, USA.

Introduction: The oldest purported evidence of eukaryotes is represented by organic molecular fossils, such as steranes, which were found in 2.5-2.7 billion-year-old bitumens in Western Australia [1]. These steranes together with methylhopanes, which are indicative of cyanobacteria, are also among the oldest evidence for the presence of oxygen on Earth [1]. 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 [2].

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 [3]. 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 [3]. 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 selectively selected and analysed. Single fluid inclusion analysis has until recently not been possible, due to the small size of most inclusions (5-50µm), including most Precambrian (> 500 million years ago) inclusions. 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.

Results: As a proof-of-concept, 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. The micrographs and the ToF-SIMS ion images collected before, during and after analysis verified that the correct inclusion was opened and analysed, and that all organic signals originated from the inclusion. ToF-SIMS spectra from the analysed inclusions showed a large number of organic peaks that are characteristic for crude oils [4], including all major diagnostic peaks for several hopanes and steranes (Fig. 1). The agreement with respect to mass accuracy (<50 ppm) and fragmentation pattern between these peaks and those observed in spectra from standard samples and from hopanes and steranes in a Siljan seep oil, provide strong evidence for the presence of hopanes and steranes in the analysed single fluid inclusions [5].

Fig. 1. Positive ToF-SIMS spectra of hopane and sterane standards (a, d, g), Siljan seep oil (b, e, h) and Siljan inclusion oil (c, f, i).

To our knowledge, it is the first time hopanes and steranes have been detected in single oil-bearing fluid inclusions. We are currently applying this approach for analysis of single inclusions in Precambrian rocks, in search of organic biomarkers that could help to answer questions regarding early evolution of life on Earth, including the first appearance of the eukaryotes on Earth.