ToF-SIMS analysis of hopanes and steranes in single oil-bearing fluid inclusions

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Hopanes and steranes are key biomarkers when tracking early evolution of life on Earth. A potential contamination-free source of such biomarkers is oil-bearing fluid inclusions as the oil has been secluded from the environment since the the inclusion was trapped. Using extraction-based techniques (GC/MS, LC/MS), it is, however, problematic to assign the extracted biomarkers to specific inclusions, due to the presence of often several generations of inclusions. As yet, it has not been possible to selectively analyse syngenetic inclusions for their biomarker content, because of their small size (5-30 µm in diameter). Here we present an approach employing time-of-flight secondary ion mass spectrometry (ToF-SIMS) to open and directly analyse the picoliter content of individual oil inclusions in petrographic thin sections of the target rocks.

A number of oil-bearing inclusions (20-30 µm in diameter) from hydrothermal veins in the Siljan impact structure, Sweden, were analysed. The approach consisted of the following steps; i) localization of a suitable inclusion in a thin section using optical microscopy, ii) opening of the inclusion by ion etching with a C_{60}^+ sputter gun inside the ToF-SIMS instrument while recording in real-time the opening of the inclusion and, iii) 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 [1], including all major diagnostic peaks for several hopanes and steranes.

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

[1] Siljeström *et al.* (2009), *Organic Geochemistry* **40**, 135-143.

Geochemistry of stream sediments from an abandoned Sn-W mine area, northeast Portugal

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The Mina da Ribeira is an abandoned Sn-W mine located in northeast Portugal. The mineralized quartz veins contain cassiterite + wolframite + scheelite + pyrite + arsenopyrite + sphalerite + chalcopyrite + manganocolumbite + bismuthinite. The rejected materials and tailings were deposited in the northern-margin of a stream (Ribeira de Viveiros), which cross the mining area and is affluent of the Sabor River. A small stream crosses the tailings deposit. The stream sediments were collected along the Ribeira de Viveiros, in the small stream, in the Sabor River and in other streams not affected by mine workings, to follow the mine contamination along the Ribeira de Viveiros and in the Sabor River (1km away from the rejected materials).

The results show that the highest contents of Cu, Zn, As, Nb, Sn, Sb, Ba, Ta, W, Pb and Bi occur in the sediments of the small stream crossing the tailings and in the sediments of the Ribeira de Viveiros, located downstream the mining area. The sediments of the Sabor River show enrichment to the regional sediments higher than 35% for Cu, Zn, As, Sn, Sb, W and Bi. The NASC normalized profiles show accentuated positive anomalies for Sn, Cs and W for all the sediments. These anomalies reflect the existence of small mineralizations disperse in the region and the influence of mine workings as they are much higher in the sediments directly related with the mine workings and in the Sabor River sediments. These and those directly related to mine workings also show a pronounced positive anomaly for As, not shown in the regional sediments.

The sediments from the small stream crossing the tailings deposit show higher La/Lu_n (11.35-14.82) and higher ΣREE (250.34-283.58 ppm) than all the other sediments, which have La/Lu_n=8.68-10.05 and ΣREE=137.71-185.86 ppm.