The use of coupled image analysis and laser-ablation ICP-MS in fission track thermochronology

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Strategies for the interpretation of fission track data from natural minerals, especially apatite, and the quantitative techniques for forward modeling of thermal histories based on data, have advanced enormously over the past two decades. However the actual techniques used to acquire these data have changed little in this time. Moreover the limitations of that data in terms of both quality and quantity are now providing significant constraint on the further development of fission track thermochronology. Two very important technological developments are currently taking place in fission track analysis that are likely to transform the practice of this technique, and are likely to lead to significant improvements in data quality, inter-user consistency and the efficiency of data acquisition.

The first of these is the emergence of autonomous microscopy and automatic image analysis for the recognition and counting of fission tracks in minerals such as apatite [1], along with new tools for the enhanced measurement of fission track lengths. The second is the adoption of Laser-Ablation ICP-Mass Spectrometry for direct determination of ^{238}U abundances in the same mineral grains, in place of the conventional method using neutron induced fission tracks to measure ^{235}U as a proxy.

Switching from the conventional external detector method to using image analysis and LA-ICP-MS means that a new set of analytical and calibration issues must be addressed. These include practical matters such as transfer of grain coordinates from the microscope to the ablation stage, avoiding ejection of etched grains from the mount during laser ablation, and choice of the most appropriate ablation pattern to adequately sample the ^{238}U distribution. In addition a number of analytical strategies such as optimising instrument settings and developing suitable matrix-matched standards must also be resolved. Working solutions to all of these issues have now been developed.

Limitations of the conventional method for fission track analysis include: laborious and demanding procedures, limited counting statistics, and extremely long sample turnaround times due to the required neutron irradiation (typically several months), as well as safety issues due to the handling of irradiated materials. In contrast, the new approach using automated image analysis and LA-ICP-MS can produce better counting statistics, reduced demands on the analyst and dramatically improved sample turn-around times. In addition only one track density need be measured instead of three with the conventional method. Further, the combination of LA-ICP-MS and fission track data opens the potential for routine double-dating using both U-Th-Pb and FT systems, or even triple dating with (U-Th)/He analysis on the same grains . These advances mean that more data can be collected, with greater consistency and much more rapidly, providing higher quality input for thermal history modelling.

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Sulfate reduction and methanogenesis in coal microcosms

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There is considerable interest in stimulating microbial methanogenesis from coal *in situ*, but limited information available on the interactions of the metabolic groups of organisms involved in this process. In most freshwater systems with sufficient sulfate, sulfate reducing bacteria (SRB) will outcompete methanogens for available acetate and H_2 due to their higher substrate affinity and growth yields . However, SRB can function both as fermenters and syntrophically with methanogens in the absence of sulfate , so their role in coal degradation may depend entirely upon reservoir conditions. In this study we examined the role of SRB in methanogenic coal degradation experiments through the use of variable sulfate concentrations (50 µM – 1mM) and metabolic inhibitors (5 mM molybdate for SRB). We hypothesized that with increasing sulfate concentrations SRB would outcompete methanogens for both the acetate and hydrogen resulting from coal fermentation, and that the absence of sulfate, or presence of molybdate, would enhance methanogenesis relative to the uninhibited, sulfate-amended experiments. Results from these experiments suggest that SRB did not outcompete methanogens for available acetate or hydrogen. Roughly 4-6 µmol sulfate was consumed in each experiment amended with sulfate, regardless of its starting concentration. Experiments performed with molybdate and in the absence of sulfate did not produce more methane than experiments amended with up to 1mM sulfate, suggesting that SRB did not compete with methanogens for the same substrate. Changes to the microbial consortium were montitored using qPCR for the mcrA and dsrA genes for methanogens and SRB, respectively, as well as by phospholipid fatty acid (PLFA) and phospholipid ether lipid (PLEL) analysis. Stable carbon isotope analysis of the microbial phospholipids will help to elucidate carbon flow pathways in these experiments as well. Results from this work help elucidate the microbial carbon transformation pathways that might stimulate in situ methanogenesis from coal.

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