

***Ex situ* studies of nanominerals by Secondary Ion Mass Spectrometry**

L.B. WILLIAMS^{1*}, R.L. HERVIG¹ AND J. SRODON²

¹Arizona State University, Box 871404, Tempe, AZ 85287, USA (*correspondence: lynda.williams@asu.edu)
²Inst. Geol. Sci PAN, Senacka1, PL-31 002, Krakow, Poland

Analyses of nanominerals that are difficult to separate from sediments in quantities sufficient for conventional isotopic analyses are well suited for analysis by SIMS because of the high useful yields for this technique. Separation of clay minerals <20nm is feasible [1], but requires several days of centrifugation to separate a few mg of fundamental clay particles. A 5 μ l suspension of 1mg pure, 20nm illite crystals in deionized water and dried on a glass slide provides ample material for multiple SIMS analyses. The surface tension of water orients the clays with basal (a-b) planes parallel to the surface, creating flat surfaces when dried. Using a defocused primary beam averages many crystals, and multiple analyses maximizes analysis precision.

Such *ex-situ* analyses of an Ordovician bentonite from the Baltic Basin, were performed on different size fractions (<20nm, 20-100nm, 100-200nm) of illite-smectite (I-S). Isotope ratios varied up to 10‰ among the size fractions, relating to changes in fluid composition during crystal growth. Across the basin isotopic trends follow a paleo-temperature gradient [2]. Clay with isotopically heavy B ($\delta^{11}\text{B} \sim +10\%$) occurs near higher temperature (200°C) parts of the basin grading to -3‰ in cooler regions (120 °C). In the same samples, Li-isotopes show an opposite trend; increasing from -10‰ (200°C) to +30‰ (seawater) in cooler sediments.

The Cambrian Alum shale is a source rock for hydrocarbons (HC) in the Baltic Basin. The thermal maturity of this unit has been evaluated based on the H/C ratios and vitrinite reflectance [3]. A suite of samples ranging from immature (H/C = 1.16) to mature (H/C = 0.14) organic matter (OM) was evaluated for B and Li isotope composition in comparison to the bentonite.

OM contributes 50% of the B and Li in the Alum shale. The OM $\delta^{11}\text{B}$ decreases from -0.4 to -28.4‰ with increasing maturity, while OM $\delta^7\text{Li}$ increases from -20 to +4‰. These opposing trends suggest that isotopically heavy B is first released from OM in the 'oil window' for hydrocarbons, while isotopically light Li is generated. Because the organic signatures of both elements are lighter than natural waters, isotopically light B and Li signatures in diagenetic illites may reflect inputs from organic sources during thermal evolution of the basin.

[1] Clauer *et al.* (1997) *Clay Mins.* **32**, 181–196. [2] Srodon *et al.* (2009) *Clay Mins.* **44**, 361–387. [3] Buchardt & Lewan (1990) *AAPG Bull.* **74**, 394–406.

Micro total analysis system development for *in situ* chemical exploration of Titan and Mars

P.A. WILLIS¹, A.M. FISHER¹, H.F. GREER¹, M.F. MORA¹, D. MAIR² AND H. JIAO³

¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA (*correspondence: Peter.A.Willis@jpl.nasa.gov)

²Fluigence, LLC, Santa Clara, CA 95054, USA

³Los Gatos Research Inc., Mountain View, CA 94941, USA

This contribution summarizes our ongoing efforts in the design, fabrication, and implementation of micro total analysis (i.e. 'lab on a chip') systems intended for the payloads of future robotic explorers to destinations such as Mars or Titan. Chemical analyses performed in these microfluidic-based systems is aimed at the determination of the extent of past or present life on these worlds, or the extent of prebiotic chemical evolution that may have taken place. Samples are to be provided by the robotic platform carrying the instrument, either via drilling into regolith and treatment with liquid water (Mars and Titan) or possibly direct sipping from hydrocarbon lakes (Titan). Organic species are mixed with stored buffer solutions, and then separated from one another on-chip electrophoretically (via capillary electrophoresis or capillary electrochromatography) and detected via laser-induced fluorescence, or alternatively via nanoelectrospray ionization and mass spectrometric analysis. Automated capillary electrophoresis analysis of this type for Mars exploration was brought to an intermediate level of automation by Skelley using fluorescamine dye for labeling of amino acids. Current work focuses on the use of Pacific Blue dye, but now in an automated fashion, in which the derivitization process is performed on chip using dried reagents deposited in dedicated reaction reservoirs. Capillary electrochromatography (CEC) analysis is also performed for the determination of polycyclic aromatic composition, utilizing porous polymer monoliths as the separation medium. Nanoelectrospray ionization is performed using conventional pulled capillaries as well as micromachined nozzles. We perform required liquid sampling handling operations (mixing, derivitization, dilution, etc.) required for these automated analyses using circuits comprised of monolithic diaphragm valves.

[1] Willis *et al.* (2008) *Lab Chip* **8**, 1024–1026. [2] Aubrey *et al.* (2008) *Astrobiology* **8**, 583–588. [3] Skelley *et al.* (2005) *PNAS* **102**, 1041–1048.