## LA-ICP-MS Sr isotope ratio analysis of individual fluid inclusions

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This pilot study addresses the feasibility of precise and accurate Sr isotope ratio analysis by laser-ablation multiple collector ICP-MS of fast transient signals as obtained from the ablation of individual fluid inclusions. We used synthetic (Na±Ca)Cl inclusions containing variable amounts of SRM 987 Sr and Rb.

The principal analytical and data reduction procedures follow those reported in Pettke *et al.* [1] and Burla *et al.* [2]. Masses 83, 84, 85, 86, 87, 88 were recorded on Faraday detectors at 0.2s integration intervals. Raw readings were first corrected for incongruent amplifier response using the quadratic tau correction scheme [1]. Background correction is followed by interference correction, altogether removing overlap by Kr, Ca-argides and Ca-dimers. <sup>87</sup>Rb overlap is then corrected by peak stripping using fractionated Rb based on mass bias values obtained for Sr, and the resulting <sup>87</sup>Sr/<sup>86</sup>Sr ratio is then mass bias corrected.

Evaluation of results based on individual readings reveals incongruent signal intensity evolution for <sup>85</sup>Rb and <sup>86</sup>Sr across the fluid inclusion signal. Tau- and interference-corrected <sup>87</sup>Sr/<sup>86</sup>Sr data are constant (at given analytical precision) across the transient fluid inclusion signal, however.

<sup>87</sup>Sr/<sup>86</sup>Sr ratios of synthetic fluid inclusions with variable Rb/Sr abundance ratios were obtained by bulk signal integration. As for synthetic fluid inclusions Sr isotope equilibrium between phases prevails, uncertainties of <sup>87</sup>Sr/<sup>86</sup>Sr ratios could be minimized by cutting off low-intensity and thus imprecise transient signal tails.

Final  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  ratios correlate with  ${}^{85}\text{Rb}/{}^{86}\text{Sr}$  ratios. The least squares linear fit intercept is at  ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.71028 \pm 0.00019$ , identical to the nominal value of SRM 987 = 0.710245. The correlation could be eliminated by adjustment of  ${}^{85}\text{Rb}/{}^{87}\text{Rb}$  to 2.58676, a value very close to that reported earlier [3], suggesting that an offset in mass bias between Sr and Rb by 5.3% in  $\beta$  values can account for the observed trend.

 Pettke, T. *et al.* (2011) *J. Anal. Atom. Spectrom.* 26, 475.
Burla, S. *et al.* (2009) *Terra Nova* 21, 401. [3] Jackson, M.G. Hart, S.R. (2006) *EPSL* 245, 260.

## Association of amino sugars (chitin) with Fe oxyhydroxides in mycorrhizal mat soils – A STXM/NanoSIMS investigation

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Amino sugars and polymers such as chitin represent a major constituent of fungal cell walls and hydrolyzed soil organic matter. Despite their potential importance in soil nitrogen and carbon cycling, comparatively little is known about their dynamics in soils. Here we present the results of an investigation into the mineral interactions and micro-scale behavior of chitin in ectomycorrhizal mats - a system adapted to rapid cycling of amino sugars. The aim of this study was to follow the micro-scale dynamics of <sup>13</sup>C- and <sup>15</sup>N-labeled chitin during a 3-week incubation in mycorrhizal mat soil collected from a Oregon andic soil under Douglas-fir forest. Based upon previous findings, we hypothesized that the isotopic label would accumulate in bacterial cells associated with fungal hyphae due to their ability to rapidly process amino sugars. In contrast, nano-scale secondary ion mass-spectrometry (NanoSIMS) imaging of hyphae-associated soil organic matter, minerals, and bacteria revealed a preferential association of <sup>15</sup>N with Fe-rich particles at the end of the experiment. Synchrotron-based Scanning Transmission X-ray spectromicroscopy (STXM/NEXAFS) at the C, N and Fe Kedge suggests that these hyphae-associated microstructures consist of thin coatings of amine N on Fe (oxyhydr)oxides. Our results are consistent with recent observations of preferential binding of amine N to Fe-rich minerals and suggest a role of Fe (oxyhydr)oxide surfaces in N cycling of organic layers soils. No enrichment of <sup>13</sup>C was found at these locations, possibly due to the lower levels of overall <sup>13</sup>C abundance. We further discuss advantages and challenges (e.g. data representation, replication, appropriate controls) of the combined application of isotopic and spectroscopic imaging techniques for the investigation of soil C and N cycling.

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