

## Development of a novel TOF-SNMS to analyze sub-micron noble gas distribution

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### Overview of the instrument

Ion beam for secondary ion mass spectrometry (SIMS) down to 10 nm can reveal new perspectives for cosmochemistry and material sciences. We have developed LIMAS (Laser Ionization Mass Nanoscope [1]) that is a time-of-flight sputtered neutral mass spectrometer (TOF-SNMS) with non-resonant laser post-ionization system. LIMAS is mainly composed of Ga focused ion beam (FIB) for sputtering, femtosecond laser for post-ionization of the sputtered particles, and high mass resolution multi-turn mass spectrometer of which mass resolving power of  ${}^4\text{He}^+$  ( $m/z=4$ ) is 8,500 (FWHM) after 90 cycles.

One of our goals is to determine micro-distribution of noble gases in solids derived from solar wind (SW) irradiation. An ultra-fine ion probe and post-ionization procedure should reveal the processes of the solar-gases were implanted and the surface layer was lost by space weathering because SW implanted layer is less than 100 nm and high spatial resolution *in situ* He analysis has never been done.

The spatial resolution for  ${}^4\text{He}$  was achieved  $\sim 50$  nm which was evaluated by using  ${}^4\text{He}$  implanted Si-wafer (dose:  $2 \times 10^{16}$  ions/cm<sup>2</sup>). A detection limit of the present system is about  $10^{18}$  atoms/cm<sup>3</sup> for  ${}^4\text{He}$ . The performance of LIMAS should be improved towards higher sensitivity and lower background noises because bulk concentrations of solar-He in gas-rich meteorite are  $10^{16}$ – $10^{18}$  atoms/cm<sup>3</sup> [2] for rocky material (density  $\sim 3$  g/cm<sup>3</sup>).

[1] Ebata *et al.* (2012) *SIA*, **44**, 635–640. [2] Goswami *et al.* (1984) *SSRv*, **37**, 111–159.

## The association between iron and carbon in freshwater colloids

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Iron and carbon are important constituents of natural colloids, which intimately links the fate of these two elements in riverine systems. Iron may strongly affect the binding of trace metals by organic matter, e.g. through competition for binding sites, which highlights the importance of a correct appreciation of the Fe speciation in surface waters. However, the chemistry of Fe and C in natural colloids is complex and depend on many factors including the pH, the Fe:C ratio, and the redox speciation of Fe [1-3].

Two areas with a contrasting Fe chemistry were studied: a lowland area with widespread seepage of iron-rich groundwater, and an upland peat area. Samples of ten oxic, well-mixed streams were subjected to cascade filtration using conventional filtration (1.2  $\mu\text{m}$ , 0.45  $\mu\text{m}$ , 0.1  $\mu\text{m}$ ) and cross-flow ultrafiltration (CFF; 5 kDa). The colloidal fraction, here operationally defined as between 0.45  $\mu\text{m}$  and 5 kDa, was isolated by CFF and subsequently freeze-dried. The speciation of colloidal Fe was determined by EXAFS spectroscopy at the Fe K-edge (MAX-lab, Lund, Sweden).

In the rivers draining upland peat, Fe and C were predominantly recovered in the fraction between 5 kDa and 0.1  $\mu\text{m}$ . Conversely, in the rivers draining the lowland with extensive seepage of iron-rich groundwater, Fe was most abundant in the  $>0.1$   $\mu\text{m}$  fraction, whereas C was predominantly present  $<0.1$   $\mu\text{m}$ . The EXAFS data reveal that colloidal Fe speciation is different in both study areas. It exists as mononuclear Fe complexed by dissolved organic matter, as colloidal hydrous ferric oxides (likely stabilized by adsorbed organic matter), or as a mixture of these. The colloidal Fe concentrations show considerable seasonal variability. Overall, this study contributes to a better understanding of colloidal Fe speciation and of its interaction with organic C.

[1] Sjöstedt *et al.* (2013) *Geochim Cosmochim Acta* **105**, 172-186. [2] Allard *et al.* (2004) *Geochim Cosmochim Acta* **68**, 3079-3094. [3] Lyvén *et al.* (2003), *Geochim Cosmochim Acta* **67**, 3791-3802.