

## Location of cation impurities in NGRIP deep ice revealed by cryo-cell UV-laser-ablation ICPMS

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The nature and location of cations impurities in ice cores provide useful insights about paleoclimate. Proxies for sea ice extension, dust atmospheric supply and the identification of annual layers are based on seasonal variabilities of soluble and not soluble impurities in ice. Furthermore, impurities play an important role in ice grain growth, which generally increases with depth, but is interrupted by many periods where the grain size sharply decreases, in correspondence of glacial-interglacial transitions [1]. The distribution of different impurities, led by this phenomenon, has never been directly observed in experiments on ice [2].

Using a recently developed methodology unique at Royal Holloway University of London [3], *in situ* chemical analysis of ice with unprecedented spatial (and thus time) resolution is achievable using cryo-cell UV-laser ablation inductively-coupled-plasma mass spectrometry (UV-LA-ICPMS). A volume of NorthGRIP ice (50x11x11 mm, HxWxD) have been analysed by using a series of 2D grids of laser spots at a resolution >300 µm over the surface of the volume. The sample surface (depth ~ 2717 m) has been smooth and cleaned using a metal free ZrO<sub>2</sub> blade mounted on a custom-built teflon vice used to remove ~2mm of ice to avoid contamination. A small liquid nitrogen reservoir covered by a teflon worksurface has been embedded in the proximity of the cryo cell, for keeping samples below -20 °C during loading procedures. N<sub>2</sub> is constantly blown on samples via a custom-made hood fitted with a vent, preventing contamination and refroosting from air.

Major elements indicative of sea salt contribution (Na, Mg) and dust concentration (Al, Ca, Fe, K) were measured simultaneously. Results proves the reliability of the technique in identify where impurities preferentially lies and which type of impurity they are (soluble or insoluble).

[1] Durand *et al.*, (2006). JGR-Earth Surface, 111(F1), F01015.

[2] Ohno *et al.*, (2005). EPSL, 232(1-2), 171-178. [3] Müller

*et al.*, (2011). JAAS, 26(12), 2391-2395.

## Lithium isotopic composition of the dissolved load in the Amazon River basin

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Silicate weathering reactions constitute a major aspect of the Earth's engine as they consume atmospheric CO<sub>2</sub> and influence the composition of the ocean and continental crust over long time scales. The investigation of past climatic variations requires geochemical proxies of silicate weathering. Lithium isotopes are a promising new geochemical proxy for silicate weathering and have notably been used recently to demonstrate the change of weathering regime during the Cenozoic based on the marine record [1]. However, the parameters controlling the extent of Li isotope fractionation during continental weathering and the associated fractionation factor are still poorly known. Here, we report the Li isotope composition of river-borne material in the largest Earth's River system, the Amazon River basin to characterize Li isotope fractionation at continental scale.

The Li isotopic composition of the dissolved load ( $\delta^7\text{Li}$ ) is highly fractionated toward heavy values (up to 31‰) compared to river bed sand (-1.39 to +3.85‰) and suspended sediments (-6.80 to -0.50‰). The dissolved Li concentrations are the highest in the headwater of the Beni River that drains shale rocks (0.3 to 2 µmol.L<sup>-1</sup>) and the lowest in the rivers draining the shield areas (< 0.1 µmol.L<sup>-1</sup>). In the Madeira basin, the  $\delta^7\text{Li}$  of the dissolved load increases from the Andes to the floodplain and displays a global inverse relationship with the Li/Na ratio. The fraction of Li incorporated into secondary weathering products during the contemporary weathering cycle is the dominant control of the dissolved Li isotope composition and is related to the geomorphic regime. This work has important implications for the determination of weathering mass budget based on Li isotope and about the importance of secondary product formation.

[1] Misra and Froelich (2012) *Science*, **335**(6070), 818-823