Sr isotopic investigations of calcium-rich matrices by LA-MC-ICPMS

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The use of $^{87}Sr/^{86}Sr$ ratios is a powerful tool in the field of analytical ecogeochemistry, above all for the investigation of migration, mobility and movement due to its outstanding properties of regional difference and Sr abundance in nature. Only recently, variation of the $^{86}Sr/^{88}Sr$ ratio due to natural fractionation processes induced by weathering and temperature effects were reported, as well.

Laser ablation coupled to multiple collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) stands out due to its attributes as a semi-invasive means for the fast and direct investigation of Sr isotope ratios and marginal sample preparation required. However, direct stable Sr isotope ratio measurements in calcium phosphates and carbonates suffer from significant matrix-related interferences such as molecular ions, e.g. $(^{40}Ca\text{-}^{31}P\text{-}^{16}O)^+$, $(^{40}Ar\text{-}^{31}P\text{-}^{16}O)^+$, $(^{43}Ca\text{-}^{44}Ca)^+$ as well as in many cases concomitant atomic ions, e.g. $^{87}Rb^+$, $^{174}Hf^{2+}$. Interferences on Sr isotopes analyzed by LA-MC-ICPMS have been subject to numerous debates and discussions among scientists during the last couple of years. Interpretations of generated data are highly diverse regarding the trustworthiness of LA-MC-ICPMS, as corrections are approached in different ways and diverse sources of interferences are presumed. The major part of observations report trends towards higher $^{87}Sr/^{86}Sr$ ratios for LA-MC-ICPMS compared to solution-nebulisation based MC-ICPMS when analyzing apatite matrices and lower ratios in case of calcium carbonate matrices.

This study is dedicated to the systematic investigation of the effect of interferences and instrumental mass discrimination on Sr isotopic investigations using LA-MC-ICPMS and the assessment and validation of possible correction strategies. This includes evaluating the potential of the implementation of externally added elements (e.g. Zr) for mass bias correction.

The major focus was set on analyzing human tooth samples, fish hard parts and geological carbonates. Laser ablation data and corresponding data established using solution nebulisation based approaches were compared and potential sources of interferences identified by e.g. using high resolution ICPMS. The combined corrections of interferences and adequate mass bias correction procedures lead to accurate data even though increased uncertainties have to be taken into account. The obtained results are discussed along with coexisting approaches for data correction in laser ablation analysis.

Speciation and Localization of Cd in the Hyperaccumulator Plant *Arabidopsis halleri* Grown in the Field and in Controlled Conditions by XAS Techniques

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Some higher plants naturally grow on metal contaminated soils due to their ability to cope with metal toxicity. They can be used in phytoremediation to extract (phytoextraction) or stabilize (phytostabilization) metals accumulated in soils. These techniques can be an alternative to invasive physico-chemical remediation techniques. However, to develop phytoremediation, it is necessary to understand the mechanisms involved in metal accumulation, and particularly the way that plants transfer and store metals. These mechanisms have not been elucidated yet [1]. In this context, synchrotron radiation based techniques, and particularly micro-focused X-Ray Fluorescence (μXRF), and X-ray Absorption Spectroscopy (XAS) appear as powerful tools to determine the localization and the chemical forms of metals in plants, and thus the mechanisms involved in the metal accumulation capacity [2, 3]. In this study, we have investigated the Zn, Cd hyperaccumulator *Arabidopsis halleri*, which naturally develops on some contaminated soils in Europe. This work presents the application of μXRF and Cd μXANES to determine the distribution and speciation of Cd in *Arabidopsis halleri*, in combination with bulk Cd EXAFS/XANES spectroscopy. We particularly compared *Arabidopsis halleri* collected on the field and in various controlled conditions. Results show that Cd is mainly located in veins and mesophyll of leaves and that hot spots are found in trichomes (epidermal hairs), although this compartment is not a major compartment of storage for the metal. The speciation of Cd varies with the various conditions of Cd treatments but also differs from the plants originated from the site. This study highlights the difficulty to extrapolate the laboratory experiments to the field in a remediation context.

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[2] Lombi and Susini (2009) *Plant Soil* **320**, 1-35.
[3] Isaure et al. (2006) *Spectrochimica Acta Part B* **61**, 1242-1252.