Quantifying micro-niche behaviour in sediments:- Precise and accurate measurements of DGT gels by laser ablation high resolution laser ablation ICPMS

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New developments in micron-scale measurements of trace metals and sulphur contents within sediments by DGT (diffusive gradients in thin-films) have revealed micro-niche structures. The origin of micro-niches is unclear and it is important to understand the relative roles played by inorganic and biological processes in the localised remobilisation of metals. We have undertaken a S and Fe isotope study of micro-niches, to better understand their mechanisms of formation. With their inbuilt pre-concentration, element selection and simple matrix, DGTs are an ideal medium for laser ablation ICP-MS. In contrast to analysis of mineral phases, fully matrix-matched standards can be easily made. We have initially concentrated on the measurement of S isotopes and will also present experiments where Fe isotopes have been measured in DGT gels. S and Fe isotopes were measured on a Neptune at mass resolutions of >9000. A New-Wave UP-213nm laser was used with Ar as the carrier gas. Instrumental mass bias (IMB) for S was corrected for using sample-standard bracketing. Ablation experiments on two S DGT gel standards, 10Hz, 40% power, 170µm wide line, scan speed 70µms-1, show in-run $\delta^{34}S$ precisions for DGT gels with 2.1 µmol/cm^2 S (3V of ^{32}S) of <0.2‰ (2SE). There is no observed correlation between $\delta^{34}S$ and ^{32}S intensity. Reproducibility on $\delta^{34}S$ for individual analytical sessions (4-8 standards) is better than 0.3‰ while the reproducibility over 4 sessions is 0.19‰. Further tests to mimic ablation over micro-niches (continuous ablation across a gel with two isotopic compositions) show similar internal precisions and only slightly worse reproducibility - 0.48‰ (2SD; n=6). The accuracy of the LA $\delta^{34}S$ measurements on a $BaSO_4$ gel relative to the reference value of the starting $BaSO_4$, bracketed by a AgI gel of known isotopic composition, is better than 1‰, showing negligible S isotopic fractionation during gel deployment. $\delta^{34}S$ variations in micro-niches can be easily resolved at the 1‰ level and 100µm scale whereas variations in natural micro-niches are expected to be 10‰ or more. Fe measurements, using external normalisation to a $^{60}Ni/^{61}Ni$ ratio and an exponential law to correct for IMB, suggest internal precisions and external reproducibility of <0.15‰ (2SE) and 0.07‰ (2SD) should be possible.