

Significant observed copper isotopic abundance variations in biological materials.

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Copper is an essential nutrient in both flora and fauna and has proven to be critical in maintaining homeostatic balance by participating in many metabolic processes. Copper has two naturally occurring stable isotopes, ⁶³Cu and ⁶⁵Cu. The ratio between the amounts of these two isotopes can be used to indicate the source of copper to an organism, give insight to cycling processes as well as metabolic pathways. Natural variations in copper isotopic composition have a measured range of 9 ‰ in geological materials and 3 ‰ in water samples [1, 2]. Recent evidence has shown that the assimilation and subsequent use of copper in an organism may cause further fractionation. This has been demonstrated in mice where it was shown that modified gene expression caused a shift in isotopic composition of copper in the brain [3]. In a recent study, participants with Parkinson's disease demonstrated differences in the metabolism of copper isotopes [4].

In order to explore the copper isotope variability in living systems, select samples were analyzed: exotic wood samples, wild animal hair, and hair and fingernails samples from local Calgary residents. Wood samples were analyzed as part of an ongoing project to determine if isotopic systems can be used to identify the geographic origins of the wood in an effort to prevent illegal trading. Hair samples from wildlife in Alberta were analyzed to determine if copper isotopes can be used to identify the dominant source of food. Hair and nail samples from local Calgary residents were also analyzed and compared to the local drinking water. A range in $\delta^{65}\text{Cu}$ of over 20 ‰ was observed.

[1] Larson, P.B., Maher, K., Ramos, F.C., Chang, Z., Gaspar M., Meinert, L.D. (2003) *Chemical Geology* **201**; 337–350. [2] Borrok, D.M., Nimick, D.A., Wanty, R.B., Ridley, W.I. (2008). *Geochim Cosmochim Acta* **72**; 329–344. [3] Büchl, A., Hawkesworth, C.J., Ragnarsdottir, K.V., Brown, D.R.; (2008) *Geochem. Trans.* 1-7. [4] Lerner, F., Sampson, B., Rehkamper, M., Weiss, D.J., Dainty, J., O'Riordan, S. (2013) High precision isotope measurements show poorer control of copper metabolism in parkinsonism. *Metallomics*, **5**; 125-132.

Construction of high-resolution trace element time-series in slow growth speleothems by ELA-ICP-MS: Challenges, new approaches and validation strategies

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Speleothems hold important potential to record terrestrial paleoclimate variations over millennial scales, as increasingly supported by monitoring studies of modern karst systems. Trace element variations in drip waters and corresponding plate calcite samples demonstrate the potential for subannual resolution in settings having well-expressed seasonality (rainfall, temperature). The high sensitivity and rapid peak-hopping capabilities of quadrupole ICP-MS, integrated with the superior coupling capacity and high spatial accuracy of modern excimer 193 nm laser ablation systems (ELA-ICP-MS line scans), offers an efficient means for constructing high-resolution chemical time-series in growth-banded speleothem calcite. However, application of the technique becomes increasingly challenged with decreasing speleothem growth rates, a factor that has relegated most high-resolution trace element studies to growth rates exceeding 100 $\mu\text{m}/\text{yr}$. Slow-growth speleothem records (< 50 $\mu\text{m}/\text{yr}$) present three significant challenges to ELA-ICP-MS, namely: (1) growth banding is often not visible by standard petrographic techniques, let alone via imaging of the laser ablation system; (2) the crystallographic fabric comprising growth bands develops as successions of rhombohedral overgrowths, the scale and geometry of which can compromise the goal of obtaining unaliased stratigraphic sampling; and (3) achieving counting statistics capable of resolving subannual chemical signals is more difficult due to the need for small apertures (lower signal-to-noise) and because of more limited “dwelling” time within growth band intervals associated with rapid chemical gradients. Parallel-offset line traverses, a well-established approach for evaluating reproducibility of chemical signals, often do not show high correspondence due to such localized sample aliasing – raising the question “We know what we are targeting, but do we know what we are hitting? We reiterate the importance of locating laser ablation line scans from the informed perspective of oriented growth band fabric imagery, and developing analytical validation strategies that demonstrate the capacity to resolve slow-growth chemical waveforms.