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An experimental approach to investigate isotope fractionation of metals by amino acid complexation

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Background: The transition metals nickel (Ni), copper (Cu) and zinc (Zn) are critical to numerous biological functions because they act as protein cofactors. Recent work [e.g., 1, 2] on organisms spanning phytoplankton to mammals has demonstrated that biological activity can fractionate the isotopes of these metals. The extent of this fractionation appears to depend on factors like metabolic state, nutrition, and disease. It has been hypothesized that metal isotope fractionation at the cell-level arises due to equilibrium fractionation effects among biomolecules within the cell. To assess isotope effects associated with the formation of metal-biomolecule complexes, and to validate *ab initio* calculations commonly used to estimate these effects, we devised an experimental approach to quantify metal isotope fractionation by complexation with amino acids commonly found in protein metal-binding sites. This presentation will describe our experimental design and report results on metal isotope effects imparted by amino acid ligation.

Materials and Methods: The transition metals Ni, Cu, and Zn were reacted with either cysteine (sulfur ligand), histidine (nitrogen ligand), glutamate or aspartate (oxygen ligands). Solutions contained metal ions and amino acids at a ratio of 100 µM:200 µM. After reacting for 1 day, free and bound metal ions were separated via equilibrium Donnan dialysis using a cation-permeable membrane. Both pH and electrolytic medium were varied to investigate how these factors affected amino acid binding and metal adsorption to the membrane. Dialysis was carried out until mass and isotopic equilibration was reached. Isotope ratios of the metal solutions were measured via multicollector inductively coupled mass spectrometry (MC-ICP-MS) following column purification under clean laboratory conditions.

Results and Discussion: Our experimental approach effectively separated complexes of amino acids and Ni, Cu, or Zn. The experimental results indicated that the presence of a suitable background ion was required to facilitate the exchange of metal ions across the membrane in the Donnan dialysis procedure. Ultimately, experimentally resolving metal isotope fractionation effects associated with distinct biomolecules can facilitate development of metal isotopes as biomarkers of microbial metabolism and human disease.

[1]Albarede et al. 2016. *Metallomics* 8(10): 1056-70.

[2]Lemaitre et al. 2022. *Earth and Planetary Science Letters* 584: 117513.