Magnesium Stable Isotope Fractionation in Biological Cycles

Chlorophyll is one of the most important biomolecules for life on earth, being the primary light absorbing pigment that plants and microorganisms use to capture light for photosynthesis. Magnesium is the metal center of chlorophyll and is thus central to this process. Magnesium has three stable isotopes with a large natural abundance ($^{24}\text{Mg}: 78.7\%; ^{25}\text{Mg}: 10.1\%; ^{26}\text{Mg}: 11.2\%$). If a biogenic fractionation of the stable isotopes of magnesium were preserved in the chlorophyll molecule it may be possible to use the magnitude of this fractionation as a marker of environmental/physiological processes, and potentially as a tracer of the origins of photosynthetic life on Earth. In my work at UC Davis I have used a state-of-the-art high resolution multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS, Nu Instruments) to precisely measure the isotopic ratios of magnesium in chlorophyll extracted from various microorganisms and higher plants. Figure 1 plots the results from cultures of a cyanobacteria (*Synechococcus elongatus*) on a three-isotope diagram, showing that the isotopic composition of chlorophyll-a is mass dependently depleted in the heavy isotopes of magnesium relative to the culture medium in which the cyanobacteria were grown. Further work is being conducted to determine the nature of this fractionation, whether is it represents a kinetic fractionation during the biosynthesis of chlorophyll; kinetic fractionation during the uptake and transport of magnesium by an organism; or an equilibrium fractionation of the magnesium isotopes in chlorophyll relative to the reservoir.

Figure 1: High-precision measurement of the magnesium isotope composition of chlorophyll-a, extracted from *Synechococcus elongatus*, relative to the culture medium and international standards (Black, Yin and Casey, 2006). ORTEP representation of the chlorophyll-a molecule shown to the right.
In further laboratory studies we have followed the magnesium stable isotope chemistry during the growth cycle (pictured below) of wheat (*Triticum aestivum* L.) (Black, Epstein, Rains, Yin and Casey, 2008). The wheat preferred to take up the heavy isotopes of magnesium, and reaches an isotopic equilibrium with its nutrient supply with a fractionation factor of 1.0004 to 1.0007 in $^{26}\text{Mg}$ (Figure 2). The preference of plants for heavy magnesium isotopes suggests that a difference might exist in the bioavailable magnesium of agricultural and natural soils due to the periodic removal of heavy magnesium isotopes by harvest, and may account for the sink of heavy magnesium seen in measurements of runoff from major river systems around the world. Our goal in undertaking the coupled research on cyanobacteria and higher plants is to constrain the biological controls on fractionation.

![Day 6, Day 12, Day 21, Day 29 plants](image)

**Figure 2.** Evolution of the stable isotope composition of the nutrient solution as a function of the fraction of magnesium left in the nutrient over time. The linear evolution indicates an equilibrium is established across the plants roots with a preference for the heavy isotopes concentrating in the plant.