

Multiple isotope effects associated with biogeochemical networks

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In a prior study (Farquhar et al., 2003) we adapted a standard treatment of isotopic flow through biosynthetic networks (c.f., Hayes, 2001) to describe the way that the four isotopes of sulfur are affected by metabolic processes. In a study that followed (Johnston et al, in press), we reported additional data for sulfate reducers and new data for sulfur disproportionators and expanded our treatment of these effects. Although our focus has been on sulfur isotopes, we note that the same principles apply to other multiple isotope systems such as O, Fe, and Se.

Here, we will describe our approach, beginning with an explanation of the mass-balance and fractionation relationships that form the underpinnings for the calculations. We will present graphical representations of several calculations to illustrate the sensitivity of the isotopic compositions of intermediate pools to the metabolic network structure, and we will illustrate this by building progressively more complex dissimilatory network examples. We will also include a generalized discussion of the principles of nesting network components and specific predictions. These predictions provide a basis to use this approach to map out the structure and the magnitude of the fractionations for the dissimilatory metabolisms. The combination of mathematical treatment and graphical solutions is meant to provide the necessary framework for adaptation of this approach to other systems and we point out that our solutions are neither restricted to biosynthetic networks nor to the sulfur isotope system. The same principles apply to reaction networks for other elements with two or more isotopes and at scales extending from that of a single-cell to that of a global biogeochemical network.

References:

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Decoupled fractionation of even- and odd-mass isotopes of Pb in TIMS

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High-precision Pb isotopic analyses of the standard SRM-981, spiked with ²⁰²Pb and ²⁰⁵Pb, were undertaken to further evaluate the anomalous fractionation of ²⁰⁷Pb relative to even-mass isotopes in thermal ionisation mass spectrometry, reported by Thirlwall 2000 (Chem.Geo. 163, 299) and Doucelance and Manhès 2001 (Chem.Geo. 176, 361). The analyses were performed using Triton TI mass spectrometer at the GSC in static multicollector mode using three different silica gel formulations: silicic acid (Merck - Gerstenberger and Haase 1997, Chem.Geo. 136, 309); hydrolysis of silicon tetrachloride, and hydrolysis of sodium orthosilicate. Ratios involving the even-mass isotopes (²⁰²Pb, ²⁰⁴Pb, ²⁰⁶Pb and ²⁰⁸Pb) obey standard mass-dependent fractionation laws over a wide range of fractionation (²⁰⁸Pb/²⁰⁶Pb between 2.160-2.172). In contrast, isotopic ratios involving odd and even isotopes (e.g. ²⁰⁵Pb/²⁰⁶Pb or ²⁰⁷Pb/²⁰⁶Pb), exhibit mass-independent fractionation when normalized to ²⁰⁸Pb/²⁰⁶Pb, and systematically decrease as the sample approaches exhaustion. The relative change of normalized ²⁰⁵Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb are between 0.02-0.05% for the Merck and silicon tetrachloride gel, and up to 0.16% for the sodium orthosilicate gel. The relative deviations of both ratios are strongly correlated, with the slope of correlation lines close to one. Thus, the fractionation between odd isotopes is similar to the mass-dependent fractionation between even isotopes, but the behaviour of even- and odd-mass isotopes is decoupled. For example, the ratio ²⁰⁶Pb/²⁰⁸Pb, normalized to ²⁰⁵Pb/²⁰⁷Pb, does not vary with sample exhaustion. If the ratio ²⁰⁷Pb/²⁰⁶Pb, most important for high-precision Pb-isotope dating, is normalized to ²⁰⁵Pb/²⁰²Pb or ²⁰⁷Pb/²⁰⁴Pb in a double-spike procedure, the ²⁰⁷Pb bias is reduced by 1/3 but not removed completely.

The cause of the mass independent fractionation appears related to a higher volatility and/or ionization efficiency of Pb atoms with non-zero nuclear spin. Large differences in ionization of even vs. odd isotopes have been noted for a number of elements in laser resonance ionization mass spectrometry (e.g. Wunderlich et al. 1992 Anal. Chem 65, 1411). However it remains unclear how the process by which silica gel enhances ionization is affected by nuclear spin.