

## Isotopic anatomies of organic molecules

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Most organic molecules exist in an astonishingly large and diverse variety of isotopologues, i.e., considering all possible site-specific and multiple isotopic substitutions. These species are fractionated from one another by physical, chemical and biological processes. Thus isotopic variations of organics must involve an extraordinarily large number of independent compositional dimensions. Full analysis of even a fraction of this diversity presents a complex, challenging problem, but would potentially yield much new information about sources, conditions, reaction mechanisms and perhaps other variables.

Several emerging technologies make such measurements: chemical and/or pyrolytic preparations; IR spectroscopy, SNIF-NMR; and novel instruments and methods of mass spectrometry. Each has strengths and weaknesses, but none to date is capable of examining both site-specific and multiple-substitutions in small quantities (ng-mg) of species larger than  $\sim$ C<sub>3</sub> hydrocarbons. Most isotopic diversity of most organic compounds remains out of reach.

We describe instruments, methods and initial results of an experiment to expand this field to encompass the isotopic anatomies of organics up to  $\sim$ 300 amu, potentially bringing into play fatty acids, amino acids, isoprenoids, and similar sized compounds. The experiment uses the MAT 253 Ultra, a prototype high resolution ( $M/\Delta M \sim 25,000$ ) multi-collector gas source mass spectrometer, and the Thermo DFS, a very high resolution (up to  $\sim$ 80-100,000) single collector gas source mass spec that is generally used for identification of organic compounds. We use the Ultra to precisely determine the intensity ratios of ion beams that include all isotopologues of a given compound (or its fragment ions), free from isobaric interferences by contaminant species, and then use the DFS to perform rapid scans over a narrow mass window, measuring relative proportions of isotopologues of that species at each cardinal mass. Combination of these data constrains proportions of each isotopologue at each cardinal mass. Initial experiments on butane indicate that this approach may be able to constrain  $\delta^{13}\text{C}$  of ion fragments with precision of  $\pm 0.1$ - $0.2$  ‰ and  $\delta\text{D}$  with precision of  $\pm 2$ - $3$  ‰. We intend to combine this approach with recently invented methods for analysis of multiply substituted and position specific isotopologues of alkanes on the Ultra to create a set of techniques for characterizing proportions of a large number of isotopologues of moderate-sized organic molecules.

## The impact of climate on land derived nutrient fluxes to the ocean

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Weathering and denudation influence greatly the global elemental cycles. There are two main sources of nutrients in the oceans, recycling due to microbial degradation and influx of nutrients from terrestrial runoff [1]. Some elements are essential nutrients for photosynthesis (N, P, Si, Ca, Mg, etc) while other, such as Fe, V, and Mo catalyse biochemical transformations at key points in the carbon and nitrogen cycles. Chemical denudation is positively correlated with runoff and atmospheric temperature [2]. In this study, we demonstrate the different effects climate has on the individual elemental fluxes, derived from silicate weathering in six basaltic river catchments in NE Iceland, of which three are of glacial origin and three are non-glacial rivers.

Concentrations of suspended sediments, major dissolved elements, and some trace elements are discharge dependent while concentrations of most trace metals are discharge independent. Due to the distinct behavior of the particulate and dissolved elements, some are more sensitive to climate change than others. The climate dependence of elemental fluxes is also different between the glacial and direct-runoff rivers.

Data regression of  $\sim$ 40 years of chemical and flow was used to determine the influence of temperature and runoff on the annual fluxes of elements transported to the oceans. The fluxes of the major elements, and Sr and Mo, depended less on the climate than those of the fluxes of trace elements, including the micro-nutrients Fe and V. A change of one °C changes 1) major element, Sr and Mo fluxes, and 2) micro-nutrient fluxes by 13 – 15%, and 15 – 19%, respectively in the non-glacial rivers and by 4 – 14% and 8 – 19% in the glacial rivers. A 10% incremental runoff increase, within the runoff range of the individual river, changed the same fluxes by 7 – 9% and 10 – 15% in the non-glacial rivers and by 2 – 8% and 9 – 16% in the glacial rivers. These results show that elemental fluxes of glacial rivers are more sensitive to climate change than those of non-glacial rivers.

[1] Falkowski (2004) Vol. 8. Treatise on Geochemistry (eds. H.D. Holland and K.K. Turekian), pp. 185 – 213. [2]. Eiriksdottir *et al.* (2013), *EPSL*, **107**, 65 – 81.