Natural organic matter and our current capacity to depict molecular dissimilarity in complex mixtures

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Natural organic matter (NOM) is the most abundant fraction of organic carbon on earth. NOM occurs in all terrestrial ecosystems such as soils, sediments, freshwater and marine environments, in the atmosphere and, throughout the universe, in the form of prebiotic organic matter synthesized by interstellar chemistry. NOM is an exceedingly complex mixture of organic compounds that collectively exhibits a nearly continuous distribution of properties (size-reactivity continuum).

NOM incorporates the hugely disparate characteristics of abiotic and biotic complexity. While biotic complexity derives from a plethora of evolutionary tested molecules with a rich three-dimensional structure designed to execute specific functions, abiotic molecular complexity is rather governed by “mathematical synthesis” which maximizes compositional diversity under given conditions of reaction partners, radiation and temperature. Molecular level NOM composition and structure at first depend on system characteristics and exhibit far more variance than anticipated from often rather uniform bulk parameters. Nevertheless, all NOM on earth is connected in a boundless carbon cycle.

Successful non-target molecular-level analyses of NOM attempts to characterize the entire molecular complement present in NOM by means of information-rich detection methods, like NMR spectroscopy (provides unsurpassed insight into short-range molecular order) and FTICR mass spectrometry (provides depiction of the compositional space with unsurpassed resolution).

This presentation provides an overview how modern organic structural spectroscopy can reveal key characteristics in composition and structure of various NOM. Examples will include secondary organic aerosols (SOA) as well as marine organic matter and NOM in organic chondrites.

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Variations of Δ^{17}O in terrestrial rocks

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Large mass independent effects in Δ^{17}O are well known for extraterrestrial and stratospheric substances. Small variations in Δ^{17}O are expected in terrestrial rocks and minerals due to variations in the triple isotope fractionation exponent [3]. In this contribution we demonstrate that high-precision measurements of Δ^{17}O allow identification and quantification of the interaction between rocks and ancient meteoric water.

We have developed a technique to measure Δ^{17}O in silicates with a precision of 5 ppm (1σ SD), which is an order of magnitude better than had been achieved previously. To characterize the Δ^{17}O composition of the Earth we have measured minerals from mantle xenoliths and a variety of crustal rocks and minerals. Our sample set included peculiar gneiss samples from Karelia, Russia with $\delta^{18}O = -25‰$ [2].

Silicate samples do not plot on a single terrestrial fractionation line (TFL), as frequently assumed. This is explained by differences in triple isotope fractionation exponent in high- and low-T fractionation processes as well as by interaction between reservoirs with different Δ^{17}O.

Rock assemblages that have interacted with water fall on well-defined arrays in the Δ^{17}O vs. δ‘^{18}O space. These arrays can be utilized to reconstruct the original oxygen isotope composition of both, the samples and the hydrous fluid.

We apply our finding to reconstruct the composition of water from low-δ^{18}O rocks from Karelia (Russia) that likely interacted with glacial melt waters during a snowball Earth event.

[1] Young *et al* (2002) *GCA* **66;** [2] Krylov (2008) *Doklady Earth Sci*. **419A.**

DOI:10.1180/minmag.2013.077.5.8