

Molecular characterisation of soil organic matter by laser-desorption ionization Fourier-transform ion cyclotron resonance mass spectrometry (LDI-FT-ICR-MS)

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Soil organic matter (SOM) characterisation has been an analytical challenge for decades. On one hand, methods like humic substances extraction describe large pools of molecules, but these extractions target operationally- rather than chemically-defined pools. On the other hand, specific compound analysis provides a more precise overview on the molecules present in the soil, but the sum of these molecules represents only a minor portion of the soil organic matter. Despite these shortcomings, soil organic matter characterisation is used in many concepts of soil science. For example, the soil aggregation hierarchical model describes the physical organisation of soils into fractions bound together by organic matter of different quality for each size fraction. Due to the method inadequation, most of these concepts still need to be validated.

We took advantage of a unique analytical set-up coupling laser-desorption ionization (LDI) to ultrahigh-resolution mass spectrometry via the Fourier-transform ion cyclotron resonance technique (FT-ICR-MS) to further characterise soil organic matter and to validate the soil aggregation hierarchical model. Soil aggregates (3-5 mm) were collected from two soils, a cambisol (32 % clay, 4.2 %C), and a loess-derived soil (15% clay, 1.6 %C). Aggregates were fractionated by fast wetting into <63, 63-125, 125-250 and > 250 μm fractions. These fractions were air-dried and ground to powder prior to analysis. LDI-FT-ICR-MS analyses were performed on otherwise untreated samples. Thousands of molecular formulae were identified in each samples, many of them could be associated with polyphenolic structures. The combination of LDI with ultrahigh-resolution FT-ICR-MS offers fundamentally new insights into soil organic matter, one of the largest organic matter pools on Earth.

Cadmium isotopes in Banded Iron Formations and early life in the Precambrian ocean

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The exact genesis of Banded Iron Formations (BIFs) is not fully understood, yet there is a consensus that they are seawater precipitates and as such provide valuable archives of Precambrian ocean chemistry, its oxygenation and perhaps clues to early life. Here we explore Cd stable isotope fractionation in BIFs to try to assess the degree of biological activity in the ancient oceans. Cadmium isotopes are particularly suited since (1) they trace differences in biological productivity between biogeochemical provinces in the modern oceans [1], (2) in contrast to Cr and Fe isotopes, Cd isotopes are not redox sensitive, and (3) they are not fractionated by Fe-Mn oxide precipitation.

Two suites of BIFs from Isua (3.8 Ga) and South Africa (2.2 Ga) were analysed using a Cd double-spike technique at MPI. Exceedingly low Cd concentrations (20-60 ng/g) are found in all BIFs, except one Isua sulfidic facies sample, independent of their provenance and age. Such concentrations are two orders of magnitude lower than found in modern Fe-Mn deposits, supporting extreme trace metal depletion in the early oceans. The Cd isotope ratios, expressed as $\epsilon^{112/110}\text{Cd}$, are varied but systematic, ranging from essentially negative values (-3.7 to -0.3) in the 3.8 Ga-old Isua samples, except for the single sulfidic facies sample, to exclusively positive values (+0.9 to +5.5) in the 2.2 Ga-old South African samples.

The Cd isotope range of the Isua BIFs is consistent with that of modern seafloor hydrothermal systems and contrasts markedly with that of the Proterozoic. The isotope effect during the Proterozoic is similar in magnitude to that observed in the present-day oceans and seems to mark the onset of biological productivity following the Great Oxidation Event. Additional data will be crucial for constraining the timing of oxygenic photosynthesis in the early Earth.

[1] Abouchami *et al.* (2011) doi:10.1016/j.epsl.2011.02.044