

Ultrahigh-resolution mass spectrometry of natural organic matter from hydrothermal springs

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Natural organic matter (NOM) is a highly complex mixture of organic compounds abundant and speciated in all environmental compartments (atmosphere, soils, sediments and water environments). The formation and decomposition of NOM is driven by abiotic and biotic reactions and its continual interactions with its environment. Thus the unique NOM signature reflects several key ecosystem characteristics.

Sulphur with oxidation states ranging from -2 to +6 is an essential element for any terrestrial life and an important constituent of NOM. Processes like microbial sulphate reduction, pyrite precipitation and polysulphane formation demonstrate the pivotal role of environmental sulphur chemistry for microbial life and its coupling to abiotic redox cycles. Furthermore, sulphur is crucial for environmental metal binding. The sulphur signature of NOM therefore reveals critical insights into important biogeochemical processes.

As shown recently, Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) is a powerful tool to unravel the diverse characteristics of abiotic and biotic complexity of various NOM [1-4]. This contribution will demonstrate the capabilities of high-field FTICR mass spectra to elucidate the significant role of organic sulphur chemistry to hydrothermal springs, which feature ecosystems conditions resembling in many aspects those supposedly found in the early earth's history.

[1] Schmitt-Kopplin *et al.* (2010) *Anal Chem* **82**, 8017-8026.

[2] Gonsior *et al.* (2011) *Water Res* **45**, 2943-2953.

[3] Hertkorn *et al.* (2013) *Biogeosciences* **10**, 1583-1624.

[4] Schmitt-Kopplin *et al.* (2010) *PNAS* **107**, 2763-2768.

Chemical and Hf/W Isotopic Consequences of Lossy Accretion

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The late stages of planetary accretion involve stochastic, large collisions [1]. Many of these collisions likely resulted in hit-and-run events [2] or erosion of existing bodies' crusts [3] or mantles [4]. Here we present a preliminary investigation into the effects of lossy late-stage accretion on the bulk chemistry and isotopic characteristics of the resulting planets.

Our model is composed of two parts: (1) an N-body accretion code [5] tracks the orbital and collisional evolution of the terrestrial bodies, including hit-and-run and fragmentation events; (2) post-processing evolves the chemistry in light of radioactive decay and impact-related mixing and partial equilibration.

16 runs were performed using the MERCURY N-body code [5]; each run contained Jupiter and Saturn in their current orbits as well as ≈ 150 initial bodies. Collisional outcomes are modified from [6,7]. The masses of the core and mantle of each body are tracked throughout the simulation. All bodies are assigned an initial mantle mass fraction, y , of 0.7.

We track the Hf and W evolution of these bodies. Radioactive decay occurs between impacts. We calculate the effect of an impact by assuming an idealized model of mixing and partial equilibration [8]. The core equilibration factor is a free parameter; we use 0.4. Partition coefficients are assumed constant.

Diversity increases as final mass decreases. The range in final y changes from 0.66–0.72 for \approx Earth-mass planets to 0.41–1 for the smallest bodies in the simulation. The scatter in tungsten anomaly increases from 0.79–4.0 for \approx Earth-mass to 0.11–18 for the smallest masses. This behavior is similar to that observed.

We find there is no simple relationship between the single-stage core formation time derived from the final tungsten isotope anomaly and the actual growth history of an object.

[1] Agnor *et al.* (1999), *Icarus* 142, 219–237. [2] Asphaug *et al.* (2006), *Nature* 439, 155–160. [3] O'Neill & Palme (2008), *PhilTransRSocLondA* 366, 4205–4238. [4] Benz *et al.* (2007), *SpSciRev* 132, 189–202. [5] Chambers (2013), *Icarus*, 224, 43–56. [6] Genda *et al.* (2012), *ApJ* 744, 137. [7] Leinhardt & Stewart (2012), *ApJ* 745, 79. [8] Nimmo *et al.* (2010), *EPSL* 292, 363–370.