

## **‘Geo-metabolomics’ — A key for understanding function and reactivity of dissolved organic matter**

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Dissolved organic matter (DOM) in the ocean contains as much carbon as the earth atmosphere. This huge pool of energy- and nutrient-rich compounds provides an important base for microbial life in the water column. We hypothesize that the microbial community shapes DOM composition (and vice versa), thereby determining the dynamics of individual molecules and the entity of DOM. The entity of DOM is considered as a population of compounds, each characterized by a specific function and reactivity in the cycling of energy and elements. We propose ‘geo-metabolomics’ as the principle that a most comprehensive characterization of molecular DOM composition and its abiotic and biotic sources and sinks reveals a correlation of properties and behavior, ultimately allowing for the prediction of function and reactivity.

We present results from a long-term study of molecular DOM composition in the open North Sea. Ten-thousands of molecular formulae were identified in DOM by ultrahigh resolution mass spectrometry analysis (FT-ICR-MS, Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry). For the ‘geo-metabolomics’ approach we include abiotic environmental factors and information on abundance and composition of phytoplankton and microbial communities.

The DOM pool in the North Sea is highly dynamic and influenced by a complex interplay of processes that produce, transform and degrade dissolved molecules. Phytoplankton blooms significantly change the molecular composition of DOM, strongly increasing the inherent molecular diversity. The temporal variability of individual molecular formulae in the ‘geo-metabolome’ provides novel information on their function and reactivity. This is a crucial step towards assigning structures to molecular formulae and finally the key for understanding DOM dynamics and interactions.

## **Near-source compositions of Italian kamafugite melt**

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Within the wide compositional spectrum of K-rich magmatism in Central Italy, kamafugitic rocks in the Intra-Appennine Volcanic Province constitute the most alkalic, Si-undersaturated end-member, showing the highest enrichment in many incompatible trace elements. Longstanding debate concerning magmagenesis and geodynamic controls has been fuelled by questions concerning the extent to which crustal-interaction processes modified primary melt compositions. Here we present the results of a detailed study of melt-inclusions (MI) and host olivines from a representative kamafugite specimen from San Venanzo, that enabled us to constrain the primary composition (s) of mantle-derived melt.

Olivine phenocrysts show complex textures indicative of drastic late-stage changes in the crystallization regime. Pristine core parts, characterized by Fo<sub>93-90</sub>, low CaO (0.2-0.3 wt.%) and Cr-spinel inclusions (Cr# ~ 0.7) are considered to have crystallized from primary mantle-derived melt. Modified rim zones, showing a strong compositional gradient of decreasing forsterite (down to Fo<sub>70</sub>) and increasing CaO (up to 1.8 wt.%), and hosting compositionally deviating MI, point to re-equilibration in response to drastic compositional changes induced by interaction with carbonate-rich rock types at shallow crustal levels.

Melt inclusions in the unmodified central parts of the olivines have compositional characteristics consistent with mantle derivation (8-12 wt.% MgO) but span a continuous range between 3 and 9 wt.% K<sub>2</sub>O. The K-richest MI have compositions are relatively enriched in Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. The K-poor end-member is characterized by very high CaO contents (up to 22 wt.%). From an average of the entire group of MI (n=25) the approximate volatile-free composition of the kamafugite parental magma is 43.0% SiO<sub>2</sub>, 12.1% Al<sub>2</sub>O<sub>3</sub>, 2.15% TiO<sub>2</sub>, 6.5% FeO, 0.11% MnO, 8.9% MgO, 17.6% CaO, 6.8% K<sub>2</sub>O, 1.9% Na<sub>2</sub>O, 0.95% P<sub>2</sub>O<sub>5</sub>.

We propose that this kamafugite composition represents an assembly of primary melts with differentiated compositions controlled by small-scale variations in the source. These would fit with different imprints by siliceous potassium-rich and carbonate-rich metasomatic agents derived from subducted carbonate-bearing metapelitic sediments.