The biohopanoid soil proxy: Recent developments and future directions

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The growing need to understand carbon dynamics and reactions involving organic matter at the land-ocean interface has lead to the development of new proxies such as the BIT index [1] in order to allow the contribution of terrestrial organic matter to the marine sedimentary environment to be estimated.

We have recently proposed a new approach based on the analysis of bacterially derived biohopanoids (BHPs) in a range of terrestrial materials (soils, peat) and aquatic sediments [e.g. 2, 3]. We identified a group of compounds related to adenosylhopane [3] which are abundant components in soils but generally scarce or absent in lacustrine sediments. Further investigations have shown that these compounds are ubiquitous in soils from around the globe and comprise a mean average of 28% of the total biohopanoid pool [4] in all samples analysed to date. Conversely they were found to be absent in many lacustrine systems and open marine sediments [2]. We subsequently proposed that the relative contribution of this group of compounds to the sedimentary BHP pool could be used as a proxy for terrestrial organic matter input [4].

Here we will present a summary of new developments in our knowledge and understanding of the occurrence and significance of these compounds, both in terrestrial source material and in riverine, estuarine, deltaic and some coastal marine sediments. We will then consider the fate of these molecules in the marine system and discuss some of the major outstanding questions driving the future directions of this research.

[1] Hopmans *et al.* 2004. *EPSL* **224**, 107-116. [2] Talbot & Farrimond (2007) *Org. Geochem* **38**, 1212-1225. [3] Cooke *et al.* (2008) *Org. Geochem.* **39**, 1347-1350. [4] Cooke *et al.* (2008) *Org. Geochem.* **39**, 958-971.

Application of oxygen isotopes in phosphate for soil studies

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Phosphorus (P) is a key nutrient essential for all living forms, and orthophosphate is the preferred source of P. Abiotic (precipitation-dissolution, adsorption-desorption) and biotic (mineralization-immobilization) processes control P concentration in soil and, thus, determine P status and availability. Although several approaches are employed to study the P distribution and the biological processes affecting P cycle in soils, research suffers from the lack of appropriate methods to identify and understand the dynamics of the P cycle. A potential and promising tool for soil sciences is given by the analysis of the oxygen isotope signature of phosphate (δ^{18} O-PO₄), first used on biogenic apatite [1], and only recently used to characterize biological processes both in experimental essays and in the marine environment [2, 3].

In order to analyze δ^{18} O-PO₄ by TC/EA-IRMS, PO₄³⁻ must be extracted, purified, and precipitated as silver phosphate (Ag₃PO₄). The use of methods successfully applied to marine waters and sediments on soil samples [3, 4] leads to the precipitation of Ag₃PO₄ together with residues of organic matter. The presence of an exogenous source of oxygen produces erroneous and not reproducible isotope measurements. We present an improved purification protocol, optimized for the production of pure Ag₃PO₄ from soil samples. After extraction, PO_4^{3-} is purified with ion exchange resins and multiple mineral precipitations. The efficiency of the method was tested by comparing yields of oxygen of Ag₃PO₄ standards and of Ag₃PO₄ obtained from soil and fertilizer samples. The difference in isotope values in samples treated with both the old and the new purification methods confirms the presence of oxygen of organic origin. Preliminary isotopic results show that differences in origin of the fertilizers and in P status in soils are readily expressed in the δ^{18} O-PO₄.

 Longinelli (1965) Nature 207, 716-719. [2] Blake et al.
(2001) PNAS 98, 2148-2153. [3] Colman et al. (2005) PNAS
102, 13023-13028. [4] McLaughlin et al. (2006) Marine Chemistry 98, 148-155.