

## Geochemical studies in Piraeus port sediments, Greece

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### Introduction and methodology

Piraeus port surface sediments were geochemically studied. Total metal content and metal partitioning [1] were determined by Atomic Absorption Spectrophotometry. Metal partitioning is presented as percentages in pie diagrams. The DOM aqueous extracts were characterized by fluorescence spectroscopy for distinguishing different classes of organic components. Mono dimensional spectra [2] and contour plots (EEMS) are given.

### Discussion of Results

Sediments show a high metal enrichment, especially in the outer part of the central port for Fe, Pb, Zn, Cu, Cd and Sn while seawards the outer cargo terminal for Mn, Ni, Cr and Zn. In all samples there are significant easily hydrolyzed Zn, Cu and Cd components, easily available to the biota. A carbonate related contribution of Mn and Ni was found. More than half of Cu is either bound to various forms of organic matter and/or present in sulphide minerals.

DOM consists of either simple aromatic units [2, 3] (phenolic- like, hydroxyl substituted benzoic and cinnamic acid derivatives, coumarins and alkaloid-like hydroxyquinolines) or compounds such as humic- and fulvic-like moieties and protein derived materials [4].

- [1] Tessier *et al.* (1979) *Analytical Chemistry* **51**, 844–851.  
[2] Senesi *et al.* (1991) *Soil Science* **152**, 259–271.  
[3] Wolfbeis (1985) *Molecular Luminescence Spectroscopy*, 167–370. [4] Baker & Genty (1999) *Journal of Hydrology*, **217**, 19–34.

## Iron isotope composition of the Middle Eocene ooidal-oncoidal ironstones and the associated lateritic paleosols from the Bahariya Depression, Western Desert, Egypt

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The Middle Eocene ironstones of the Bahariya depression, Western Desert, Egypt are subdivided into two marine sequences. The lower ironstone sequence consists mainly of peritidal stromatolitic and ooidal-oncoidal ironstone facies that were later subjected to subsurface alteration by acidic hot groundwater. The upper ironstone sequence consists mainly of mud-ironstones. The upper surfaces of these ironstone sequences were exposed to subaerial weathering processes, along which lateritic iron ores and paleosols were formed.

Iron isotope measurements were used to differentiate between the subaerial and subsurface alteration processes affecting the original marine ironstones. The iron isotope composition of the lateritic paleosols displays low  $\delta^{56}\text{Fe}$  values of  $-0.15\text{‰}$  to  $-0.85\text{‰}$ , while the stromatolitic and ooidal-oncoidal ironstones have high  $\delta^{56}\text{Fe}$  values of  $+1.14\text{‰}$  to  $+2.28\text{‰}$ . The negative  $\delta^{56}\text{Fe}$  values of the paleosol are compatible with the simple internal redistribution of originally light (i.e. organically- bound) iron by dissolution-reprecipitation processes in a closed system. Multiphase iron recycling through multiple oxidation and reduction steps may have resulted in lower  $\delta^{56}\text{Fe}$  [1, 2]. The negative  $\delta^{56}\text{Fe}$  may have been preserved by complete or near-complete oxidation of low  $\delta^{56}\text{Fe}$  aqueous  $\text{Fe}^{2+}$ . The positive  $\delta^{56}\text{Fe}$  values of the marine ironstones are most probably related to a secondary subsurface alteration by ascending acidic groundwater. The acidity and the redox gradient of the groundwater resulted in the oxidation of pyrite pockets of the Cenomanian glauconitic clastics. This process involved transport of aqueous  $\text{Fe}^{2+}$  through the marine ironstone sequences. The production of high  $\delta^{56}\text{Fe}$  values can be attributed to partial oxidation of low  $\delta^{56}\text{Fe}$   $\text{Fe}^{2+}_{\text{aq}}$  in a close proximity to an aqueous anoxic-oxic boundary. The high  $\delta^{56}\text{Fe}$  values for oxides indicate an open system with respect to Fe [3]. Our findings indicate that the application of iron isotopes may provide important information about environmental conditions dominated during the Middle-Eocene ironstone formation and helps to determine precisely the paleoweathering surfaces within the marine ironstone sequences.

[1] Fantle & DePaolo (2004) *EPSL* **228**, 547-562.

[2] Emmanuel *et al.* 2005) *Chem. Geol.* **222**, 23-34.

[3] Yamagushi *et al* (2007) *EPSL* **256**, 577-587.