

## Speciation of Fe adsorbed on and incorporated into soil and aquatic bacteria: XAS structural study

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This work is devoted to the interaction of important oligo-element and nutrient, iron, with major planktonic (cyanobacteria) and soil (rhizospheric *Pseudomonas aurefaciens*) microorganisms via structural study of metal adsorption on and incorporation into cells. Three typical cyanobacteria (*Synechococcus* sp., *Planctothrix* sp. and *Gloeocapsa* sp.) were used both in assimilation ( $\text{Fe}^{3+}$ -containing nutrient solution) and adsorption ( $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ -containing inert electrolyte) experiments. Experimental details are presented elsewhere [1]. Our experiments demonstrated that Fe uptake during growth of exopolysaccharides (EPS)-producing and EPS-poor cultures yields octahedral oxygen environment of trivalent iron with no polymers of Fe-O-Fe structures even to pH 7 (*P. aurefaciens*) and 10.5 (cyanobacteria). Intracellular Fe storage in the form of Fe(III) phosphate is the most likely scavenging mechanism during growth at high concentration (10-100 mg/L of Fe(aq)). In case of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  adsorption at pH = 5-8 and 2-6, respectively, mostly Fe(III) form isolated octahedra linked to carboxylate, and, probably, phosphoryl groups of the external surface layers. Our results strongly suggest that, in the presence of surface organic ligands, the oxidation of divalent iron does occur but the polymerization of formed Fe(III) oxyhydroxides is inhibited and the adsorbed iron present in the form of individual Fe atoms attached to organic moieties. This implies that Fe(III) adsorbed on the cell surface is potentially more bioavailable when follows from thermodynamic prediction on the equilibrium with Fe(III) solid oxyhydroxides.

[1] Pokrovsky, Viers & Emnova *et al. Geochim. Cosmochim. Acta* **72**, 1742-1757.

## Origin of Rare Earth Elements in atmospheric aerosols

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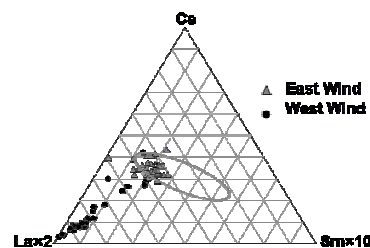
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The main objective of this study is to evaluate the effect of the oil refinery activity in atmospheric aerosols. To this end, fine and coarse PM, were sampled during 5 years in four villages located around an important petroleum refinery industrial state in the Algeciras Bay (Gibraltar Strait).

Previous works have demonstrated that emissions of catalyst employed in the FCC operations in the refineries, are the primary cause REEs enrichment in atmospheric PM. As reported earlier [1], it is necessary to characterize the employed catalyst in each study area due to catalyst chemical characteristics are being continuously changed to enhance their performance. Exhaustive data on the elemental composition of the catalyst employed in the study area is provided in this study. The relative abundance sequence of dominant REEs in the FCC emissions analyzed from the refinery in Algeciras, were identical ( $\text{La} > \text{Ce} > \text{Nd} > \text{Pr} > \text{Gd} > \text{Sm} > \text{Dy}$ ) as previous catalyst compositions reported by other authors [1,2].

The Lanthanum and dominant lanthanoid mass concentrations in PM were illustrated by LaCeSm triangular plots employing the method proposed by Moreno *et al.* [3]. As shown in Figure 1 there is a clear Lanthanum enrichment in PM<sub>10</sub> in the Puente Mayorga station. Inspection in the diagram reveals that the impact from industrial emissions occurs simultaneously with a predominant West wind direction.



**Figure 1:** LaCeSm triangular diagram for PM<sub>10</sub> data from Puente Mayorga station.

The results demonstrate that the oil refinery activities are a considerable source of REEs in the Algeciras Bay, having a significant contribution to PM in the study area.

[1] Kulkarni *et al.* (2006) *Atmosph. Env.* **40**, 508-520.

[2] Kitto M.E. *et al.* (1992) *Env. Science & Technology* **26**, 368-375. [3] Moreno *et al.* (2008) *Atmosph. Env.* **42**, 7851-7861.