Adsorption of organophosphorous compounds on well-characterized iron mineral nanoparticles

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Particles of iron (hydr)oxides in the eartht's crust are highly reactive towards phosphates, and sorption of organophosphorous (OP) compounds constitutes an important part of the anthropogenic phosphor cycle [1]. In this study, three different polymorphs of well-characterized nanoparticles were chosen as model systems for iron minerals, i.e. hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and and goethite (α-FeOOH). Comparative studies of structure-specific sorption processes were performed using three OP compounds, namely trimethyl phosphate (TMP), triethyl phosphate (TEP) and dimethyl-methyl phosphonate (DMMP). Using *in situ* infrared vibrational spectroscopy, calibrated OP adsorption measurements were performed in a temperature controlled system under different conditions: Dry sorption with and without irradiation by simulated sunlight, and sorption under controlled humidity with and without sunlight.

The surface reactivity was shown to be strongly dependent on detailed bonding coordination of the central P atom, the structre of iron mineral surface, and environmental parameters (humidity and sunlight). All OPs were found to adsorb through the phosphoryl O atom on unsaturated iron cation surface sites (Lewis acids) on hematite and maghemite. In contrast, on goethite hydrogen bonding to surface OH (Brønstedt acid sites) dominates. On the iron oxides dissociative adsorption is facile yielding predominantly methoxy and formate reaction intermediates (oxidative pathway), and predominantly methoxy and phosphoric acid on the hydroxide (hydrolysis). The reactivity increases in the order goethite < maghemite < hematite. Addition of water blocks reactive adsorption sites, whereas sunlight strongly promotes OP dissociation on all minerals. Absence of water favours oxidation on hematite and maghemite, whereas presence of water during sunlight irradiation yields a combined oxidation/hydrolysis pathway.

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Microbiological investigation of the Iron-containing floculent mats in various deep sea environments

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It is believed that most important energy source in ocean crust or subseafloor is vastly abundant iron. Therefore, it is suggested that the iron-oxidizing chemolithoautotrophic microbe is a key player for the microbial ecosystem. However, there were no direct evidences because cultivation of iron oxidizer was difficult.

Recently, '*Mariprofundus ferrooxidans*' belong to the ζ (zeta)-proteobacteria [1] was isolated. This microbe can oxidize ferrous iron as the elctron donor and can be widely observed in various deep-sea low-temperature hydrothermal fields [2].

However, the diversity, distribution and role of these iron-oxidizing ζ-proteobacteria are still unknown. In addition, it is still unclear how these microbes cope with iron predominantly from oceanic basalts.

Therefore, to clarify these questions, we have investigated several iron-containing flocculent mats from deep-sea hydrothermal fields in the Mariana Vocanic Arc and the Okinawa Trough. Culture independent analysis of these mats demostrated that ζ-proteobacteria was the most dominant phylotypes. The X-ray analysis (XANES and EXAFS) revealed that the abundance of potentially biogenic Fe-oxides-species would be relevant with the abundance of ζ-proteobacteria population in the iron-containing flocculent mats. These results strongly supported that iron-oxidizing chemolithoautotrophs have significant ecological roles for iron and carbon cycles in deep-sea low-temperature hydrothermal systems.

[1] Emerson D. *et al*. (2007) *PLoS ONE* **2**, e667. [2] Emerson D. & C. L. Moyer (2010) *Oceanography* **23**, 148-163.