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有機物の影響による bacteriogenic iron oxides(BIOS) へのヒ素吸着能の低下
Decrease of arsenate adsorption onto bacteriogenic iron oxides (BIOS) by the presence of organic material

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The adsorption behavior of trace elements onto iron (Fe) oxides has been well demonstrated for their importance in water chemistry. Especially, bacterial-induced Fe oxides (Bacteriogenic iron oxides: BIOS) are of common interest because of their ubiquity and characteristics of adsorption of various ions. Indeed, it is previously reported that the adsorption of heavy metal ions onto BIOS exhibited adsorption trend different from synthetic iron oxides [1]. In this study, arsenate adsorption behavior onto (A) synthetic ferrihydrite, (B) natural BIOS collected from Okinawa hydrothermal vent, and (C) synthetic BIOS obtained by incubation of iron-oxidizing bacterium (*Mariprofundus ferroxydans*) were compared. BIOS synthesis was performed using a set of diffusion cells by which we can obtain pure BIOS free from other inorganic and organic materials which are abundant in natural BIOS (e.g., silica, clay minerals, and other ions adsorbed on BIOS). Adsorption experiments were performed under sea water condition (I: 0.70 M; initial arsenate concentration: 70 mg/L; adsorbent: approx. 0.5 mg) as a function of pH 4-10. Iron mineral species of iron oxides were specified by Fe K-edge X-ray absorption fine structure (XAFS) [2] and adsorption structure of arsenate was examined by As K-edge XAFS analysis.

Iron K-edge XAFS analysis revealed that both natural and synthetic BIOS consisted mainly of ferrihydrite with 45-55 % of highly amorphous Fe hydroxides that is characterized by the primitive Fe hydrothesis stages. The crystal size was nano-scale which was smaller than the synthetic ferrihydrite. Thus, it was expected that BIOS should have more arsenate adsorption capacity than synthetic ferrihydrite. However, the amount of arsenate adsorbed onto each iron oxides decreased in the order of synthetic ferrihydrite > natural BIOS = synthetic BIOS with a same adsorption trend as a function of pH. XAFS and micro-XRF analysis indicated that arsenate was mainly adsorbed onto Fe phase within natural and synthetic BIOS forming inner-sphere complexation to the Fe oxides. These results were consistent with previous results on As adsorbed onto synthetic ferrihydrite. Contrary to their reduced crystal particle size, specific surface areas of synthetic BIOS was decreased by 25% from synthetic ferrihydrite, which is possibly caused by the coprecipitation of Fe oxides with organic materials [3]. Thus, it is suggested that strong aggregation of Fe particles by the presence of organic materials reduces (i) the surface area and/or (ii) the active adsorption site within BIOS, which may ultimately result in the decrease of the arsenate adsorption onto BIOS. These results also suggest that direct and indirect effects of organic materials should be taken into account to evaluate the anion adsorption onto BIOS.

[1] Katsoyiannis et al. (2006) *Water Research* 40, 3646.
[2] S. Kikuchi et al. (2011) *Chem. Lett.* 40, 680-681.
[3] Mikkuta et al. (2008) *Geochim. Cosmochimi. Acta.* 72, 1111.

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