Nano-sized biogenic iron oxides produced by neutrophilic Fe-oxidizing bacteria and its implications for biogeochemical cycling

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Neutrophilic microaerophilic Fe-oxidizing bacteria (NMFeOB) are thought to play a significant role in global biogeochemical cycling of Fe and associated elements. They are commonly found at redox boundaries in both of freshwater and marine iron-rich environments, and produce extracellular iron biominerals that interact with various elements. However, ecophysiology of NMFeOB is still poorly understood due to the difficulty of cultivation. Recently, *Ferriphaselus amnicola* strain OYT1 and *Ferriphaselus* sp. strain R-1, which produce a unique twisted-ribbon-like extracellular iron biomineral structure called a stalk, have been reported (Krepski et al., 2012; Kato et al., 2014). The present study demonstrates the strains OYT1 and R-1 also produce extracellular nano-sized biogenic iron oxides (nanoBIOS), which are morphologically distinct from stalks. Energy dispersive X-ray spectroscopy indicates that the nanoBIOS contain P, as well as the stalks. Given the chemical and morphological characteristics, nanoBIOS may contribute to P, Fe and other metal transport in the environment as a vector. Furthermore, the first genome sequencing of stalk-forming NMFeOB was performed in the present study. Comparative genomics propose potential genes involved in the formation of stalks and nanoBIOS, which are similar to genes involved in extracellular polysaccharide production, and potential genes in iron oxidation, which have been previously suggested as key iron oxidation genes in other NMFeOB. These genes can be used as marker genes for detection of NMFeOB producing iron biominerals. Overall, the detailed microscopy and first genomic analysis of the freshwater stalk-forming NMFeOB provide novel insight into the ecophysiology and biomineralization of enigmatic NMFeOB.

Keywords: Fe-oxidizing bacteria, Nano-sized iron oxides, Biogeochemical cycling

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Cyanobacterial extracellular polymeric substances (EPS) control stromatolite and thrombolite formations

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Stromatolite and thrombolite are the major components of microbialite. Stromatolite is abundant in Meso- to Neoproteozoic successions, while it declined in the early Paleozoic and thrombolite became dominant alternatively. The cause of this transition was previously considered to be due to the bioturbation of evolved metazoans, but recently most of thrombolites are considered to be the primary structure. Therefore, the reconsideration is necessary for the cause of microbialite transition in the early Paleozoic. However, stromatolite and thrombolite are rare in the modern environments, and moreover, there had been no report for the site where they both are formed together. Nonetheless, such example has been found recently from the tufa site in Okayama Prefecture. The present study therefore examined this site for revealing the factors controlling microbialite fabrics.

Water chemistry at the depositional sites of stromatolite and thrombolite are similar, and microelectrode measurement revealed that they both are mainly formed by photosynthesis-induced $CaCO_3$ precipitation. Confocal laser scanning microscopy observation and DNA analysis indicated that cyanobacteria colonizing the stromatolite are mostly *Phormidium* sp., and their extracellular polymeric substances possess acidic group to provide mineral nucleation sites, and resulted in the stromatolite formation. On the other hand, cyanobacteria colonizing the thrombolite are mostly *Leptolyngbya* sp., and their extracellular polymeric substances does not possess acidic group to be unsuitable for the mineral nucleation sites, and resulted in the thrombolite formation. These results indicate that chemical characteristics of extracellular polymeric substances are crucial for the formation of microbialite fabrics.

By simply applying the results above, we can hypothesize that the evolution of cyanobacteria lacking acidic extracellular polymeric substances caused the microbialite transition in the early Paleozoic. Nonetheless, further investigation is necessary for validating this hypothesis.

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Lysine polymerization on amorphous silica: A thermodynamic evaluation

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When, where and how did life on the Earth originate? To resolve that fundamental question, one must first ascertain the reactivity of biomolecules, and the response of reactivity to changing environmental conditions such as pH, temperature, dissolved composition, and mineral surfaces. Amino acids are building blocks of proteins, which are fundamental to life. Therefore, the polymerization behavior of amino acids has been a topic of many experimental and theoretical works (Shock, 1992).

This study focuses on thermodynamic effects of minerals on amino acid polymerization. To date, widely various oxide minerals and clays has been examined for their roles in this reaction (Cleaves et al., 2012). Results have demonstrated their positive influences with regard to reaction rate, peptide length, and the amounts of polymers synthesized. However, reported experiments have mostly emphasized catalytic properties of minerals. Consequently, in most cases, experiments have been terminated before polymerization reaches its steady state. It remains unclear whether minerals promote polymerization in thermodynamics as well as kinetics.

To examine the thermodynamic effects, we have evaluated adsorption behaviors of amino acids and peptides on minerals by using extended triple layer model (ETLM; Sverjensky and Fukushi, 2006). Obtained adsorption parameters are used, by combining thermodynamic parameters for amino acids and peptides in aqueous solution, to predict amino acid/peptide equilibria on mineral surfaces. In this presentation, we will present our findings for a lysine/amorphous silica system.

Keywords: Adsorption, Lysine, Silica

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A role of ferruginous ocean in photochemical synthesis of organic compounds

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Photochemistry is important for the origin of life and the early earth's environment. Previous photochemical experiments suggest that the reaction initiated by UV in CO-rich atmosphere can produce simple organic compounds mainly formaldehyde and methanol (Bar-Nun and Chang, 1983). The amount and speciation of organic molecules are known to depend on the redox state of the atmosphere. The reducing ocean containing ferrous iron may also control the redox state of the ocean-atmosphere system, though the role of ferruginous ocean for abiotic UV synthesis is poorly understood. We have conducted photochemical experiments simulating the reducing atmosphere and Fe(II)-bearing ocean. The results of our experiment suggest that formate, acetate, propionate, and normal alkanes are synthesized under CO-atmosphere. When irradiating UV under the presence of Fe(II)-bearing water, the production rate of formate is about three times faster than the simple CO-H_2O system without ferrous iron. Furthermore, formate is formed even when the gas phase is pure CO_2 when liquid-phase contains Fe(II). These results suggest that the production rate and speciation of organic matter depends on the availability of H_2O as well as total redox state of the whole atmosphere and ocean system. Based on the results, we have modeled the reaction pathway and estimate the flux of each organic compounds supplied to early ocean.

Keywords: origin of life

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Selenium and cesium adsorption onto biogenic iron oxyhydroxides:Comparison with inorganic iron oxyhydroxides

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Iron(Fe) oxyhydroxides are considered to be important sorbents of trace elements in surface environment. This widely view mainly extends from many laboratory studies using inorganic Fe oxyhydroxides. However, most of the natural Fe oxyhydroxides are referred to as biogenic Fe oxyhydroxides(BIOS) which are complex mixtures with various organic matters. The presence of organic matters in BIOS can cause unique adsorption behaviors of trace elements for BIOS, but they have not been characterized well. This study aims to reveal adsorption characteristics of trace elements onto BIOS.

Biogenic Fe oxyhydroxides were collected from Sambe hot-spring in Shimane prefecture. The samples consist of very fine particles of two-line ferrihydrite, coexisting with biogenic organic matters including stalks, extracellular polysaccharides, and bacterial cells. We have conducted adsorption experiments of selenium(Se) and cesium(Cs) on BIOS and synthesized ferrihydrite in a batch system. Our experiments revealed significant differences in Se and Cs adsorption between BIOS and inorganic Fe oxyhydroxides in a wide range of pH, even though they have similar Fe mineralogy. In the case of positively-charged Cs, BIOS showed larger adsorption than inorganic Fe oxyhydroxides. In contrast, negatively-charged Se showed smaller adsorption on BIOS compared with that on inorganic Fe oxyhydroxides. Especially, the decrease of Se adsorption on BIOS compared to inorganic Fe oxyhydroxides was more significant in Se(VI) than in Se(IV), corresponding to their formation of different surface complexes. We consider that the unique adsorption behaviors of Cs and Se on BIOS and their difference with inorganic Fe oxyhydroxides can be explained by the electrostatic effect caused by the coexisting biogenic organic matters in BIOS.

Keywords: iron oxyhydroxides, bacteria, adsorption behavior

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Limiting factor for weathered granitic rocks to be ion adsorption ore

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Main rock of ion adsorption type deposit which is important as rare earth element (REE) resource is weathered granite, from which we can extract REE readily using aqueous solution such as ammonium chloride or ammonium sulfate solution, because REE can be extracted from weathered granite by ion exchange reaction. Previous studies of the ion adsorption type REE deposit has been carried out mainly using weathered granite found in the Southeast Asia, but there are few studies on the weathered granite present in Japan in terms of the REE deposit. In addition, there are no studies which clarify the relationship between REE chemical state and extraction properties in the weathered granite at molecular level. Therefore, the aim of this study is (i) to clarify the relationship between the extraction characteristic of REE in the weathered granite and its chemical state at the molecular level using XAFS method and molecular orbital calculation and (ii) to study the dependence of extraction rate of REE on the degree of weathering of the granitic rocks. In this study, we analyzed granite or weathered granite samples collected in Hiroshima, Shimane, and Tottori in Japan, Sri-Lanka, and Myanmar. The collection of the samples from various sites are strongly needed to cover granitic rocks having various degrees of weathering. Initially, the mineral and major element compositions were examined by XRD and X-ray fluorescence (XRF) analyses. After the analysis, local chemical state of Y, one of REE, was determined using bulk XAFS and μ-XRF-XAFS method at SPring-8 and KEK-PF, scanning electron microscopy (SEM), and molecular orbital calculation. As a result, it was suggested that REE in the samples with high CIA can be readily extracted and the REE chemical state suggested by Y K-edge EXAFS is outer-sphere complex adsorbed weakly in the weathered granite. The μ-XRF-XAFS and SEM analyses showed that REE was mainly adsorbed on phyllosilicates such as halloysite and weathered biotite. On the other hand, the extraction ratio of REE in the samples with low CIA are low and its REE chemical state is inner-sphere complex, or REE incorporated possibly into primary minerals or phosphate. The ratio of outer-sphere complex among total REE determined by the fitting of EXAFS spectra in k space is positively correlated with that of REE extraction ratio. In addition, weathered granite with higher REE extraction ratio exhibits larger negative Ce anomaly, suggesting that REE with negative anomaly in aqueous phase was adsorbed to the granitic rocks, which finally induces the correlation between the degree of negative Ce anomaly and REE extraction ratio. Thus, it is suggested that the degree of negative Ce anomaly is one of the characteristics of ion adsorption type REE deposit. However, strongly weathered granite samples with CIA values higher than 85 do not show high REE extraction ratio. Mineralogy of the samples is dominated by kaolinite and gibbsite, which suggests that the fraction of REE adsorbed on clay minerals is minimal for the strongly weathered granites compared with intermediately weathered granitic rocks with CIA value around 70. Thus, we can conclude that medium weathering characterized by the presence of vermiculate/smectite with CIA value around 70 is an important limiting factor to establish the sample as an REE ion adsorption ore.

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Adsorption behavior of organoarsenic compounds in soils
- Influence of organic matters -

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Anthropogenic originated organoarsenic compounds such as diphenylarsinic acid (DPAA) are a water pollution source as well as naturally occurring inorganic ones. For example, DPAA polluted well water caused serious health problems in Kamisu, Japan. However, their adsorption behavior in soils is still well unknown. In general, the adsorption property of chemical compounds influences its migration process in natural environments such as soil-water system. In soils, organic matters (OMs) affect adsorption behavior of trace metals on minerals. Thus, it is important to understand the adsorption mechanism of the arsenic compounds with taking account of influence of OMs to predict future fate of them in environment. In this study, we conducted adsorption experiments for several soils which have different contents of Fe/Al-(oxyhydr)oxides and OMs, and adsorption amounts and structures were analyzed by ICP-MS and As K-edge XAFS measurements. The same experiments and analysis were conducted with OM extracted soils to understand the influence of OMs. The As K-edge EXAFS spectra for arsenic compounds adsorbed on soil samples were well fitted with corresponding EXAFS spectra As adsorbed on Fe- and Al-(oxyhydr)oxides. The fact indicates that these arsenic compounds adsorbed on these minerals mainly. The adsorption ratios for Fe- and Al-(oxyhydr)oxides were estimated by the fitting, and the deviation of the ratio from the Fe/Al content was larger with increasing the OM content in soils. In addition, in most cases, the adsorption amounts of arsenic compounds increased by removing OMs. Thus, it is considered that the OMs prevent arsenic compounds from being adsorbed on minerals by covering their surface. However, even though OMs were removed from soils, the adsorption ratios were still not always reflected Fe/Al content ratio by removing OMs depending on the arsenic compounds. This fact indicates that the affinity of arsenic compounds for Fe/Al-(oxyhydr)oxides is different.

Keywords: organoarsenic compound, adsorption, soil, XAFS

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Change processes of microfabrics in the Nankai Trough muddy sediments from several centimeters through several hundreds meters in burial depths

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Microfabrics in deep-sea sediments prior to incorporation in an accretionary prism give us important visual information for deformation fabric analyses. Analyses of primary sedimentary fabrics and compaction processes of deep-sea sediments are a key to understanding formation processes of the decollement zone. This paper discusses the microfabric development processes of unconsolidated hemipelagic sediments and mass transport deposits (MTDs) during early diagenesis from deposition, burial compaction-cementation, and deformation by means of microfabrics observations and physical/mechanical property measurements using drilling core samples and submersible samples as follows.

1) The submersible samples were collected from the landward trench slope in the Nankai Trough using a MBARI-type corer. The water depths were from 2500 to 3000 m. The sediment cores of 3K#1345C-1, -2, -3, -4 and 3K#1346 C-1 were mostly 20 cm in length. We measured physical and mechanical properties in the core sediments.

2) The drilling core samples were collected in the Nankai Trough using a Hydroric piston corer. The water depths were from about 3000 m. The sediment cores of C0018A were 314.5 m in length. C0018A is divided into Unit IA is composed Hemipelagic mud layer that is frequently volcanic ash layer is sandwiched between and six MTD layer volcanic ash layer is caught. Unit IB is composed of a sandy turbidite layers. In addition, it deals only Unit IA in this announcement. Mechanical properties in the core sediments were used on board data.

The main objective of this paper is to understand the microfabrics changing processes in the Hemipelagic sediments from several centimeters to several hundreds meters in depth during long-term burial compaction. The burial compaction processes have been mainly studied using consolidation tests in laboratories for a short-term, although, sediments are consolidated gradually during geologic time as an age effect. Microfabrics changing processes by age effects are not well understood. Hemipelagic sediments are the best examples for long-term compaction study, because they have mostly constant sedimentation rates through geologic time and homogeneous structures and components.

The samples for microfabrics observation were treated by freeze-drying and embedding methods in order to avoid volume shrinkages by air-drying. The microfabrics in the Hemipelagic sediments and MTDs are mainly constituted of clay aggregations (ped) and clay linkages (connector) as shown in below.

1) In the Hemipelagic mud layers, the microfabrics are characterized by a horizontal preferred orientation of clay flakes in Face-to-Face contact.

2) In the MTD layers, most of the clay flakes constitute in regular/irregular aggregations. The regular aggregations range from 1 to 5 μm and irregular aggregations are larger than 20 μm in diameter.

Keywords: Microfabric, Nankai trough, Mass transport deposits

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Chemical forms of arsenic in marine sediments and dissolution mechanisms into porewater of Kumano Basin, Nankai Trough

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The purpose of this study is to clarify the accumulation process of arsenic and the behavior during an early stage of diagenesis in modern marine sediments.

The cored sediments and porewaters at Sites C0002 and C0022, Nankai Trough. At the Site C0002 (0-1050mbsf), sediments at <800mbsf was composed of forearc basin sedimentary rock (terrestrial sediment) and the lower part was of accretionary prism.

In the Site C0002, total arsenic concentrations of sediments increased at 0-330mbsf with depth. The highest concentration was recorded at 330mbf (13ppm). Then, the concentration decreased, and became constant about 5ppm below 500mbsf. Total arsenic concentration was higher in forearc basin sedimentary rocks than the underlying accretionary prism sediments. It suggest that the primary arsenic was mostly derived from subareal region via detrital fragments.

The result of BCR sequential extraction analysis showed that about 40% of As in the sediment was fixed in insoluble phases, i.e., structure of sulfide and/or silicate minerals. Arsenic in insoluble phase was >80% in the sediment at 1000mbsf, implying that the arsenic was fixed in authigenic pyrite in the deep part of the sediment column.

The ratio of dissolved arsenic arsenic $_{\text{(porewater)}}$ to Total arsenic of the sediment was especially high at those depth. Thus, the arsenic dissolution was promoted at those depth. Similar high dissolved arsenic ratio was shown at 100-200mbsf, Site C0022, suggesting the same mechanisms to release arsenic in the sediment at these depth.

Speciation of arsenic-being phases in the adsorbed fractions onto sediment particles were analyzed by HPLC and analyzed by ICP-MS/MS. Arsenate, arsenite, MAA, and AsB were only detected from the sediments at C0002, C0022. Total concentration of these arsenic compounds was 60% of total arsenic of the sediment, and most of them were arsenate and arsenite. It indicate that over half of total arsenic in the sediment was adsorbed as inorganic arsenic onto the mineral surface. The concentration of arsenite increased below 100mbsf, suggesting that the arsenate was reduced below this depth. The MAA was not large compared to the total arsenic, however, it is important to evaluate the contribution of microbiological activity to the arsenic cycle in the marine sediments. As mentioned above, arsenic fixed in the sediments releases into the porewater at 100-200mbsf. Decomposition of organic matters are extensive in 0-150mbsf evidenced by increasing concentration of NH_4^+ of porewater and Br^- (accumulate in red algae). Thus, MAA would be a product of decomposition of organic arsenic compounds, such as arsenosugar contained in algae.

Below 200mbsf, increasing pH controlled arsenic dissolution. The average of pH was 7.79 in 0-200mbsf, then graduate increased below this depth. It’s peak was about 7.98 at 400mbsf. Surface potential of iron oxyhydroxides/oxides changes at pH=7.9. Negatively changed arsenic (mainly arsenate) was intensely released into the solution at pH>7.9. Observation of this study showed that the small change of pH considerably controls the dissolved arsenic in porewater.

This study demonstrates the importance of input of subareal detrital materials for the arsenic cycle in the crust through hydrosphere and microbiological activity to change the arsenic phases in the marine sediments at the very early stage of diagenesis.

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Keywords: arsenic, IODP, porewater

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Selenite sorption on magneaium oxide under the highly alkaline conditions

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Selenium occurs widely throughout nature. It is one of essential the elements for human, but it shows toxicity at degree to double of the necessary quantity. Selenium is environmental standard designation item.

After earthquake disaster, the contribution of the nuclear power generation in the electricity source of supply in Japan decrease, while that the thermal power generation increases. In coal-fired station, the selenium concentrations more than industry waste water regulation (100ppb) in the drainage has been reported to occur in a desulfurization processes of the gases which is generated during burnt coral (Central Research Institute of Electric Power Industry, 2005). The solutions used in the desulfurization processes is kept alkaline in order to facilitate the dissolution gases.

Selenium mainly exists as selenite($H_xSeO_4^{2-x}$, Se(Ⅵ)) or selenite($H_ySeO_3^{2-y}$, Se(Ⅳ)) in solution. Most of selenium exists as selenite in waste water in desulfurization process (Central Research Institute of Electric Power Industry, 2005). A general selenite removal method in the solution includes the adsorption on iron oxide. However, adsorption significantly decrease under the alkali condition because the surface charge of iron oxide become to minus at alkaline conditions (Fukushi, 2008). Therefore, the effective removal of selenite under the alkali condition is expected.

The anions of which oxygens coordinate to the center atom are called oxyanions. There are many oxyanions which cause the water pollutions, e.g., arsenite and bronate. It is reported that magnesium oxide (MgO) has ability for the removals of aresnite and bronate (Liu et al., 2011; Fuente and Eugenio, 2006). It can be expected that MgO has ability for removal for selenite in solution. MgO is metastable phase under the Earth surface environmental, and it transforms to brucite ($Mg(OH)_2$) in solution with time (Yabe et al., 2011). Liu et al., (2011) studied the removal of arsenite from solution by MgO with high sace area. They suggested that the tranformation in solution is related to the uptake of arsenite, i.e., the sorption mechanism of aresenite on MgO under the high arsenite concentration condition is formation of an “arsenite-Mg compound” following transformation to $Mg(OH)_2$. Their study was conducted under the very high sorbate concentration (>1ppm) condition. There were no arguments about the mechanisms under the low concentration condition with sub-ppm order. The water pollution related to selenium mainly becomes problem with low concentration around the waste water satandards (100ppm order). It is thought that understanding the sorption behavior in the low concentration condition is necessary. I conducted bacth sorption experiments of selenite by MgO and magnesium hydroxide which is stable phase in this study to examine the selenite uptake behavior and mechanism on MgO.

Keywords: Selenite, Magnesium Oxide, Metastable Phase, Magnesium Hydroxide, Alkaline Conditions

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Predictive model for Pb(II) adsorption on soil minerals (oxides and low crystalline aluminum silicate) consistent with spectroscopic evidence

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Mobility of Pb(II) in surface condition is governed by the adsorption processes on soil minerals such as iron oxides and low crystalline aluminum silicates. It has been documented that the adsorption effectiveness and the surface complex structures of Pb(II) sensitively varies with the solution conditions such as pH, ionic strength, Pb(II) loadings and electrolyte anion types. Present study aims to construct the quantitative model for Pb(II) on the soil minerals, which can predict the adsorption effectiveness and surface complex structures under any solution conditions by means of extended triple layer model (ETLM).

The Pb(II) adsorption data on goethite, ferrihydrite, quartz and low crystalline aluminum silicate (LCAS) were analyzed with ETLM to retrieve the surface complextion reactions and these equilibrium constants. The adsorption data on goethite, ferrihydrite and quartz come from previous studies. Those on LCAS were measured in present study under wide range of pH, ionic strength and Pb(II) loadings in $NaNO_3$ and NaCl solutions. All adsorption data can be reasonably regressed by ETLM with the assumptions of inner-sphere bidentate complexation and inner-sphere monodentate ternary complexation with electrolyte anions, which are consistent with the previously reported spectroscopic evidences. The predictions of surface speciation under wide range of solution conditions by ETLM revealed that the inner-sphere bidentate complex is predominant species at neutral to high pH conditions. The inner-sphere monodentate ternary complex becomes important at low pH, high surface Pb(II) coverage and high electrolyte concentrations, of which behavior is consistent with the spectroscopic evidences.

The comparisons of the obtained adsorption constants on goethite, ferrihydrite and quartz exhibited good linear relationships between the reciprocals of dielectric constants of solids and adsorption constants. The linear relationships enable the predictions of the adsorption constants of all oxides based on Born solvation theory. The adsorption constants of LCAS are comparable to those of goethite. The comparisons of the adsorption constants of soil minerals suggest that the ferrihdyrite, goethite and LCAS are three most important sorbents for Pb(II). Ferrihydrite and goethite are ferric oxides which are unstable in reducing conditions while LCAS is insensitive to the redox changes. The present study also implies that adsorption of Pb(II) in subsurface soil conditions may be governed by LCAS.

Keywords: soil minerals, surface coplexation modeling, Pb(II), oxides, low crystalline aluminum silicate

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