

Siderophore sorption to clays

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Abstract Siderophores are low molecular weight organic ligands exuded by some aerobic organisms and plants to acquire Fe under Fe-limited conditions. The hydroxamate siderophores may sorb to aluminosilicate clays through a variety of mechanisms depending upon the nature of the clay and of the siderophore along with solution conditions such as pH, ionic strength, and presence of metal cations. They may also affect metal binding to clays. Here, we review previous studies of siderophore sorption to aluminosilicate clays; briefly discuss how the techniques of X-ray diffractometry, Fourier-transform infrared spectroscopy, and X-ray absorption spectroscopy may be applied to such studies; review effects of siderophores on metal sorption to clays; and highlight some areas for future research.

Keywords Siderophore · Clay · Sorption · Metals · XRD · FTIR · EXAFS

Introduction

Many aerobic microorganisms and graminaceous plants exude siderophores, which are low molecular weight organic ligands that bind Fe^{3+} with 1:1 binding constants as high as 10^{52} (Albrecht-Gary and Crumbliss 1998; Raymond and Dertz 2004). In addition to binding Fe^{3+} , siderophores may form strong complexes with a variety of other metals and radionuclides (e.g., Evers et al. 1989). In recent years, a good deal of research has focused on siderophore sorption to and/or dissolution of a broad range of minerals, including: Fe(hydr)oxides (e.g., Holmén and Casey 1996; Kraemer et al. 1999; Kraemer 2004); the Fe-rich aluminosilicate mineral hornblende (e.g., Liermann et al. 2000); the aluminosilicate clays kaolinite and smectite (e.g., Neubauer et al. 2000; Rosenberg and Maurice 2003; Haack et al. 2008); the Mn oxides (Duckworth and Sposito 2005) and the Pb-phosphate mineral pyromorphite (Maneck and Maurice 2008).

Many studies of siderophore interactions with minerals have relied on use of the trihydroxamate desferrioxamine (DFO) siderophores (Fig. 1). The structure of the hydroxamate group is exemplified by acetohydroxamic acid (aHA; Fig. 1). DFO-B and DFO-D₁ have the same fundamental structures, but different terminal groups make DFO-B cationic (pK_a of terminal amine group is 11.7; Duckworth and Sposito 2005) and DFO-D₁ neutral over a broad pH range, respectively. DFO-E has the same basic

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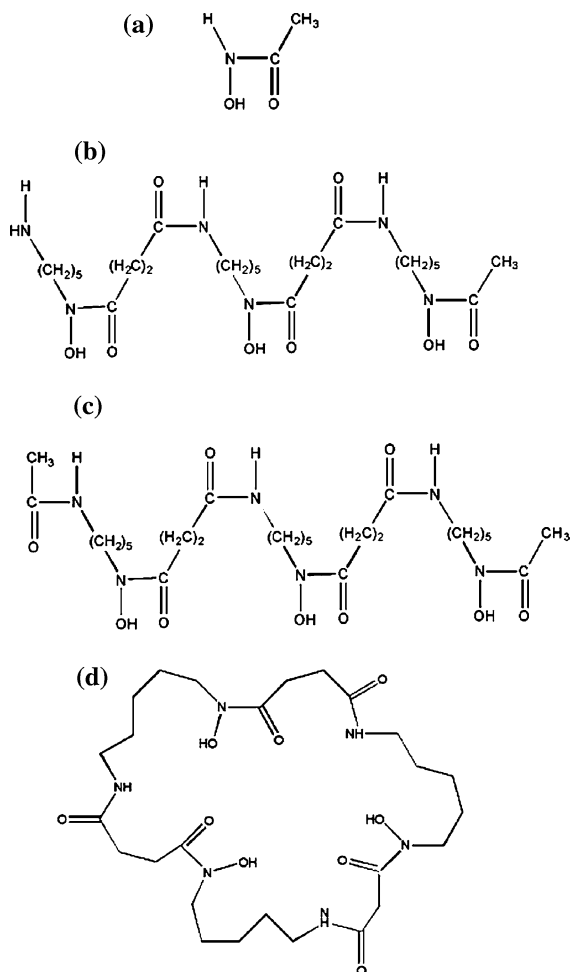


Fig. 1 a aHA, b DFO-B, c DFO-D₁ and e DFO-E structures

structure as DFO-B, but forms a ring and does not have a terminal group. DFO-B, which is the most widely studied trihydroxamate siderophore, complexes Fe strongly to form predominantly the HDFO-B-Fe⁺ cation over the pH range from 1 to 12 (e.g., Neilands et al. 1987; Edwards and Myneni 2005).

In this paper, we focus on DFO sorption to the aluminosilicate clays kaolinite and smectite. First, some properties of the clays important to sorption are reviewed. Second, some key methods of analysis are discussed, with a focus on application to siderophore-clay studies. Third, results of adsorption experiments are discussed. Fourth, we review research on siderophore-metal-clay sorption. Finally, we identify some important topics for future research.

Some notes on terminology

The term *sorption* is used when the mechanism by which a given species (the *adsorbate*) accumulates at an interface (the *adsorbent*) is unknown, or to refer to more than one process. The term *adsorption* is applied to a process in which individual species or small clusters accumulate in a two-dimensional fashion at an external surface. *Absorption* refers to accumulation that goes into a particle, such as into micropores or clay interlayers. *Precipitation* refers to a three-dimensional accumulation process associated with a surface (heterogeneous nucleation) or in the surrounding solution (homogeneous nucleation). For a non-swelling clay such as kaolinite, organic compounds may adsorb or precipitate. But, for a swelling clay such as montmorillonite, many organic compounds may also absorb into the clay interlayers. Swelling clays and micas with negative permanent structural charge density resulting from isomorphic substitution may undergo *cation exchange* and often have high cation exchange capacities (CEC).

Kaolinite and montmorillonite structure and surface properties

Kaolinite (Al₂Si₂O₅(OH)₄) has one silica tetrahedral sheet linked through oxygen atoms to one aluminum octahedral sheet to form a 1:1 structure with the thickness of the two-layered unit ~7 Å (Fig. 2). Hydrogen bonds form between protons exposed on the surface of one layer and oxygens on the next, so that kaolinite is a non-expanding clay. Natural kaolinite tends to be close to stoichiometric, although small amounts of structural or sorbed Fe may occur or Fe may be present in an additional solid phases. Ams et al. (2002) showed that an aerobic *Pseudomonas mendocina ymp* bacterium produced siderophores in the presence of kaolinite, in order to acquire Fe present in trace quantities.

Si–O–Si sites on the basal plane surfaces of kaolinite are generally considered to be unreactive to ionic adsorption, although they may adsorb nonpolar organics. A small amount of structural charge due to isomorphic substitution can create diffuse negative charge allowing for minor cation exchange on some samples. Metal cations may associate with the ditrigonal cavities on the siloxane basal-plane surfaces. Sites on the basal plane where a

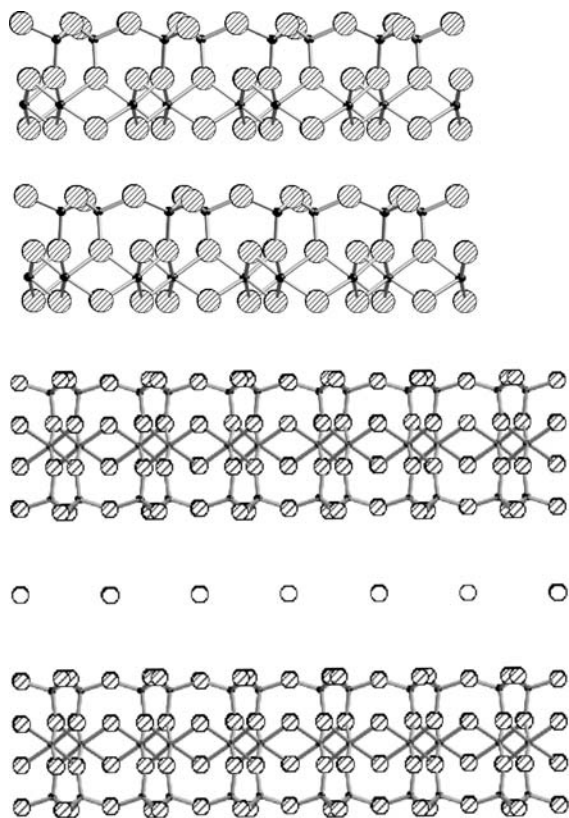


Fig. 2 The kaolinite (*top*) and montmorillonite (*bottom*) structures. From Maurice (2009)

hydroxide group is bridged between two Al atoms (Al–OH–Al) also can permit cation adsorption. Edge sites tend to be far more reactive for ion sorption, and may include aluminol sites, Al(III) · H₂O, and silanol sites, Si(IV)OH. The H₂O on the aluminol sites can be replaced by hydroxide at relatively high pH (Sposito 1984). The pH of the point of zero net proton condition (pH_{p.z.n.p.c.}) of Georgia kaolinites is in the vicinity of five (e.g., Sutheimer et al. 1999).

The term *smectite* refers to a group of clay minerals described by the general equation (Al, Mg, Fe³⁺)₂((Si,Al)₄O₁₀)(OH)₂, with montmorillonite an important example [(Na,Ca)_{0.3}(Al,Mg)₂Si₄O₁₀(OH)₂ · *n*(H₂O)]. There are two silica tetrahedral layers on either side of an aluminum octahedral layer, so that montmorillonite has a 2:1 structure (Fig. 2). Substitution of Mg²⁺ for Al³⁺ and of Al³⁺ for Si⁴⁺ leads to substantial permanent negative structural charge. The thickness of the interlayer spacing may change with conditions such as relative humidity, and identity and concentration of interlayer cation(s) and of molecules

absorbed in the interlayer. Smectites show an affinity for organic cations that exceeds that for inorganic cations, and they also can represent important sorbents for neutral organic compounds, especially when polar (e.g., Karickhoff 1984; Pereira et al. 2007). The CEC of montmorillonite can be as high as ~100 mEq 100 g⁻¹.

Some key methods for investigating siderophore sorption to clays

X-ray diffractometry, XRD

XRD is a method for determining the arrangement of atoms within a crystalline solid based on the scattering of an X-ray beam by (primarily) the electrons associated with atoms within the solid. XRD is useful for determining how interlayer spacings in swelling clays change upon different treatments such as during organic absorption experiments (e.g., Sheng et al. 2002). Absorption of organic molecules or ions into the smectite interlayer has traditionally been evidenced by changes in the *d*(001) spacing of the clay in the presence of an organic sorbate versus the same clay saturated with an inorganic cation such as Na⁺ or Ca²⁺. Using conventional XRD, samples reacted in bulk solution are prepared for analysis as air- or oven-dried powders or films, and the *d*-spacing reflects the interlayer hydration state, which is a function both of the hydration energy of the saturating cation and of the relative humidity (e.g., Dontsova et al. 2004).

When organic cations are absorbed into the smectite interlayer, the *d*-spacing depends on the size and structure of the cation, its conformation in the interlayer, relative humidity, and any interactions between the clay and absorbed organic molecule that may inhibit swelling. The *d*-spacings of smectites have been well studied when organic amines and ammonium cations are sorbed (e.g., Yariv and Lapidés 2005). For example, the hexadecyltrimethylammonium (HDTMA⁺) cation may take on different orientations in the interlayer, depending on sorption density (He et al. 2006). HDTMA⁺ may be oriented parallel between opposing siloxane layers (i.e., lateral monolayer), in paraffin formation (with the alkyl chain oriented 31° to the siloxane surface) or in intermediate orientations, resulting in different *d*-spacings. Interlayer absorption of organic compounds often affects

montmorillonite expansion upon rehydration. Haack et al. (2008) applied XRD in a study of DFO-B and DFO-D₁ sorption to montmorillonite, and dehydration/hydration experiments confirmed interlayer absorption under the experimental conditions.

Pereira et al. (2007) found by comparing classical XRD with newly developed techniques allowing XRD in suspension that the sorption behavior of organic compounds can be different on air-dried versus suspended clays. Suspension XRD may represent fully hydrologically saturated environments, whereas measurements on air-dried samples may be more relevant to soil environments that are hydrologically unsaturated.

Fourier transform infrared spectroscopy, FTIR

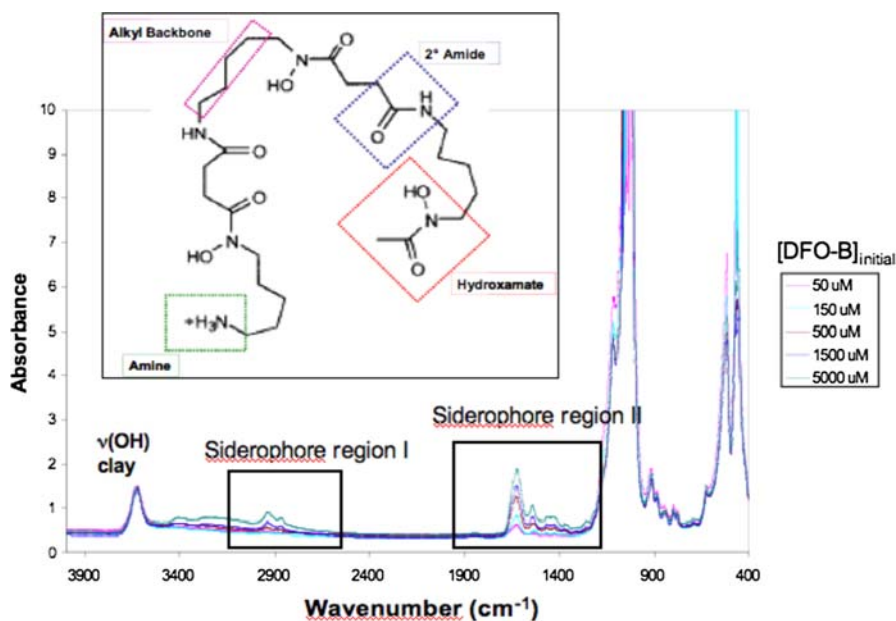
This vibrational spectroscopy, including Fourier transform analysis to account for effects of water, can provide insight into molecular interactions between organic molecules and clay external or interlayer surfaces. The vibrational motions of atoms in solution or at a surface are highly sensitive to changes in their local environment so that FTIR can provide detailed information on interactions of sorbents with sorbates.

FTIR can be used to probe both the structure of a clay and the conformation of sorbed DFO. Samples are often prepared as self-supporting films, a process

that includes air drying. The region(s) of FTIR spectra that contain diagnostic information will depend on the structure of the sorbed molecules. FTIR spectra of DFO-B and DFO-D₁ molecules are complex because of the different structural components, including the methyl backbone and the amide and hydroxamate functional groups, so that specific diagnostic bands are focused upon. For the trihydroxamate siderophores, two diagnostic regions are (Fig. 3): Region I from 1,700 to 1,300 cm⁻¹ and Region II from 3,800 to 2,800 cm⁻¹ (Haack et al. 2008). In Region I, the Amide II and $\delta(\text{C-H})$ bending vibrations are important. The Amide I [mainly resulting from the amide $\nu(\text{C=O})$] stretch and hydroxamate $\nu(\text{C=O})$ stretch bands also occur in this region. Complexation of metals can affect the positions of both of these bands, as shown for the Fe³⁺–DFO-B complex by Siebner-Freibach et al. (2005). However, changes to the shape and intensity of the Amide I and Hydroxamate $\nu(\text{C=O})$ bands for DFO upon sorption to clay are difficult to interpret because they absorb at the same energy as the $\delta(\text{OH})$ bend of water sorbed to clay. In Region II, the symmetric and asymmetric $\nu(\text{C-H})$ and the $\nu(\text{N-H})$ stretching bands can provide important information regarding the conformation of a sorbed siderophore.

Clay structure upon siderophore sorption can also be probed using FTIR. Strong bands in the FTIR

Fig. 3 DFO-B molecule and FTIR spectra of self-supporting films of Swy-2 montmorillonite with sorbed DFO-B. Two regions of interest in the FTIR spectra with respect to DFO-B sorption are indicated, and include bands assigned to the highlighted moieties of the DFO-B molecule. All spectra have been normalized to the peak area of $\nu(\text{OH})$ of clay. Data described in Haack et al. (2008)



spectrum of SWy-2 montmorillonite at 919, 883, and 850 cm^{-1} are assigned to the structural AlAlOH , $\text{AlFe}^{3+}\text{OH}$, and AlMgOH bending vibrations of the clay (e.g., Farmer 1974). Quantitative analysis of this region can be used to determine the extent of isomorphic substitution of the clay (Vantelon et al. 2001). Using quantitative FTIR, Haack et al. (2008) observed that the structural Fe^{3+} content of montmorillonite decreased upon exposure to DFO-B and DFO-D₁ for 48 h, in agreement with measurements of Fe release to solution.

Research described above was conducted on air-dried samples, and further research needs to be conducted using FTIR-ATR (attenuated total reflectance) on fully wetted samples.

X-ray absorption spectroscopy, XAS

X-ray absorption fine structure (XAFS) spectroscopy is a synchrotron-based technique that is part of the

XAS family. XAFS is an element-specific, short-range structural probe that provides qualitative and quantitative information on the local structure and coordination environment of an atom of interest in environmentally relevant conditions. The interactions illustrated in Fig. 4a result in a series of oscillatory structures (*sine waves*) which have been attributed to the presence of other atoms around the absorbing atom. By analyzing these oscillations, information about the local environment of the absorbing atom can be derived (Fig. 4b). Oscillations well above the absorption edge known as extended X-ray absorption fine structure (EXAFS) provide information about the type, number, and radial distances of the atoms surrounding the atom of interest.

X-ray absorption fine structure can be run on sample in solution or wetted, under ambient conditions. For applications to metal-siderophore sorption studies, the data range can be limited to relatively high surface loadings, and physical interpretation of

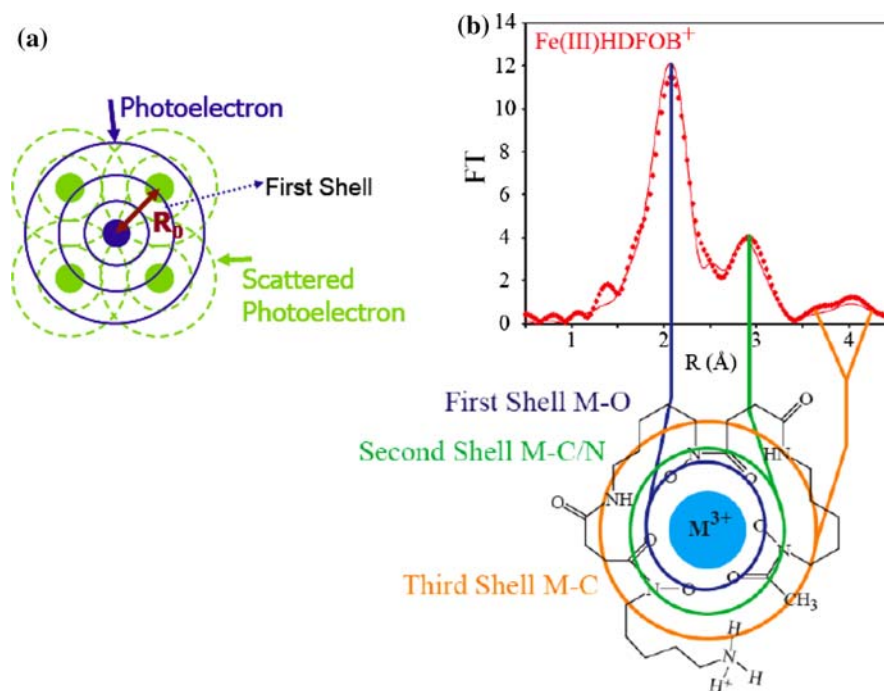


Fig. 4 **a** The principle of XAFS. The absorbing atom is shown by a solid blue circle and the neighboring atom by a solid green circle. The outgoing photoelectron wave from the absorbing atom is shown by solid red lines and the backscattered Photoelectron wave from the neighbor by the dotted lines. These two photoelectron waves interfere to give rise to XAFS oscillations. X-ray is incident on a sample resulting in the

ejection of a photoelectron from the core-hole. This photoelectron must return back to the core-hole before its decay for XAFS to happen. The figure also shows the difference between XANES and EXAFS. The inset **b** is courtesy O. Duckworth (North Carolina State University), showing the EXAFS FT fit for the Fe(III)HDFOB^+ complex

sorption data can be complicated due to overlapping contribution of different scattering paths. For DFO, C cannot be distinguished from N using metal-edge EXAFS, although O is readily distinguishable from either C or N. What this means is that if a metal binds inner-spherically to an hydroxamate group, the first shell can be identified as O (see Fig. 1 and Mishra et al. 2009), but the second shell cannot be represented exactly with C distinguished from N. Despite these limitations, XAFS is a powerful tool for probing metal-siderophore interactions with clays, especially when used in combination with other techniques such as FTIR, solid-state NMR, and quantum chemistry calculations.

EXAFS has been used to study the coordination geometry of metal-siderophore complexes in solution under a wide range of conditions (e.g., Edwards and Myneni 2006; Duckworth et al. 2009; Mishra et al. 2009). Such solution studies can provide invaluable background information for comparison in sorption studies. Duckworth et al. (2008) used EXAFS to probe the sorption mechanism of Fe(III)–DFO-B complex to layered Mn oxides. The structural modeling of Fe K edge EXAFS spectra was accomplished with three components: (1) Fe sorbed at defect sites, (2) Fe sorbed at edge sites formed on the Mn oxide layers, and (3) intact Fe(III)HDFO-B⁺. EXAFS analysis indicated that the dominant component was Fe directly sorbed to the oxide surface at the edge

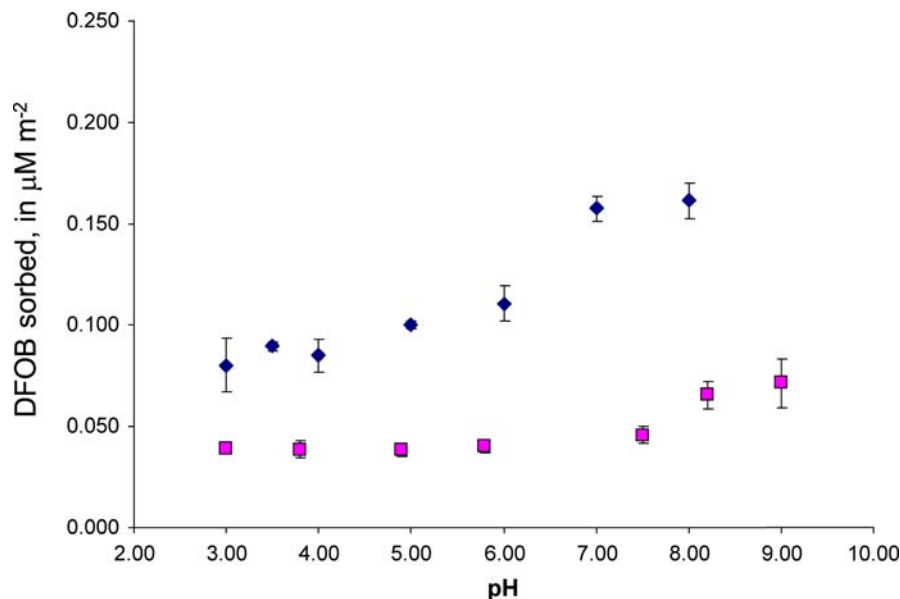
sites, and that sorption to defect sites was a minor component. Intact Fe(III)HDFO-B⁺ was found to be significant only for a biogenic Mn oxide sample (Duckworth et al. 2008). Mishra et al. (2007 and unpublished data) used EXAFS to study the interactions of Pb and Cd with kaolinite in the presence of DFO-B. EXAFS analysis indicated formation of a “Type A” ternary surface complex (i.e., siderophore–metal–clay) for Pb, but no such ternary complex for Cd.

DFO–clay sorption studies

Rosenberg and Maurice (2003) investigated the adsorption of DFO-B to Georgia kaolinite KGa-2 at pH 3–8, in 0.01 M NaClO₄. Adsorption of DFO-B to kaolinite was considerably stronger than previously observed by Kraemer et al. (1999) on goethite (Fig. 5). Adsorption of DFO-B was consistent with cation-like behavior, increasing above KGa-2's $pH_{p.z.n.p.c.} = 4.9$ and above goethite's $pH_{p.z.n.p.c.} = 8.1$. This suggests that adsorption of the DFO-B cation is at least partly electrostatically driven, although the exact mechanism(s) of DFO-B sorption to kaolinite and goethite as a function of pH and ionic strength are unknown.

Numerous studies have shown that cationic and neutral small organic molecules may absorb into the interlayers of swelling clays such as montmorillonite.

Fig. 5 Comparison of the adsorption of DFO-B to kaolinite (*diamonds*) versus goethite (*squares*). Figure after Rosenberg and Maurice (2003); using goethite data from Kraemer et al. (1999)



For example, absorption of short-chain alkylammonium cations has been widely reported (e.g., Lagaly 1981; He et al. 2006). Mechanisms that may contribute to the absorption of organic molecules to montmorillonite include cation exchange (for cationic species) and site-specific interactions between polar functional groups of the sorbed molecule and the interlayer cations, or the water molecules that surround the interlayer cations (Johnston et al. 2001, 2002; Sheng et al. 2002). Interactions between neighboring adsorbed molecules may also affect sorption. Neubauer et al. (2000) and Siebner-Freibach et al. (2004, 2005) showed that DFO-B sorption to montmorillonite tended to be significantly greater than to kaolinite over a broad pH range (Fig. 6), and they showed that DFO-B and the Fe^{3+} complex FOB (ferrioxamine B) both appear to absorb into the montmorillonite interlayer.

Haack et al. (2008) investigated the sorption of cationic DFO-B, neutral DFO-D₁ and aHA to Na-saturated montmorillonite at pH 5.5 and 0.1 M ionic strength using batch experiments coupled with XRD and FTIR analysis. Both siderophores showed a high affinity for montmorillonite, but aHA did not sorb appreciably. The extent of sorption of the siderophores was too great to be strictly adsorption to the external montmorillonite surfaces, so that absorption was deemed likely. It should be noted that DFO-D₁ is relatively insoluble and tends to precipitate with increased concentration, which had to be taken into

consideration in the design of the sorption experiments. Changes to the *d*-spacings as measured by XRD were consistent with DFO-B and DFO-D₁ absorption into the clay interlayers. Analysis of FTIR spectra of clay samples with sorbed DFO-B and DFO-D₁ indicated that the conformations of each of these molecules was distinct from its conformation in either crystalline or dissolved states. As the initial concentration of DFO-B increased to 500 μM , DFO-B absorption changed from monolayer to bilayer.

Haack et al. (2008) suggested that up to three mechanisms may contribute to the observed DFO sorption: (1) cation exchange (for DFO-B, which is cationic, but not for DFO-D₁, which is neutral), (2) specific interactions between polar and non-polar moieties on the siderophores and like sites associated with the clay interlayer surface structure, and (3) “cooperative” processes, in which siderophore–siderophore interactions or siderophore-induced changes to the clay structure enhance sorption. Some DFO sorption may also occur on the external surfaces of montmorillonites, although fewer sites are available than within the interlamellar spaces.

DFO effects on metal sorption

Neubauer et al. (2000) showed that DFO-B adsorbed only very weakly to kaolinite at pH ~ 6.5 – 9.3 and that it decreased the adsorption of Cu, Zn, and Cd. The effect of DFO-B was greatest for Cu and least for Cd, in agreement with complexation constants for these metals. Hepinstall et al. (2005) compared the effects of DFO-B, DFO-D₁, DFO-E, and aHA on Pb and Cd (excepting DFO-E) adsorption to kaolinite at pH 4.5–9, in 0.1 M NaClO_4 . At pH > 6 , all of the studied ligands decreased Pb adsorption to kaolinite: aHA by 5–40% and DFO-B, DFO-D₁, and DFO-E by 30–75%, with the effects increasing with pH. At pH > 8 , aHA decreased Cd adsorption by up to 20% and the trihydroxamates by up to 80%. Enhancement of Pb adsorption by DFO-B at pH ~ 5 – 6.0 (Fig. 7a) was also observed, perhaps due to formation of a ternary surface complex. Mishra et al. (2007 and unpublished data) demonstrated that a variety of DFO-B–Pb–kaolinite ternary surface complexes may form on kaolinite at pH > 4 (Fig. 7b). The ternary surface complex(es) that form between Pb, DFO-B, and kaolinite at pH ~ 5 – 6 apparently have greater

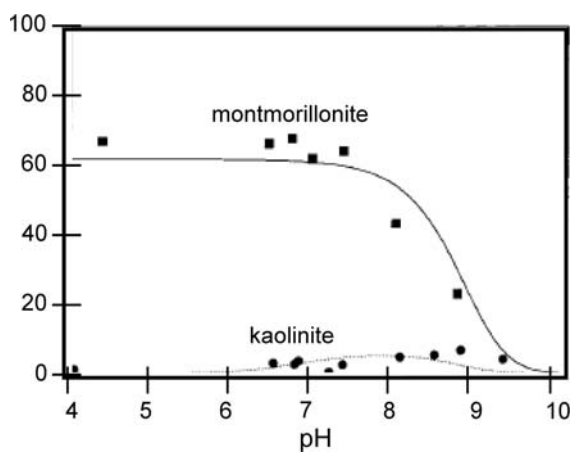


Fig. 6 Comparison of sorption of DFO-B to montmorillonite versus kaolinite. Data Neubauer et al. (2000); figure redrafted for clarity of text

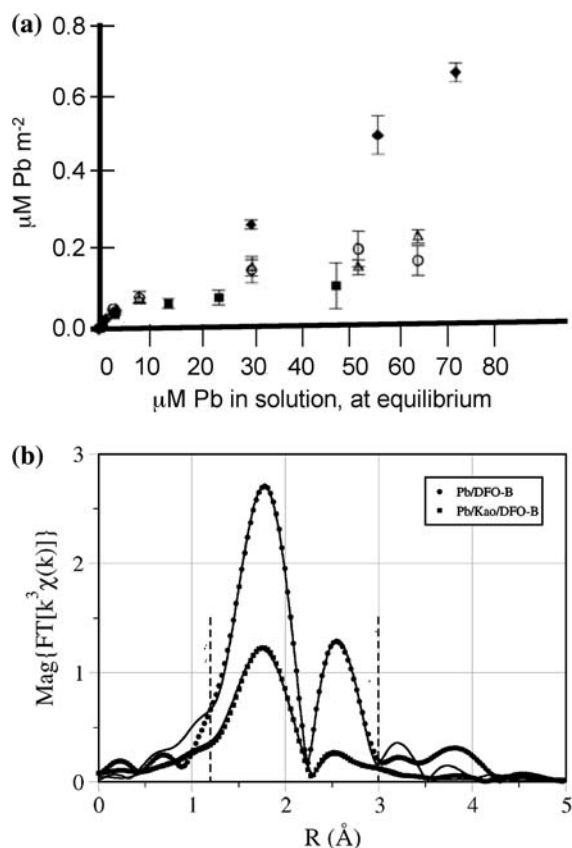


Fig. 7 **a** Top, Effects of DFO ligands on Pb adsorption to kaolinite at pH 6. Filled squares, no ligand added; open circles, aHA; open triangles, DFO-D; filled diamonds, DFO-B. After and using data from Hepinstall et al. (2005). **b** Bottom, EXAFS Data and fit of the magnitude of the Fourier Transform of Pb/DFO-B and Pb/DFO-B/kaolinite. The Pb–DFO-B/kaolinite system indicates the presence of a ternary surface complex at the sample pH (7.5). Although in the solution complex, the Pb is fully caged by siderophore, the absence of a strong second shell in the Pb/DFO-B/kaolinite surface complex indicates the unwrapping of DFO-B molecule in the presence of kaolinite surface at pH 7.5. From Mishra et al. (2007)

affinity for the kaolinite surface than inorganic Pb species at this pH range. But, the ternary surfaces complex(es) that form at $\text{pH} > 6$ apparently have lesser affinity for kaolinite than the inorganic species have at this pH range. Additional XAS analysis of the molecular-scale structure of the inorganic and organic (i.e., with DFO-B) Pb adsorption complexes is ongoing.

Wolff-Boenisch and Traina (2007) investigated the effects of DFO-B on desorption of U(VI) from kaolinite at pH 6 and 25°C . They observed that DFO-B was able to remobilize most of the U(VI) adsorbed

to kaolinite, forming a $\text{UO}_2\text{DFO-BH}$ stable neutral aqueous species that would be more likely to remain mobile in porous media.

Neubauer et al. (2000) showed that DFO-B increased the sorption of Cu, Zn, and Cd to montmorillonite at near-neutral pH. At pH greater than ~ 8 , DFO-B decreased sorption of Zn and Cd. These authors also observed differences in sorption in Ca-versus Na-containing solutions, and suggested that further study on the effects of the Ca^{2+} ion was particularly needed. Haack et al. (unpublished data) showed that DFO-B and Pb mutually enhanced each others' absorption to montmorillonite, and that the magnitude of the effects varied with pH.

Summary and suggested topics for future study

Siderophores sorb to aluminosilicate clays, and they may play a role in clay dissolution and in metal sorption. Adsorption of DFO-B to kaolinite increases above the $\text{pH}_{\text{p.z.n.p.c.}}$, suggesting that electrostatics play an important role in controlling the adsorption process. The presence of DFO-B may either enhance or inhibit metal binding to kaolinite. Both cationic DFO-B and neutral DFO-D₁ absorb to montmorillonite, and they may also affect metal sorption.

Although initial studies are showing complex and interesting results, a wider range of studies involving different metals, different solution conditions (e.g., pH, ionic strength, temperature, loading) and an array of techniques (e.g., XRD, EXAFS, solid-state NMR, FTIR, and quantum chemistry calculations) are needed to increase our understanding of metal–siderophore–clay interactions. It is particularly important to take advantage of techniques on fully-wetted samples, such as utilizing in-solution XRD, and FTIR-ATR. More study needs to be conducted on the kinetics of Fe^{3+} versus other metal exchange on DFO, and how these exchange rates may influence sorption and metal mobility. Although difficult and time-consuming, more experimentation is needed involving metabolizing siderophore-producing microorganisms, along with increased efforts towards quantifying and understanding actual field processes.

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References

- Albrecht-Gary A-M, Crumbliss AL (1998) Coordination chemistry of siderophores: thermodynamics and kinetics of iron chelation and release. In: Sigel A, Sigel H (eds) Metal ions in biological systems. Marcel Dekker, New York, pp 239–327
- Ams DA, Maurice PA, Hersman LE, Forsythe JH (2002) Siderophore production by *P. mendocina* in the presence of kaolinite: evidence for bacterial responses to Fe stress. *Chem Geol* 188:161–170. doi:[10.1016/S0009-2541\(02\)00077-3](https://doi.org/10.1016/S0009-2541(02)00077-3)
- Dontsova KM, Norton LD, Johnston CT, Bigham JM (2004) Influence of exchangeable cations on water adsorption by soil clays. *Soil Sci Soc Am J* 68:1218–1227
- Duckworth OW, Sposito G (2005) Siderophore–manganese (III) interactions: II. Manganite dissolution promoted by desferrioxamine B. *Environ Sci Technol* 39:6045–6051. doi:[10.1021/es050276c](https://doi.org/10.1021/es050276c)
- Duckworth OW, Bargar JR, Sposito G (2008) Sorption of ferric iron from ferrioxamine B to synthetic and biogenic layer type manganese oxides. *Geochim Cosmochim Acta* 72:3371–3380. doi:[10.1016/j.gca.2008.04.026](https://doi.org/10.1016/j.gca.2008.04.026)
- Duckworth OW, Bargar JR, Sposito G (2009) Quantitative-structure activity relationships for aqueous metal–siderophore complexes. *Environ Sci Technol* 43(2):343–349. doi:[10.1021/es802044y](https://doi.org/10.1021/es802044y)
- Edwards DC, Myneni SCB (2005) Hard and soft X-ray absorption spectroscopic investigation of aqueous Fe(III)–Hydroxamate siderophore complexes. *J Phys Chem A* 109:10249–10256
- Edwards DC, Myneni SCB (2006) Near edge X-ray absorption fine structure spectroscopy of bacterial hydroxamate siderophores on aqueous solutions. *J Phys Chem A* 110:11809–11818. doi:[10.1021/jp0611976](https://doi.org/10.1021/jp0611976)
- Evers A, Hancock RD, Martell AE, Motekaitis RJ (1989) Metal ion recognition in ligands with negatively charged oxygen donor groups. Complexation of Fe(III), Ga(III), In(III), Al(III), and other highly charged metal ions. *Inorg Chem* 29:2189–2195. doi:[10.1021/ic00310a035](https://doi.org/10.1021/ic00310a035)
- Farmer VC (1974) The layer silicates. In: Farmer VC (ed) The infrared spectra of minerals. Mineral Society, London, pp 331–359
- Haack EA, Johnston C, Maurice PA (2008) Siderophore sorption to montmorillonite. *Geochim Cosmochim Acta* 72:3381–3397. doi:[10.1016/j.gca.2008.03.027](https://doi.org/10.1016/j.gca.2008.03.027)
- He HP, Frost RL, Bostrom T, Yuan P, Duong L, Yang D, Yunfel XF, Klopogge JT (2006) Changes in the morphology of organoclays with HDTMA(+) surfactant loading. *Appl Clay Sci* 31:262–271. doi:[10.1016/j.clay.2005.10.011](https://doi.org/10.1016/j.clay.2005.10.011)
- Hepinstall S, Turner B, Maurice PA (2005) Effects of siderophores on Cd and Pb adsorption to kaolinite. *Clays Clay Miner* 53:557–563. doi:[10.1346/CCMN.2005.0530601](https://doi.org/10.1346/CCMN.2005.0530601)
- Holmén BA, Casey WH (1996) Hydroxamate ligands, surface chemistry, and the mechanism of ligand promoted dissolution of goethite [α -FeOOH(s)]. *Geochim Cosmochim Acta* 60:4403–4416. doi:[10.1016/S0016-7037\(96\)00278-5](https://doi.org/10.1016/S0016-7037(96)00278-5)
- Johnston CT, De Oliveira MF, Teppen BJ, Sheng GY, Boyd SA (2001) Spectroscopic study of nitroaromatic-smectite sorption mechanisms. *Environ Sci Technol* 24:4767–4772. doi:[10.1021/es010909x](https://doi.org/10.1021/es010909x)
- Johnston CT, Sheng G, Teppen BJ, Boyd SA, De Oliveira MF (2002) Spectroscopic study of dinitrophenol herbicide sorption on smectite. *Environ Sci Technol* 36:5067–5074. doi:[10.1021/es025760j](https://doi.org/10.1021/es025760j)
- Karickhoff SW (1984) Organic pollutant adsorption in aqueous systems. *J Hydraul Eng* 110:707–735. doi:[10.1061/\(ASCE\)0733-9429\(1984\)110:6\(707\)](https://doi.org/10.1061/(ASCE)0733-9429(1984)110:6(707))
- Kraemer SM (2004) Iron oxide dissolution and solubility in the presence of siderophores. *Aquat Sci* 66:3–18. doi:[10.1007/s00027-003-0690-5](https://doi.org/10.1007/s00027-003-0690-5)
- Kraemer SM, Cheah S-F, Zapf R, Xu J, Raymond KN, Sposito G (1999) Effect of hydroxamate siderophores on Fe release and Pb(II) adsorption by goethite. *Geochim Cosmochim Acta* 63:3003–3008. doi:[10.1016/S0016-7037\(99\)00227-6](https://doi.org/10.1016/S0016-7037(99)00227-6)
- Lagaly G (1981) Characterization of clays by organic-compounds. *Clay Miner* 16:1–21. doi:[10.1180/claymin.1981.016.1.01](https://doi.org/10.1180/claymin.1981.016.1.01)
- Liermann LJ, Kalinowski BE, Brantley SL, Ferry JG (2000) Role of bacterial siderophores in dissolution of hornblende. *Geochim Cosmochim Acta* 64:587–602. doi:[10.1016/S0016-7037\(99\)00288-4](https://doi.org/10.1016/S0016-7037(99)00288-4)
- Maneck M, Maurice PA (2008) Siderophore promoted dissolution of pyromorphite. *Soil Sci* 173:821–830. doi:[10.1097/SS.0b013e31818e8968](https://doi.org/10.1097/SS.0b013e31818e8968)
- Maurice PA (2009) Environmental surfaces and interfaces from the nanoscale to the global scale. Wiley, Hoboken, NJ, 494 pp
- Mishra B, Haack EA, Vasconcelos IF, Maurice PA, Bunker BA (2007) XAFS determination of Pb and Cd speciation with siderophores and the metal/siderophore/kaolinite system. *AIP Proc* 882:196–198. doi:[10.1063/1.2644472](https://doi.org/10.1063/1.2644472)
- Mishra B, Haack EA, Maurice PA, Bunker BA (2009) Effects of the microbial siderophore DFO-B on Pb and Cd speciation in aqueous solution. *Environ Sci Technol* 43:94–100. doi:[10.1021/es071011w](https://doi.org/10.1021/es071011w)
- Neilands JB, Konopka K, Schwyn B, Coy M, Francis RT, Paw BH, Bagg A (1987) Comparative biochemistry of microbial iron assimilation. In: Winkelmann G, Van der Helm D, Neilands JB (eds) Iron transport in microbes, plants and animals. VCH, Weinheim, pp 3–33
- Neubauer U, Nowack B, Furrer G, Schulin R (2000) Heavy metal sorption on clay minerals affected by the siderophore desferrioxamine B. *Environ Sci Technol* 34:2749–2755. doi:[10.1021/es990495w](https://doi.org/10.1021/es990495w)
- Pereira TR, Laird DA, Thompson ML, Johnston CT, Teppen BJ, Li H, Boyd SA (2007) Role of smectite quasicrystal dynamics in adsorption of dinitrophenol. *Soil Sci Soc Am J* 72:347–354. doi:[10.2136/sssaj2007.0081](https://doi.org/10.2136/sssaj2007.0081)
- Raymond KN, Dertz EA (2004) Biochemical and physical properties of siderophores. In: Cross JH, Mey AR, Payne SM (eds) Iron transport in bacteria. American Society of Microbiology Press, Washington DC, pp 3–17
- Rosenberg DR, Maurice PA (2003) Siderophore adsorption to and dissolution of kaolinite at pH 3–7 at 22°C. *Geochim*

- Cosmochim Acta 67:223–229. doi:[10.1016/S0016-7037\(02\)01082-7](https://doi.org/10.1016/S0016-7037(02)01082-7)
- Sheng G, Johnston CT, Teppen BJ, Boyd SA (2002) Adsorption of dinitrophenol herbicides from water by montmorillonite. *Clays Clay Miner* 50:25–34. doi:[10.1346/000986002761002630](https://doi.org/10.1346/000986002761002630)
- Siebner-Freibach H, Hadar Y, Chen Y (2004) Interaction of iron chelating agents with clay minerals. *Soil Sci Soc Am J* 68:470–480
- Siebner-Freibach H, Yariv S, Lapidés Y, Hadar Y, Chen Y (2005) Thermo-FTIR spectroscopic study of the siderophore ferrioxamine B: spectral analysis and stereochemical implications of iron chelation, pH and temperature. *J Agric Food Chem* 53:3434–3443. doi:[10.1021/jf048359k](https://doi.org/10.1021/jf048359k)
- Sposito G (1984) The surface chemistry of soils. Oxford University Press, New York, p 234
- Sutheimer SH, Maurice PA, Zhou Q (1999) Dissolution of well and poorly crystallized kaolinites: Al speciation and effects of surface characteristics. *Am Mineral* 84:620–628
- Vantelon D, Pelletier M, Michot LJ, Barres O, Thomas F (2001) Fe, Mg and Al distribution in the octahedral sheet of montmorillonites. An infrared study in the OH-bending region. *Clays Clay Miner* 36:369–379
- Wolff-Boenisch D, Traina SJ (2007) The effect of desferrioxamine B on the desorption of U(VI) from Georgia kaolinite KGa-1b and its ligand-promoted dissolution at pH 6 and 25°C. *Chem Geol* 242:278–287. doi:[10.1016/j.chemgeo.2007.03.019](https://doi.org/10.1016/j.chemgeo.2007.03.019)
- Yariv S, Lapidés I (2005) The use of thermo-XRD-analysis in the study of organo-smectite complexes: Robert MacKenzie memorial lecture. *J Therm Anal Calorim* 80:11–26. doi:[10.1007/s10973-005-0608-7](https://doi.org/10.1007/s10973-005-0608-7)