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Geomaterials (Mineralogy)

Microbial reduction of iron in smectite

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Abstract

Bacteria-mediated changes in the oxidation state of iron in soil clay minerals play an important role in determining the chemical and physical properties of soils and sediments. As structural Fe(III) in the octahedral sheet of smectites is reduced to Fe(II) by bacteria, specific surface area decreases, cation exchange capacity (CEC) increases, swelling in water decreases, reactivity with organic chemicals and pesticides increases, and the potential for mineral dissolution and transformation increases. Changes in clay mineral structure due to bacterial reduction is, however, small. Because of the large potential for the redox state of soil minerals to change with natural environmental conditions, the chemical properties of the soil must be regarded as constantly changing. The resulting dynamic nature of soil behavior must be taken into account in management strategies to maximize soil fertility and structural performance. ***To cite this article: J.W. Stucki, J.E. Kostka, C. R. Geoscience 338 (2006).***
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Résumé

Réduction bactérienne du fer dans les smectites. Les modifications que les activités bactériennes induisent dans l'état d'oxydation du fer des minéraux argileux peuvent affecter considérablement les propriétés des sols et des sédiments. En effet, lorsque le Fe(III) structural de leur couche octaédrique est réduit en Fe(II) les smectites voient plusieurs de leurs propriétés modifiées : leur surface spécifique décroît, leur capacité d'échange cationique augmente, leur aptitude à gonfler dans l'eau décroît, leur réactivité vis-à-vis des substances organiques et des pesticides s'accroît et, enfin, leur susceptibilité vis-à-vis des phénomènes de dissolution et de transformation augmente. Généralement, toutefois, les modifications structurales qui surviennent restent modestes. Comme ces minéraux argileux ont la capacité de s'ajuster aux conditions rédox qui prévalent dans leur environnement, il est indispensable de considérer que leurs propriétés ne sont pas stables. Il en résulte aussi que la gestion, tant physique que chimique, de la fertilité des sols doit dorénavant prendre en compte le caractère dynamique du comportement de leur assemblage minéralogique. ***Pour citer cet article : J.W. Stucki, J.E. Kostka, C. R. Geoscience 338 (2006).***
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Mots-clés : Bactéries ; Rédox ; Gonflement ; Charge structurale ; Surface spécifique ; Pesticides

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1. Introduction

Reduction of structural Fe in clay minerals by bacteria was first reported by Stucki, Wu, and co-workers [23,38,42,46]. Iron-reducing bacteria are ubiquitous in soils and sediments and are likely the dominant mediator of redox cycling of Fe in the environment, which plays a key role in the transformation of soil minerals and the fate of other soil constituents and contaminants. In recent years, increased attention has focused on the role of microorganisms in catalyzing Fe redox cycling in smectite clay minerals, including reduction of Fe(III) in the clay mineral structure and the dissolution and transformation of Fe (hydr)oxides. Studies involving abiotic Fe reduction, primarily using dithionite as the reducing agent, have shown strong links between clay surface chemistry and structural Fe oxidation state. Do bacteria assert a similarly large influence on the chemical and physical properties of soil clay minerals through bacteria-mediated Fe reduction in soil minerals? The purpose of this paper is to summarize some of the recent findings related to the effects of bacterial reduction on clay properties and behavior.

2. Iron reduction coupled with carbon oxidation

The stoichiometry for formate oxidation by Fe^{3+} in solution is given by:

$$2\,Fe^{3+} + HCOO^- + H_2O \rightarrow 2\,Fe^{2+} + HCO_3{}^- + 2\,H^+$$

in which $2\,Fe^{3+}$ ions are reduced to Fe^{2+} for each molecule of formate that is oxidized. For lactate oxidation, the corresponding reaction is:

$$4\,Fe^{3+} + CH_3CHOHCOO^- + 2\,H_2O \rightarrow 4\,Fe^{2+} + CH_3COO^- + HCO_3{}^- + 5\,H^+$$

in which $4\,Fe^{3+}$ ions are reduced to Fe^{2+} for each molecule of lactate that is oxidized. Kostka et al. [25] found similar stoichiometries when the smectite was reduced by bacteria with either formate or lactate as the electron donor and carbon source, viz.:

$$0.73\,[Fe(III)_{2.73}]_{smectite} + HCOO^- + H_2O \rightarrow 0.73\,[Fe(II)_{2.73}]_{smectite} + HCO_3{}^- + 2\,H^+$$

$$1.47\,[Fe(III)_{2.73}]_{smectite} + CH_3CHOHCOO^- + 2\,H_2O \rightarrow 1.47\,[Fe(II)_{2.73}]_{smectite} + CH_3COO^- + HCO_3{}^- + 5\,H^+$$

where (0.73×2.73) and (1.47×2.73) are almost equivalent to 2.0 and 4.0 moles of Fe(III) in the smectite reduced for each mole of formate or lactate oxidized, respectively.

They pointed out that these results are strong evidence that structural Fe(III) reduction in the clay is a product of bacterial respiration and that the bacteria directly couple carbon oxidation with Fe(III) respiration. Further investigation [24], revealing that the bacteria can grow when Fe(III) in the smectite is the sole electron acceptor, supports this hypothesis.

Still undetermined is whether this coupling occurs because of close membrane contact with the clay surface or through an electron shuttle. Some studies of bacterial cultures have reported an increased rate or extent of structural Fe reduction if an electron shuttle (e.g., AQDS or other humic substance) is added to the culture medium [8,9,25,30]. While the presence of a non-bacterial electron shuttle enhances bacterial reduction of smectite, its presence apparently is required in order to reduce structural Fe in illite [8].

3. Effects of bioreduction on clay properties and chemical behavior

3.1. *Specific surface area*

One of the most important properties imparted by clay minerals to soils and sediments is a large, chemically active surface area. Lear and Stucki [27] reported that dithionite reduction of structural Fe in smectite decreases its specific surface area, which led Kostka et al. [26] to investigate whether such a phenomenon occurs if reduction is mediated by bacteria. Their results (Fig. 1) illustrate that bioreduction decreases specific

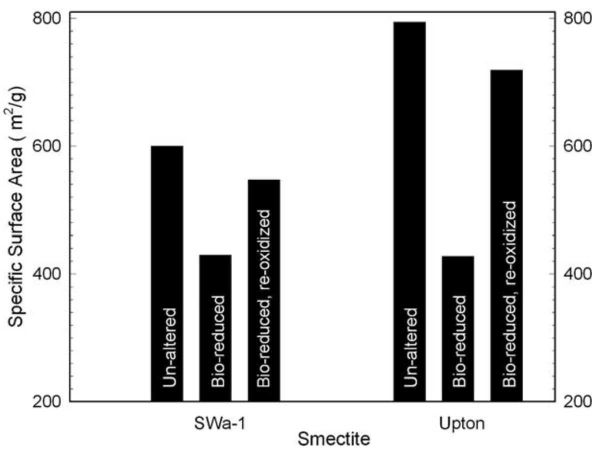

Fig. 1. Effects of bacterial reduction of structural Fe on specific surface area of ferruginous smectite (SWa-1) and Upton, Wyoming, montmorillonite (data from [26]).

Fig. 1. Effets d'une réduction bactérienne sur la surface spécifique d'une smectite ferrifère (SWa-1) et de la montmorillonite d'Upton (Wyoming, USA) [26].

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