

## Review of Microbially Mediated Smectite-illite Reaction

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### 생지화학적 스멕타이트-일라이트 반응에 관한 고찰

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스멕타이트-일라이트 (SI)의 전이 반응은 쇄설성 퇴적암 지역에 흔히 볼 수 있는 광물 반응이다. 지난 40여년 동안 SI 전이 반응의 중요성에 대한 논문들이 많이 출간되었는데 이는 스멕타이트가 일라이트로 변하는 정도 즉 “illitization” 이 석유의 개발, 퇴적물의 화학적 변화 및 물리적 성질변화에 많은 연계성이 있기 때문이다. 기존의 S-I 상전이에 대한 메커니즘 연구에서는 layer-by-layer reaction 에 의한 solid state 반응 혹은 dissolution/precipitation 반응으로 집약되지만 박테리아 반응의 역할을 전혀 고려하지 않았다. 무산소 환경에서 박테리아와 점토광물의 반응에 대한 연구, 특히 스멕타이트와 철 환원 박테리아의 반응 작용에 대한 연구에서는 철 환원 박테리아가 스멕타이트 구조 속에 있는 철을 환원시켜 에너지를 얻는다고 밝혀졌다. 최근 발표된 논문들은 미생물의 철 환원 작용에 의하여 S-I 상전이가 일어날 수 있다고 보고되었는데, 이는 기존의 상전이에 대한 개념에 즉 고온, 고압, 오랜 시간이 S-I 전이의 필수 조건이라는 일반적인 해석에 반하는 것으로 새로운 연구 분야의 가능성을 시사하고 있다. 현재까지 발표된 논문에 의하면 박테리아가 S-I 반응을 촉진지킴으로 고온, 고압, 혹은 상당시간의 속성작용이 전제조건으로 작용하지 않을 수 있다는 가능성을 시사한다. 하지만 박테리아가 철을 환원함과 동시에 스멕타이트를 일라이트로 전이시킴에 있어서의 메커니즘에 대한 이해는 아직 미비하다. 따라서 이 논문에서는 현재까지 밝혀진 SI 반응을 살펴보고, 미생물 광물간의 반응작용에 있어서 연구 방법을 소개함을 목적으로 한다.

**주요어** : 스멕타이트 일라이트 반응, 생지화학적 반응, Fe(III) 환원작용

The smectite-illite (SI) reaction is a ubiquitous process in siliciclastic sedimentary environments. For the last 4 decades the importance of smectite to illite (S-I) reaction was described in research papers and reports, as the degree of the (S-I) reaction, termed “smectite illitization”, is linked to the exploration of hydrocarbons, and geochemical/petrophysical indicators. The S-I transformation has been thought that the reaction, explained either by layer-by-layer mechanism in the solid state or dissolution/reprecipitation process, was entirely abiotic and to require burial, heat, and time to proceed, however few studies have taken into account the bacterial activity. Recent laboratory studies showed evidence suggesting that the structural ferric iron (Fe(III)) in clay minerals can be reduced by microbial activity and the role of microorganisms is to link organic matter oxidation to metal reduction, resulting in the S-I transformation. In abiotic systems, elevated temperatures are typically used in laboratory experiments to accelerate the smectite to illite reaction in order to compensate for a long geological time in nature. However, in biotic systems, bacteria may catalyze the reaction and elevated temperature or prolonged time may not be necessary. Despite the important role of microbe in S-I reaction, factors that control the reaction mechanism are not clearly addressed yet. This paper, therefore, overviews the current status of microbially mediated smectite-to-illite reaction studies and characterization techniques.

**Key words** : SI reaction, bacterial activity, structural Fe(III) reduction

### 1. Introduction

Smectite-illite clay minerals are ubiquitous in

siliciclastic sedimentary environments. The smectite to Illite (S-I) transformation is considered to be one of the most important mineral reactions (Dong

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*et al.*, 1997), as the degree of the (S-I) reaction, termed "smectite illitization", is linked to the maturation, migration and trapping of hydrocarbons (Pevear *et al.*, 1999), the development of pore pressures (Freed and Peacor, 1989), pore water chemistry (Brown *et al.*, 2001), and the changes in petrophysical properties of sediments (Kim *et al.*, 2005). Recently, a great increase in flocculation of clay suspensions by adding the Fe-reducing bacteria was shown in our laboratory (Kim *et al.*, 2005). Consequently, these changes can impact on the macroscopic geotechnical and optic properties of the sediments. The degree of S-I transformation is also used frequently as an independent geothermometer (Pollastro *et al.*, 1993) to predict the thermal history of sedimentary basins. The S-I transformation has been thought that the reaction was entirely abiotic and to require burial, heat, and time to proceed. However recent laboratory studies provided evidence suggesting that microbes can transform smectite to illite at room temperature within 14 days (Kim *et al.*, 2004) and the role of microorganisms is to link organic matter oxidation to metal reduction, resulting in the S-I transformation. These results are of great interest because this reaction was thought to require much higher temperatures over an extended period of time. Numerous studies have emphasized temperature, pressure, and time as geological variables in either solid state or dissolution-precipitation S-I transformation mechanisms (Bethke and Altaner, 1986), but none have considered microbial reactions. Data from previous studies may support microbially mediated illite formation. For example, an increasing percentage of illite layers in mixed-layered smectite-illite (S-I) with increasing  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in Cretaceous bentonites was reported (Eslinger *et al.*, 1979); however, the authors were unable to identify the cause for the varying  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio. A small amount of illite-like phase (1.0-nm spacing) also was observed (Russell *et al.*, 1979) when Fe-rich smectite was chemically reduced by dithionite. However, dithionite is not likely to occur in abundance or to play a significant role in iron reduction in natural soil environments. In abiotic systems, elevated temperatures are typically used in laboratory experiments to accelerate the smectite to illite reaction in order to compensate for a long geological time in nature (Huang *et al.*, 1993). In

biotic systems, bacteria may catalyze the reaction, and elevated temperature or prolonged time may not be necessary.

The previous studies should change the fundamental understanding of the S-I reaction and has significant implications for sediment diagenesis and petroleum exploration. Consequently, the results will be directly applicable to sediments well below the water-sediment interface (e.g., stratigraphic layers below those that contain methane hydrates) and hydrocarbon-laden basins. Despite the significant developments of understanding the microbial process in S-I reaction, the mechanism of structural Fe(III) reduction is not still clear. Some studies (Lee *et al.*, 2006; Stucki and Kostka, 2006) demonstrated the solid state reduction mechanism while other groups (Dong *et al.*, 2003; Kim *et al.*, 2004; Jaisi *et al.*, 2007; Furukawa and O'Reilly, 2007) provided the evidence of clay mineral structure dissolution associated with microbial Fe(III) reduction. In this paper, the current status of microbially mediated S-I reaction studies and characterization techniques were reviewed.

## 2. Bacterial Culture

Mesophilic *Shewanella oneidensis* bacterium previously isolated from anoxic sediment (Dong *et al.*, 2003a; Kim *et al.*, 2004; Kostka *et al.*, 2002; Lee *et al.*, 2006) was used to reduce the structural Fe(III) in smectite. Jaisi *et al.* (2007, 2008, 2009) used *Shewanella putrefaciens* for microbially reduced smectite experiments. The degree of SI reaction was also tested by Zhang *et al.* (2007a, 2007b) using thermophilic and hyperthermophilic bacterium which requires extreme anoxic environment. In general, conditions for clay reduction experiments using mesophilic bacterium were as follows: a single, well-isolated colony was grown aerobically overnight at 22°C in liquid LB medium and harvested by centrifugation. Introduction of the culture to anaerobic conditions was done incrementally by resuspension in sterile minimal (M1) medium (pH 7.4), supplemented with 20-mM lactate as the electron donor and 80-mM Fe(III) citrate as the terminal electron acceptor (TEA). The culture then was incubated for 72 hours at 22°C under anaerobic conditions. Bacteria were pelleted by centrifugation, washed twice with M1 media, and transferred

into 15 ml of fresh M1 medium containing 20-mM lactate to a density of a 0.5 MacFarland Standard ( $1.5 \times 10^8$  cells  $\text{ml}^{-1}$ ). Fe(III) citrate was not present in M1 medium used for reduction experiments. Sterilized nontronite (4 mg  $\text{ml}^{-1}$ ) was added as the sole TEA and a 5 ml aliquot was placed into a sterile 50 ml centrifuge tube. The tubes were loosely capped and incubated anaerobically in an anaerobic chamber at 22°C.

For smectite reduction experiments at high temperature (68°C) thermophilic *Thermoanaerobacter ethanolicus* bacterium was used (Zhang *et al.*, 2007a). The composition of the medium (Prowe and Antranikian, 2001) contained (per liter of deionized water)  $\text{Na}_2\text{HPO}_4$ , 0.5 g;  $(\text{NH}_4)_2\text{SO}_4$ , 1.5 g;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.1 g;  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.05 g; vitamin solution 141 (DSMZ), 10 mL; trace element solution 141 (DSMZ), 10 mL; yeast extract, 0.2 g; and resazurin, 0.0001 g. In order to promote the S-I reaction, an external K and Al source was added. The structural Fe(III) in nontronite (5 mg/mL, final concentration) was then used as the sole electron acceptor, lactate (20 mM, final concentration) as the sole electron donor, and anthraquinone-2,6-disulfonate (AQDS) as an electron shuttle.

### 3. Characterization Techniques

#### 3.1. Aqueous Chemistry

Iron dissolution caused by microbial reduction during the batch experiments can be monitored over time by analyzing the aqueous Fe concentration using the ferrozine method for total and speciated Fe (Fe(II) and Fe total are measured directly and Fe(III) is determined by difference) (Jaisi *et al.*, 2009; Dong *et al.*, 2003; Kim *et al.*, 2004; Furukawa and O'Reilly, 2007). Aqueous concentrations of major elements such as Al and Si can be measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). The amount of Fe(II) adsorbed to the surface of the reduced solid or newly generated illite was determined by X-ray photoelectron spectroscopy (XPS) which is a surface sensitive technique. If significant amounts of released Fe is re-adsorbed to the surface of the clay solids, further chemical extraction or desorption studies may be used to determine the lability of the sorbed Fe. The zeta-sizer, an instrument for simultaneous particle size and

surface electrokinetic analysis for suspended particles and aggregates, can be used to characterize the charge of the experimental system.

#### 3.2. S-I Transformations

S-I transformation can be monitored using X-ray Diffractometer (XRD), environmental cell (EC) transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). The percent of illite in mixed-layer I-S in the reaction products can be quantitatively determined in XRD patterns by comparing experimental and calculated patterns using NEWMOD program (Moor and Reynolds, 1997). The illite peak will be intensified by polyvinylpyrrolidone (PVP) treatment and Mudmaster program (Eberl *et al.*, 1998) can be followed to calculate crystal size distribution to further delineate the smectite illitization mechanism. Analysis of high-resolution lattice fringe, selected area electron diffraction, and EELS can be carried out in each sample at selected time point to determine the structural changes due to the structural Fe(III) reduction. EELS technique is capable of determining the Fe oxidation state at nano-scale (Kim *et al.*, 2009 in review). These data allow direct determination of S-I ordering based on their layer spacings because EC-TEM allow the direct measurement of layer spacing of S-I layers in hydrated native state excluding any artifacts resulted from dehydration during conventional TEM observation.

#### 3.3. Mechanism of Microbially Mediated S-I Transformation

Percentage of illite layers in S-I can be plotted as a function of time for both biotic and abiotic systems. The difference in the extent and rate of the S-I transformation between the two systems will reflect the effect of microbes. Although recent data have suggested that microbial reduction of Fe(III) in smectite triggers smectite dissolution and precipitation of illite, solid-state transformation may be possible. If a large amount of octahedral Fe(III) is reduced in solid state, the smectite structure may become unstable because of the imbalance of surface charge and eventually break down resulting in K fixation to produce illite. Smectite samples with a range of structural Fe(III) will allow us to determine what extent of Fe(III) reduction is needed to break-down the smectite structure. Smectite can be

dissolved by organic ligands and precipitate illite. The Si and Al release from mineral to solution will be used as an indicator to determine the dissolution rates of smectite at different temperature. The dissolution rate will be expressed in terms of mol per surface area per time. Excess Fe resulting from the reductive dissolution of Fe-rich smectite can cause the precipitation of Fe-rich minerals as by-products, because illite contains less Fe than Fe-rich smectite. XRD perform to detect these minerals.

#### 4. Microbially Mediated S-I Reaction

Reduction of Fe(III) in smectite structure associated with microbes was initiated by Stucki and coworkers (1986), and observed the collapsed layer spacings due to Fe-reduction (high charge smectite) with different petrophysical properties such as specific surface area, cation exchange capacity, and swelling property. The direct TEM measurements of layer collapse associated with the microbial Fe-reduction was made by Kim *et al.* (2003) utilizing environmental cell that maintains the hydrate state preventing the artificial layer collapse due to the high energy of TEM beam. As shown in Fig. 1 (data from Kim *et al.*, 2003), the typical rod-shaped morphology of *S. oneidensis* is intact and shows no evidence of rupture by partial decompression in the TEM column. The collapse of layer spacing associated with microbial Fe(III) reduction is displayed in Fig. 2 (data from Kim *et al.*, 2003); structural change from 1.5-1.6 nm of layer spacings in nonreduced nontronite to 1.2-1.3 nm in microbially Fe(III) reduced nontronite that was confirmed by the inset selected area diffraction (SAED) patterns. From the statistical analysis of distribution of layer spacings in nonreduced and microbially Fe(III) reduced nontronite (Fig. 3, data from Kim *et al.*, 2003), about 15% of measured spacings in microbially Fe(III) reduced nontronite samples shows 1.0-1.2 nm of layer spacings, implying mineral transformation. Nontronite with layer spacings of 1.2-1.4 nm may be high charge smectite that was observed by Stucki (1986). The smectite to illite reaction was for the first time, directly measured using TEM and XRD by Kim *et al.* (2004). The discrete packet of illite phase in smectite matrix was observed by TEM that was con-

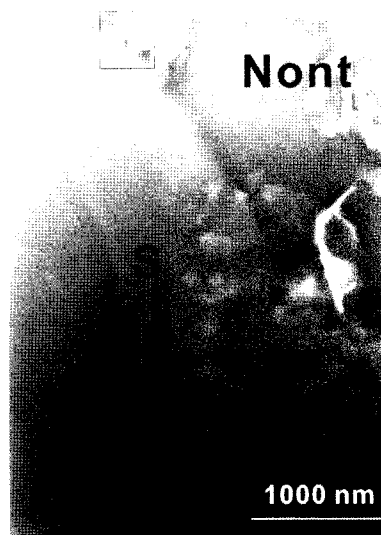


Fig. 1. EC-TEM images of *S. oneidensis*(S) with nontronite (Nont) particles, at intermediate-magnification image. (Data from Kim *et al.*, 2003).

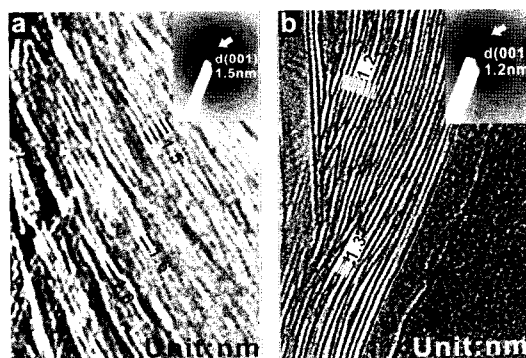
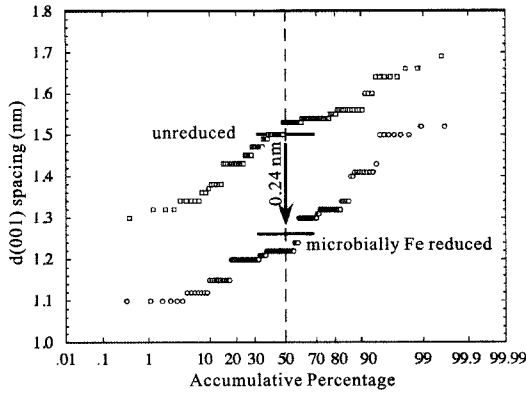
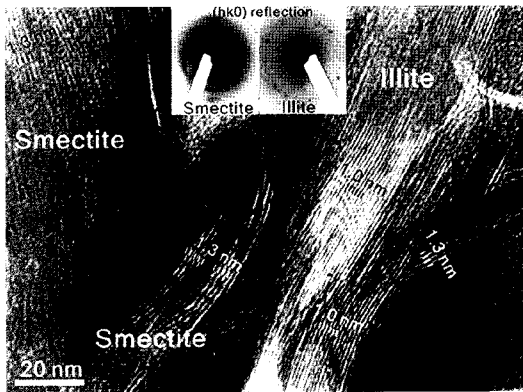


Fig. 2. EC-TEM lattice fringe images of (a) unreduced and (b) microbially Fe(III)-reduced nontronite. SAED patterns of nontronite are shown in inset. (Data from Kim *et al.*, 2003).

firmed by SAED patterns and XRD analysis (Fig. 4, data from Kim *et al.*, 2004). The changes in SAED patterns from turbostratically ordered pattern to the discrete Bragg reflections indicated the structural changes of clay minerals. These results are of great interest because this reaction is thought to require much higher temperatures over an extended period of time and the role of microorganisms is to link organic matter oxidation to metal reduction, resulting in the S-I transformation. The changes in petrophysical property of clay particles associated with S-I reaction resulted from microbial Fe(III)

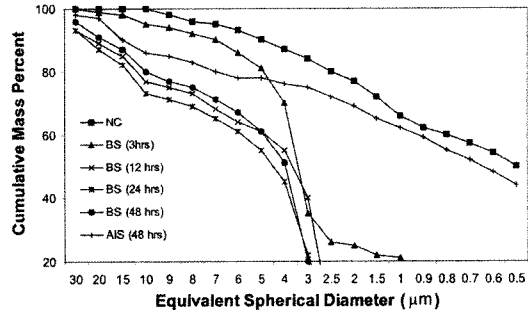


**Fig. 3.** Distribution of (001) layer spacings in unreduced and microbially Fe(III)-reduced nontronite as measured by EC-TEM. (Data from Kim *et al.*, 2003).

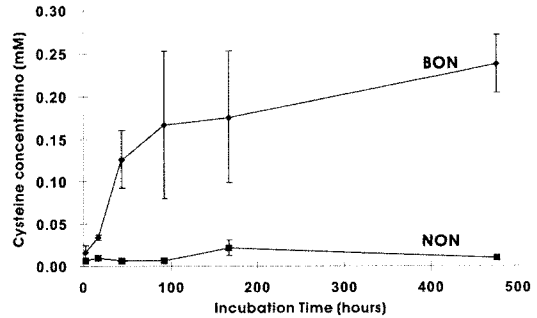


**Fig. 4.** TEM micrograph of the L.R. White resin embedded bioreduced smectite sample. Two phases of clay minerals were observed: an approximately 40-nm thick packet of 1.0-nm illite layers occurred in the smectite matrix of 1.3-nm layers. The inset selected area electron diffraction (SAED) patterns show the structural difference between these two phases in (hk0) reflections, in ring patterns (turbostratic typical of the smectite structure), and in discrete Bragg reflections (typical of the illite structure). (Data from Kim *et al.*, 2004).

reduction, specifically flocculation properties are visualized in Fig. 5 (data from Kim *et al.*, 2005). The packet size distribution and aspect ratio (thickness/length) of microbially Fe(III) reduced nontronite and controlled nontronite shows increase in mean packet size (7.28 nm to 12.23 nm) and aspect ratio (0.11 to 0.18). These results imply that change in surface charge due to Fe(III) reduction associated with microbial activity may result in promoting the aggregation property of clays which was confirmed



**Fig. 5.** Aggregate size distribution of nonreduced control (NC), microbially Fe(III) reduced nontronite suspensions (variable incubation time from 3 to 48 hours) and aerobically inoculated nontronite (AIN) suspensions using Micromeritics Sedigraph. (Data from Kim *et al.*, 2005).



**Fig. 6.** Quantities of cysteine recovered from organo clay control and organo clay+cells. (Data from Zhang *et al.*, 2007a).

later by Jaisi *et al.* (2007, 2008). The studies by Zhang and Kim (2007a, 2007b) further confirmed the S-I reaction. The release of cysteine from nontronite structure during microbial structural Fe(III) reduction indicate that smectite may be transformed to illite by the reductive dissolution of nontronite structure (Fig. 6, data from Zhang *et al.*, 2007a) and the S-I reaction may be accelerated at higher temperature which is more relevant conditions to diagenetic environment. Currently the effects of S-I reaction on the environmental relevance, changes in petrophysical properties, application in soil sciences, and bioremediation are investigated to facilitate the hypothesis of microbially mediated S-I reaction.

### 5. Topics to be Discussed

Future researches should be focused on questions

as below;

1. Do subsurface microbes accelerate the smectite to illite transformation under diagenetic conditions? The factors controlling S-I reaction for example, pH, temperature, contents of organic matter, time and type of microbe should be tested. What is the optimum conditions for promoting S-I reaction?

2. Which type of microbe is most effective? Depending on the type of microbes, the optimum conditions for S-I reaction should be investigated

3. What are the extent and rate of this acceleration? The kinetics of S-I reaction should be tested based on the chemical composition (Al, Si ratio)

4. What are mechanisms for the S-I transformation in presence of bacteria? The best scenario to explain the S-I reaction in each condition should be explained.

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