

Interactions of Kaolin Minerals in the Environment

Randall T. Cygan¹ and Kazue Tazaki²

1811-5209/14/0010-195\$2.50 DOI: 10.2113/gselements.10.3.195

The interactions of ions, organics, and microorganisms at the aqueous interface with kaolin-group minerals control many important geochemical processes in the environment. Kaolinite has both hydrophilic and relatively hydrophobic external surfaces that exhibit different adsorption phenomena. Our understanding of kaolin minerals in the environment is advancing as a result of molecular simulation and field studies. Molecular dynamics simulations reveal the structure and behavior of adsorbed ions and water molecules at the interface. The presence of microorganisms affects the formation and surfaces of kaolinite and halloysite. Mechanisms by which kaolin-group minerals complex, adsorb, and desorb radioactive pollutants in the subsurface can be understood by combining theory with observation.

KEYWORDS: adsorption, biomineralization, kaolinite, molecular dynamics, radioactivity, surface chemistry, weathering

INTRODUCTION

The adsorption of contaminants onto the surfaces of clay minerals is an important geochemical process for protecting the quality of groundwater. The fine-grained nature of clay minerals and their correspondingly high surface area promote relatively large adsorption capacities and allow clays to be used as efficient migration barriers at contaminant sites and nuclear waste repositories. The negative layer charge associated with most clay minerals is effective in controlling the adsorption of metal cations and other positively charged species (e.g. UO_2^{2+} and organic cations) under most pH conditions. Unlike 2:1 clay minerals, which can also exchange cations in the interlayer, the 1:1 kaolin-group minerals primarily adsorb species onto their external surfaces. Although impurity substitutions may impart a local charge site, kaolin-group minerals are typically neutral phases and are unable to swell in nature and develop intercalated structures like the smectite and vermiculite varieties of clay minerals. Nonetheless, kaolin-group minerals make a significant contribution to adsorption in the environment and are involved in many other important geochemical processes (Newman 1987; Dixon and Schulze 2002). Kaolinite, in particular, strongly interacts with microorganisms and can nucleate and precipitate on cell walls. Biomineralization processes—in which living organisms produce or induce minerals—can be extensive in the natural environment and could be employed in the remediation of radioactive environments, including the region near the recent Fukushima nuclear accident in Japan.

1 Geoscience Research and Applications Group
Sandia National Laboratories, Albuquerque, NM 87185-0754, USA
E-mail: rtcyan@sandia.gov

2 Department of Earth Sciences, Kanazawa University
Kanazawa, Ishikawa 920-1192, Japan
E-mail: kazueta@cure.ocn.ne.jp

KAOLIN-GROUP MINERALS IN THE ENVIRONMENT

Kaolin-group minerals include kaolinite, dickite, nacrite, and halloysite, each having the common ideal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. FIGURE 1 presents the basic structure of the mineral group as represented by the structure of kaolinite (Brindley and Brown 1980; Bish 1993). The 1:1 designation denotes the combination of a single tetrahedral sheet and a single octahedral sheet to form a kaolinite layer. The octahedral sheet is comprised of edge-sharing $\text{Al}(\text{O},\text{OH})_6$ octahedra, with vacant sites occurring once

for every two occupied sites and with Al coordinated by four hydroxyl groups and two bridging oxygen atoms. This sheet structure is similar to that of the mineral gibbsite, whose formula is $\text{Al}(\text{OH})_3$, and is often referred to as the gibbsite-like sheet. The tetrahedral sheet incorporates corner-sharing SiO_4 tetrahedra, which form a ditrigonal structure on the basal plane of the layer, and is often referred to as the siloxane sheet. The other basal plane, as expressed by the gibbsite-like sheet, is saturated with hydroxyl groups that form hydrogen bonds across the interlayer with the oxygen of the siloxane surface. The basal *d*-spacing of 0.72 nm (7.2 Å) is diagnostic of most kaolin minerals.

The polymorphs dickite and nacrite have the same basic structure as kaolinite but with different stacking sequences of the layers (Balan et al. 2014 this issue). Typically, kaolin-group minerals occur with plate-like morphologies. The

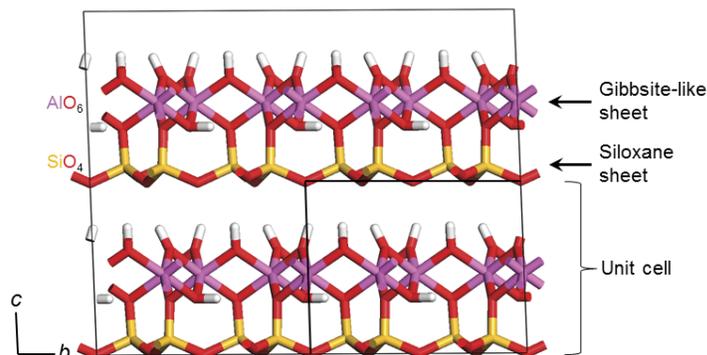
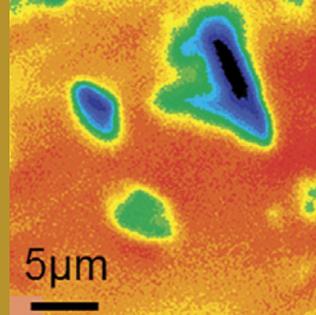


FIGURE 1 Molecular model of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as a periodic simulation cell ($1 \times 2 \times 2$ unit cells) showing the gibbsite-like and siloxane sheets and the inner and interlayer hydroxyl groups



lone exception, halloysite, has the same fundamental structure but occurs in cylindrical form when hydrated with a single water layer between sheets; the cylinders are typically 30 nm in diameter. Although all kaolin-group minerals are the result of aqueous-solution weathering or hydrothermal alteration of micas and feldspars at low-pH conditions, only kaolinite and halloysite are found in modern soils and sediments.

SURFACE CHEMISTRY OF KAOLINITE

Kaolinite, as the most common of the kaolin-group minerals, has been the focus of several studies of adsorption phenomena concerning clay minerals in the environment. On or near the Earth's surface, adsorption onto mineral surfaces is primarily determined by the surface structure, composition, and surface charge, although this conventional approach is complicated by the strong structural anisotropy (dipolarity) of the 1:1 layers. In addition to its occurrence on the basal planes of kaolinite, adsorption takes place on its edge surfaces, which are controlled by exposed $-Al-O$ and $-Si-O$ sites, where the interaction with water is different from that on basal surfaces. Using titration experiments, Brady et al. (1996) distinguished different pK values for protonation and deprotonation reactions for two aluminol edge sites and one silanol edge site and derived the corresponding site densities. By combining this information with atomic force microscopy observations of the high percentage of edge surface area for kaolinite compared to smectite and illite and with molecular models of kaolinite charge distribution, they demonstrated the significant role of surface aluminols in controlling adsorption. The basal surface makes a smaller contribution, compared to the edge sites, to the total adsorption of inorganic cations, especially at neutral- to high-pH conditions, although the adsorption of neutral species and organic compounds will involve both basal and edge surfaces.

MODELS OF KAOLINITE-WATER INTERFACES

The details of the adsorption mechanisms for kaolinite at the molecular level are poorly understood. The fine-grained nature of clay particles (typically less than 2 μm in diameter) and the difficulty in obtaining accurate crystal structures for layered phases with stacking disorder, severely limit physical observations of structure-property relationships (Balan et al. 2014). Particle-size and sample-preparation issues affect the quality of kaolinite images obtained using optical, electron, and atomic force microscopies, as well as the interpretation of measurements from many spectroscopic and diffraction methods. In the last decade, however, new molecular simulation methods have been used to supplement these experimental approaches by offering a theoretical probe of clay mineral structure, surfaces, and the clay mineral-water interface.

Adsorption Mechanisms through Simulation

Molecular simulation has been used to develop a basis for understanding adsorption on clay surfaces, with particular success in evaluating the adsorption of metal cations on the basal surfaces of kaolinite. Two general modeling approaches are used in these types of studies: (1) classical simulation methods involving an empirical description of how atoms interact with each other and (2) quantum approaches that provide a first-principles description of the electronic structure and that require approximate solutions to the Schrödinger equation. The classical approaches include molecular dynamics (MD) and Monte Carlo (MC) simulations, which incorporate many thousands of atoms and, in some cases, more than a million atoms (Thyveetil

et al. 2008). Energy force fields, such as Clayff (Cygan et al. 2004), provide an accurate set of potential energy expressions for modeling a variety of environmental phases (including clay minerals and aqueous solutions). Potential energy and atomic configurations are monitored during the simulation (time steps for MD; sample steps for MC) and used to evaluate optimized or equilibrium states. Quantum methods can be computationally expensive and therefore are limited to applications involving less than several hundred atoms. Advances in high-performance computers and quantum chemistry software, however, are allowing for more efficient, accurate, and computationally affordable quantum chemistry simulations.

Adsorption on Kaolinite

Several computational studies have examined water adsorption onto kaolinite using either classical or quantum methods. These include the recent investigations of wettability (Šolc et al. 2011), the adsorption of a water monolayer on the basal surfaces (Tunega et al. 2004), and the viscosity of nanoconfined water in a kaolinite nanopore (Haria et al. 2013). As with most simulations of kaolinite-water systems, molecular dynamics models of the adsorption of aqueous cations have usually focused on a comparison of the adsorption behavior of both basal surfaces since they offer contrasting hydrophilic and hydrophobic structures (Vasconcelos et al. 2007). Similarly, quantum methods have been used to examine the binding of organics, such as formamide ($HCONH_2$) (Scott et al. 2012) and glucose-related molecules (Lee et al. 2013), on both basal surfaces.

The molecular dynamics investigation of Vasconcelos et al. (2007) offers a comparison of the adsorption behavior at 300 K and one atmosphere for several monovalent and divalent cations interacting with the two kaolinite basal surfaces. FIGURE 2 presents the initial and equilibrated configurations for a CsCl solution in a kaolinite nanopore as represented by a modest-sized system of about 20,000 atoms. The simulation cell has periodic boundaries in all directions and cell lengths that are allowed to shorten or lengthen as the system equilibrates during the molecular dynamics simulation. The equilibrated simulation cell exhibits a smaller pore dimension, which results from contraction of the aqueous solution as the ions in solution diffuse to either of the kaolinite surfaces. In this example, Cs^+ ions migrate toward the negatively charged oxygens of the siloxane surface while Cl^- counterions are attracted to the gibbsite-like surface. Atomic density profiles traversing the nanopore are calculated by averaging the trajectories of each species over 500 picoseconds (ps) (5000 total structures) following the equilibration period (FIG. 3).

The density profiles graphically depict the equilibrium distribution of atoms in the aqueous solution and in the kaolinite substrate, and provide insight into the structure and mechanisms of ion adsorption. Inner- and outer-sphere adsorption complexes exist at both basal surfaces depending on whether water molecules are intermediate between the ion and the surface. Cesium ions bind strongly at the siloxane surface as an inner-sphere complex (Cs^+ has the lowest hydration enthalpy of the ions), whereas Na^+ , Cd^{2+} , and Pb^{2+} behave predominantly as outer-sphere adsorption complexes and are fully coordinated by water molecules. At equilibrium, all cations display finite atomic density in the bulk-solution region, illustrating the dynamics of element partitioning between being adsorbed onto kaolinite or remaining in solution. In similar fashion, Cl^- occurs as an inner-sphere complex adsorbed on the gibbsite-like surface. Interestingly, Cd^{2+} and, to a lesser extent, Na^+ exhibit ion pairing with Cl^- , which allows for some indirect adsorption of cations to the gibbsite-like

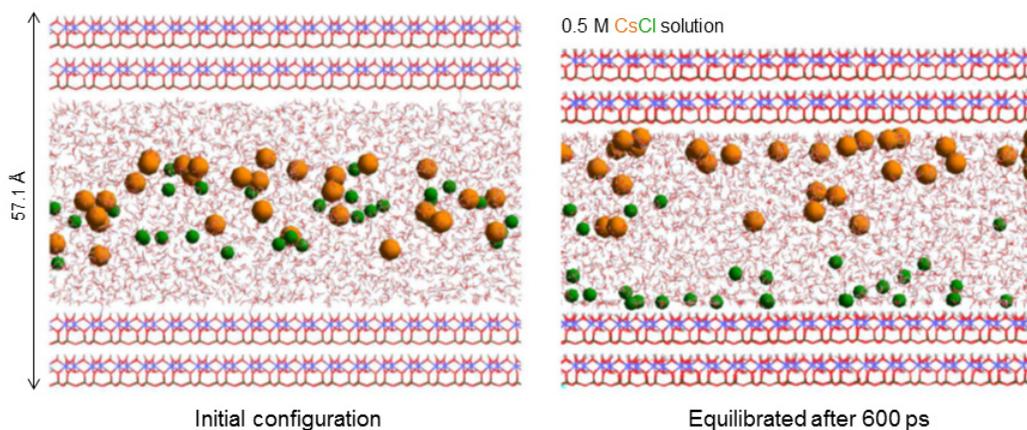


FIGURE 2 Periodic simulation cells of a kaolinite nanopore with a CsCl solution exposed to the gibbsite-like and siloxane basal surfaces of kaolinite. The equilibrated configuration from molecular dynamics shows Cs⁺ (orange spheres) mostly adsorbed

to the siloxane surface and Cl⁻ (green spheres) bound to the gibbsite-like surface (ps = picoseconds). ADAPTED WITH PERMISSION FROM VASCONCELOS ET AL. (2007). COPYRIGHT 2007, AMERICAN CHEMICAL SOCIETY

basal surface. Site densities for ion adsorption derived from these results can help improve surface complexation models for thermodynamic and reactive transport models currently being used to simulate the fate of pollutants in the Earth's surface environment.

Density profiles for water H and O (FIG. 3) readily show the formation of ordered water layers at each kaolinite surface, with the hydrophilic gibbsite-like surface exhibiting more tightly bound water than the relatively hydrophobic siloxane surface. Up to three ordered water layers occur near the gibbsite-like surface; the ordered water layers transition into a diffuse water region in the central part of the nanopore. The combination of Clayff and MD simulation offers amazing insight into the molecular details of adsorption behavior that is beyond the reach of laboratory experiments.

The present challenge in the molecular simulation of kaolinite, and of clay minerals in general, is in obtaining accurate models of edge sites, especially for variable

protonation states. Quantum chemistry simulations have been used successfully to evaluate possible kaolinite edge structures and their reactivity (Liu et al. 2012), but these have not yet been applied to examining adsorption phenomena with large-system models. Research on developing improved classical models and force field parameters for kaolinite edges is ongoing. Although one would hope that all molecular simulations are accurate depictions of real materials, it is important to stress that the validation of models by experimental findings is crucial, and perhaps their best contribution lies in helping to design or interpret the next experiment.

BIOMINERALIZATION, REDOX, AND KAOLINITE-WATER INTERFACES

Microorganisms play an important role in the concentration of elements, the crystallization of kaolin-group minerals, and the transport and sedimentation of most elements in the environment. Microbial mats of bacterial colonies complex with clay minerals in many environmental systems. Bacterial biomineralization contributes to the remediation of toxic heavy metals at abandoned mining sites (e.g. uranium and cadmium, and mercury mud ponds in gold mines) and in polluted soils and water systems (e.g. pesticides, tar sand spoils, and petroleum spills).

The occurrence of kaolin-group minerals produced in the presence of microorganisms depends on temperature, pH, oxidation-reduction potential (Eh), and the amount of dissolved ion. At the high temperatures and strongly acidic conditions associated with hot springs, microorganisms produce various clay minerals external to and within the living cell. Understanding the mechanisms of bacterial biomineralization is crucial to our understanding of the redox potentials of electron donors (fuels) and acceptors (oxidants) commonly used for microbial respiration.

Perhaps the best-known example of biomineralization is the colorful microbial mats observed in hot springs, geysers, and geothermal areas, which form at high-temperature and low-oxygen conditions (e.g. Yellowstone National Park, USA). The colored microbial mats surrounding geysers clearly exhibit specific pH-Eh-temperature dependencies. Other examples include reddish *Halobacterium* and *Halococcus* bacteria occurring in high-salinity lakes and red algae occurring on snow surfaces during winter in the Arctic. The biomineral assemblages include not only

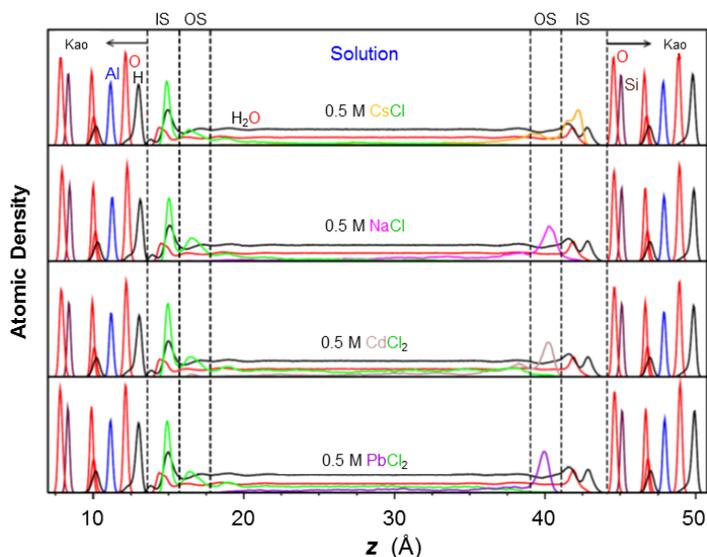


FIGURE 3 Atomic density profiles for various solution compositions at the basal surface of kaolinite (Kao) derived from an equilibrated molecular dynamics simulation. The interfacial regions for adsorption are denoted by IS for inner sphere and OS for outer sphere, as indicated by water intermediate between the ion and the surface. ADAPTED WITH PERMISSION FROM VASCONCELOS ET AL. (2007). COPYRIGHT 2007, AMERICAN CHEMICAL SOCIETY

kaolin-group minerals but also carbonates, silicates, Fe–Mn oxides, hydrated phosphates, and sulfides formed through bacterial activity (Tazaki 1997a, b).

Bacterial Biomineralization of Kaolin

In nature, the degree of order and disorder within kaolin-group minerals ranges from poorly crystalline kaolinite granules to well-oriented crystalline phases. Polymeric substances secreted by microbial cells include the crystalline surface-layer proteins, polysaccharides, and capsules that often provide nucleation sites and possibly a favorable chemical microenvironment for biomineral formation. Bacterial cells can act as nucleation sites for clay minerals. The layer of extracellular polymeric substances surrounding microbial cells can therefore act as a template in the formation of hydroxides (Tazaki 2005). Cation bridging is one mechanism in which multivalent metal cations complex with a functional group such as carboxylate (e.g. COO^-), which in turn bridges with ionic silicate species to form large aggregates. Multivalent cations may serve as cation bridges in the interaction between clays and microbial extracellular polymeric substances. The coccus- and bacillus-type bacteria transfer electrons via the pilus—a hair-like appendage—to the metal that they feed from. Transferring the electrons provides the bacteria with energy. This also changes the ionization state of the metal, producing a form that can potentially precipitate from solution.

Evidence for kaolin mineral production via bioweathering is supported by experiments with iron bacteria (*Toxothrix* and *Gallionella*) carried out using thin sections of granite. Samples of bacteria were collected from microbial mats in river freshwater. Cavities and fissures with bacilli and filamentous bacteria were immediately observed on the surface of feldspars and biotite in the granite samples, and during two months of treatment K and Si were released into solution. The Si content of the altered material was reduced at the grain edges (Si:Al modified from 3:1 to 3:2), and the material was identified as kaolinite by electron diffraction. Compared to an abiotic experiment, microorganisms associated with the release of nutrients such as K^+ accelerated the weathering of granite. The biokaolinite exhibits almost the same X-ray diffraction and energy-dispersive X-ray (EDX) patterns as hydrothermal kaolinite. Fourier transform infrared spectra exhibit absorption bands of kaolin, which is an additional indicator of organic origin (FIG. 4A) similar to that of primary kaolinite from Cornwall, UK (FIG. 4B). Optical and electron microscope observations of cultured microbes reveal that thin clay films cover areas of the bacterial cell wall after two years, and these display the 7.13 Å *d*-spacing of a halloysite-like phase, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as determined by X-ray diffraction (Asada and Tazaki 2000; Tazaki 2005).

Kaolinite and Bioremediation of Radioactive Environments

Tanzania is endowed with a variety of industrial minerals, such as kaolinite, diatomite, and rock salt, which are occasionally associated with uranium deposits. One such occurrence is the Bahi swamp area in central Tanzania, which is a dry lake or playa. Uranium is known to have variable degrees of mobility depending upon its redox state, and it accumulates in poorly oxygenated aquifers. Uranium is observed on the margins of regional uplands of uranium granites. The Bahi uranium mine is located in weathered granite and clays characterized by a high γ -ray radioactivity, with indurated-sediment cores having U_3O_8 contents of 0.23 wt%. Salt soils with Th/U ratios ranging from 2.9 to 3.7 are also found associated with abundant

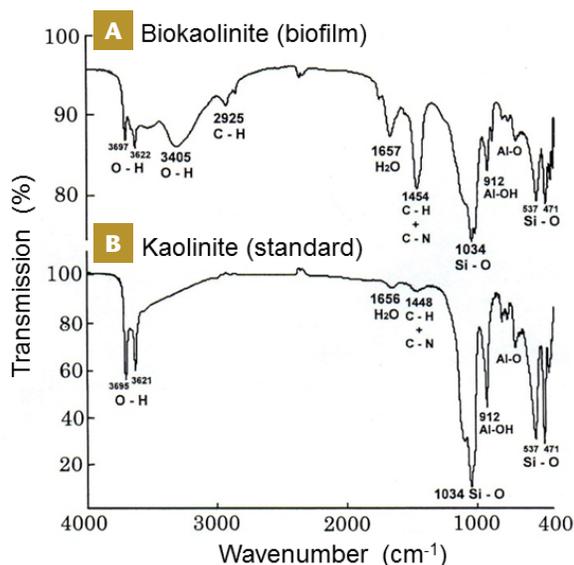


FIGURE 4 Fourier transform infrared (FT-IR) spectra of (A) biokaolinite compared with (B) standard kaolinite for reference material API62 (Cornwall, UK). The peaks at 3697 cm^{-1} and 3622 cm^{-1} are due to the structural water O–H stretch of kaolinite, whereas the peaks at 1454 cm^{-1} to 1420 cm^{-1} are due to abundant organics (C–H and C–N stretch) in the structure of kaolinite.

microorganisms. Nearby, rice paddy soils are composed mainly of halloysite, micaceous clays (10 Å), smectite (14 Å), feldspar, tridymite, and quartz.

Scanning electron microscope (SEM) imaging provides elemental maps of kaolin grains in the Bahi soils, and these show abundant Al resulting from weathered feldspar and the presence of clay components (FIG. 5A). The maps indicate a nonuniform distribution of elements within 100 μm sized grains. Elemental maps of 5 μm sized bacteria show regions of concentrated Na, Cl, S, Ca, and Sr (FIG. 5B). Some coatings on bacteria are rich in S and Ca whereas others are dominated by Ca and Sr, suggesting the occurrence of SrCO_3 and SrSO_4 nodules in the sediments. The elongated and spherical shapes suggest the presence of bacillus and coccus bacteria, respectively. Transmission electron microscopy (TEM) observation of paddy soils confirms the survival of many microorganisms under radioactive conditions. Among the microbes are filamentous bacteria (FIG. 6A) covered by submicron hexagonal precipitates of kaolinite (FIG. 6B, C). TEM micrographs and electron diffraction analysis show the initial stages of biomineralization involving coccus-type (FIG. 6D) and bacillus-type (FIG. 6E) bacteria. All bacteria observed in the radioactive paddy soils are lightly covered with kaolinite grains on the cell walls and occasionally within the cells themselves. These results suggest that kaolinite grains play an important role as a screening tool for radioactive pollutants and as a potential repository for containment.

Clay minerals are a significant component of the radioactive soils and tsunami sediments contaminated by the Fukushima Daiichi nuclear power plant accident in 2011 (Murakami and Ewing 2012). The destruction of the Fukushima power plant was the world's worst nuclear accident since the Chernobyl disaster in 1986. Kaolin minerals associated with the weathered-granite soils near Fukushima are now contaminated with high levels of radioactive material. The interaction of soils with ^{131}I , ^{134}Cs , ^{137}Cs , $^{129\text{m}}\text{Te}$, $^{110\text{m}}\text{Ag}$, ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{90}Sr pollutants is controlled by a complex interplay of surface organic chemistry, redox, pH, and microbiology. Especially

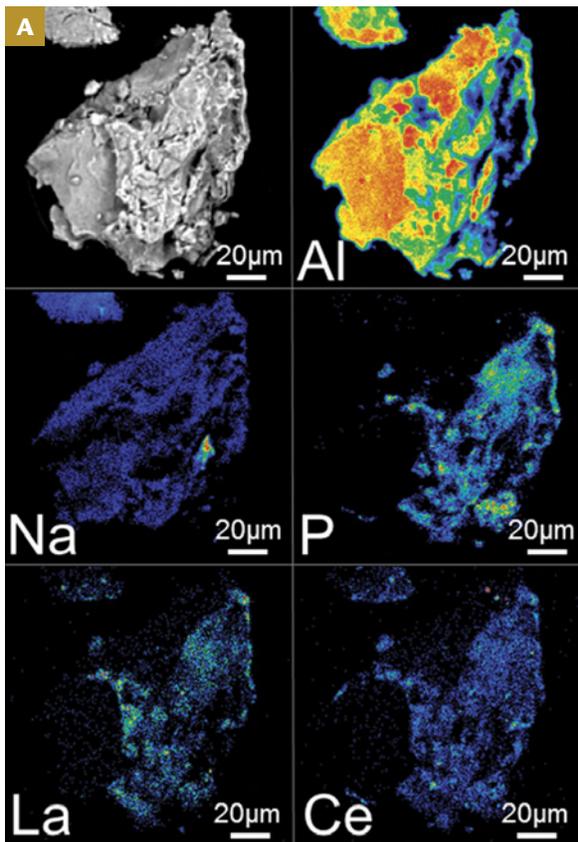
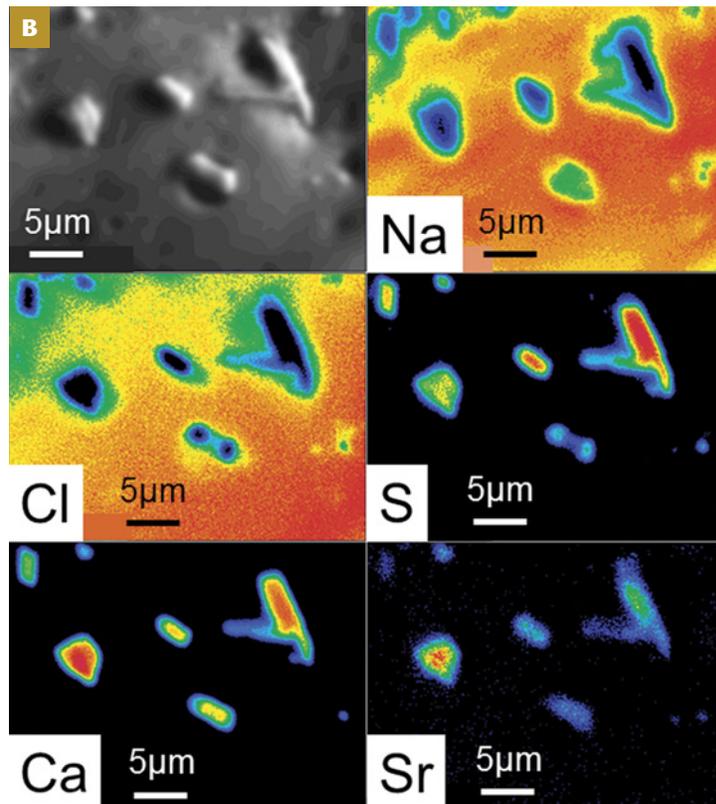


FIGURE 5 (A) Scanning electron microscope elemental color-coded maps of kaolinite grains from Bahi, Tanzania, indicating a major component of Al, lesser amounts of Na and P, and traces of La and Ce. (B) Elemental, color-coded maps of bacteria from Bahi indicating S- and Ca-rich regions in coccus-type (round shape) and bacillus-type (elongated) bacteria and a Sr-rich region in coccus-type bacteria. The background surrounding the bacteria is rich in Na and Cl because of the salty paddy soil surfaces in Bahi during the dry season. The colors indicate elements contents, red corresponding to the highest content.



common is the adsorption of 134 , 137 Cs and K onto the edge and interlayer sites of illite and mica-group minerals (McKinley et al. 2004; Pusch 2006; Asami 2013).

Salty microbial mats on the rice paddy soils at Minami Soma were exposed to radioactivity after the tsunami event at Fukushima. Electron microscope observations indicate abundant microorganisms, such as diatoms, foraminifera, and bacteria, in the severely contaminated environment (Tazaki 2013; Tazaki et al. 2013). After one year of exposure, quantitative analyses using SEM-EDX showed that diatoms and kaolin minerals held discernible concentrations of radionuclides (such as I, Cs, Ba, Nd, Th, U, Np, and Pu), indicating a capacity for adsorbing both radionuclides and stable isotopes from paddy soils polluted by radioactive materials (137 Cs, some 90 Sr, and a trace of Pu) dispersed by the Fukushima accident. The microorganism–clay–radionuclide interactions as observed in the contaminated paddy soils at Fukushima could be potentially effective in moderating the transport of low-level radioactive waste from geological repositories. Microbe–clay interaction is of concern for mediating the risk in contaminated sites for longer periods, such as the concentration of 90 Sr at various radioactive hot spots in Japan. This is significant for health issues, and especially for the safety of food sources (Steinhauser et al. 2013).

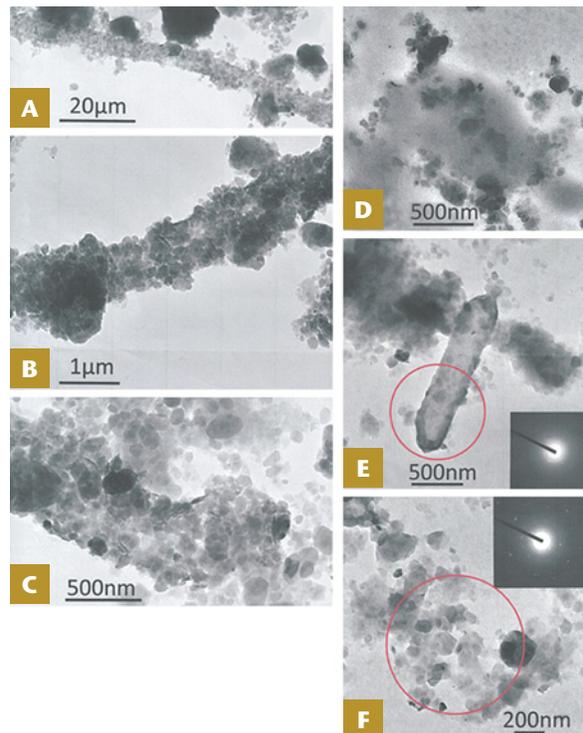


FIGURE 6 Transmission electron microscopy (TEM) micrographs. (A) Filamentous bacteria 1 μ m wide and more than 100 μ m long, which are (B) densely covered with hexagonal granular grains of kaolinite on the cell surface. One large hexagonal kaolinite crystal can be seen in the lower left. (C) Nanometer-sized kaolinite grains adhere to the bacterial surface, showing the initial stage of biomineralization. (D) Coccus-type bacteria. (E) Bacillus-type bacteria with an electron diffraction pattern (inset) for the circled area. (F) Nanometer-sized kaolinite grains with an electron diffraction pattern (inset) indicating 7 Å and 4.5 Å *d*-spacings.

OUTLOOK

Kaolinite and other kaolin-group minerals are prevalent environmental phases that control many geochemical processes, such as adsorption, nucleation and growth, redox, and induced biomineralization. The fate of heavy metals, radionuclides, pesticides, organics, and other contaminants in the environment will be partly determined by their physical and chemical interactions with kaolin and other clay materials. New developments of natural gas resources and the efficient extraction of methane from kaolin-bearing beds may potentially be improved by determining the fundamental mechanisms of gas-clay interactions. Similarly, the extraction of oil from deep sedimentary reservoirs is limited by our understanding of the wetting properties of clay mineral surfaces. The design of a geological repository for radioactive waste requires the assessment of geomicrobiological factors to better evaluate the chemical and biological reduction of radionuclide species. Within these contexts, the properties

of kaolinite are important for understanding the behavior of microorganisms in natural environments. It is clear that investment in research toward improving our understanding of such complex interactions at many spatial scales and timescales would benefit our global society.

ACKNOWLEDGMENTS

The authors appreciate the opportunity to contribute to the kaolin issue and thank the guest editors, Paul Schroeder and David Bish, for the invitation and their editorial support. Tazaki extends her gratitude to Hiroshi Onodera at JEOL for his technical assistance. The U.S. Department of Energy, Office of Basic Energy Sciences, Geosciences Research Program funded this study. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. ■

REFERENCES

- Asada R, Tazaki K (2000) Observation of bio-kaolinite clusters. *Journal of the Clay Science Society of Japan* 40: 24-37 (in Japanese)
- Asami T (2013) Fukushima Nuclear Power Plant Accident—Contamination of Soils and Foods by the Nuclides. AGNE Gijutsu Center, Tokyo, 299 pp
- Balan E, Calas G, Bish DL (2014) Kaolin-group minerals: From hydrogen-bonded layers to environmental recorders. *Elements* 10: 183-188
- Bish DL (1993) Rietveld refinement of the kaolinite structure at 1.5 K. *Clays and Clay Minerals* 41: 738-744
- Brady PV, Cygan RT, Nagy KL (1996) Molecular controls on kaolinite surface charge. *Journal of Colloid and Interface Science* 183: 356-364
- Brindley GW, Brown GC (eds) (1980) *Crystal Structure of Clay Minerals and Their X-ray Identification*. Monograph 5, Mineralogical Society, London, 495 pp
- Cygan RT, Liang J-J, Kalinichev AG (2004) Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. *Journal of Physical Chemistry B* 108: 1255-1266
- Dixon JB, Schulze DG (2002) *Soil Mineralogy with Environmental Applications*. Book Series 7, Soil Science Society of America, Madison, 253 pp
- Haria NR, Grest GS, Lorenz CD (2013) Viscosity of nanoconfined water between hydroxyl basal surfaces of kaolinite: Classical simulation results. *Journal of Physical Chemistry C* 117: 6096-6104
- Lee SG, Choi JI, Koh W, Jang SS (2013) Adsorption of β -D-glucose and cellobiose on kaolinite surfaces: Density functional theory (DFT) approach. *Applied Clay Science* 71: 73-81
- Liu XD, Lu XC, Wang RC, Meijer EJ, Zhou HQ, He HP (2012) Atomic scale structures of interfaces between kaolinite edges and water. *Geochimica et Cosmochimica Acta* 92: 233-242
- McKinley JP, Zachara JM, Heald SM, Dohnalkova A, Newville MG, Sutton SR (2004) Microscale distribution of cesium sorbed to biotite and muscovite. *Environmental Science & Technology* 38: 1017-1023
- Murakami T, Ewing RC (eds) (2012) *Fukushima Daiichi*. *Elements* 8: 181-219
- Newman ACD (1987) *Chemistry of Clays and Clay Minerals*. Mineralogical Society, London, 480 pp
- Pusch R (2006) Clays and nuclear waste management. In: Bergaya F, Theng BKG, Lagaly G (eds) *Handbook of Clay Science* 1, Elsevier, Amsterdam, pp 703-716
- Scott AM, Dawley MM, Orlando TM, Hill FC, Leszczynski J (2012) Theoretical study of the roles of Na^+ and water on the adsorption of formamide on kaolinite surfaces. *Journal of Physical Chemistry C* 116: 23992-24005
- Šolc R, Gerzabek MH, Lischka H, Tunega D (2011) Wettability of kaolinite (001) surfaces—Molecular dynamic study. *Geoderma* 169: 47-54
- Steinhauser G, Schauer V, Shozugawa K (2013) Concentration of strontium-90 at selected hot spots in Japan. *PLOS ONE*: doi 10.1371/journal.pone.0057760
- Tazaki K (1997a) Biomineralization of layer silicates and hydrated Fe/Mn oxides in microbial mats: An electron microscopical study. *Clays and Clay Minerals* 45: 203-212
- Tazaki K (1997b) A new world in the science of biomineralization: Environmental biomineralization in microbial mats in Japan. *Science reports of Kanazawa University* 42: 1-65
- Tazaki K (2005) Microbial formation of a halloysite-like mineral. *Clays and Clay Minerals* 53: 224-233
- Tazaki K (2013) Clays, micro-organisms, and biomineralization. In: Bergaya F, Lagaly G (eds) *Handbook of Clay Science* 5, Elsevier, Amsterdam, pp 613-653
- Tazaki K, Takehara T, Ishigaki Y, Nakagawa H, Nemoto N (2013) SEM-EDX observation of organisms in polluted soils by FDNPP accident in 2011. *Kahokugata Lake Science* 16: 1-20
- Thyveetil M-A, Coveney PV, Greenwell HC, Suter JL (2008) Computer simulation study of the structural stability and materials properties of DNA-intercalated layered double hydroxides. *Journal of the American Chemical Society* 130: 4742-4756
- Tunega D, Gerzabek MH, Lischka H (2004) Ab initio molecular dynamics study of a monomolecular water layer on octahedral and tetrahedral kaolinite surfaces. *Journal of Physical Chemistry B* 108: 5930-5936
- Vasconcelos IF, Bunker BA, Cygan RT (2007) Molecular dynamics modeling of ion adsorption to the basal surfaces of kaolinite. *Journal of Physical Chemistry C* 111: 6753-6762 ■