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Versatile CLAY

from functional products
to the search
for extraterrestrial life

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**Many of you probably played with clay as a child.
While you may see clay merely as an artistic medium, you're likely to change your mind after learning about clay research at NIMS.
Although clays can have a diverse array of textures and shapes, they have one thing in common: outstanding adsorption capabilities.**

Since ancient times, people have known and taken advantage of clay's excellent adsorbent qualities. Clay can be found serving a variety of purposes in our daily lives. For example, clay is used as a water purification agent in aquariums and it can also be used cosmetic face packs.

**Clay is a key component in a wide range of materials used in the food, medical and industrial fields. Despite clay's widespread use, its microstructures had been poorly understood.
However, recent technological advances have enabled more detailed structural analyses. It is now feasible to chemically modify "naturally occurring clay" and artificially synthesize it from scratch.**

Clay may even offer vital clues that could help solve a great mystery: does extraterrestrial life exist? Clay is a profoundly influential material in a variety of ways, useful in everyday life and even in reaching a more complete understanding of the universe.

Dyed water becomes clear as it passes through a clay filter capable of removing only the pigment.

Introduction

The surprising world of clay

Montmorillonite

Vermiculite

While it exists as flat and flaky crystals at normal temperature (left), heating it to 800–1,000°C causes it to expand in a manner similar to the bellows of an accordion (right).

Zeolite

What is "clay"?

What images come to mind when you think about clay? Many of you might remember playing with moist clay in elementary school art classes. However, not all clay is moist. It can have a wide variety of textures, from a dry stone-like feel to a glassy, hard consistency.

Because of the diverse array of forms clay can take, it has many different definitions. Although the definition varies somewhat from discipline to discipline, the most common definition of clay is a sediment composed of very fine-grained particles (2 μm or less in diameter). Clay generally means a sediment composed primarily of tiny clay mineral particles formed through chemical reactions between rocks and water. Different clay textures are associated with different clay mineral constituents with distinctive crystalline structures. As a side note, the moist clay used in art classes is commonly called oil clay, and is produced by adding an oil to naturally occurring clay minerals. Oil clay is designed to be easily reshaped and stretched by hand.

Clay minerals in our daily lives

Clay minerals have long been used in various products, such as ceramics, gastrointestinal drugs and cosmetics. All of these products have exploited a particular feature of clay minerals: their ability to adsorb and retain target substances.

For example, clay minerals added to gastrointestinal drugs adsorb water, preventing loose stools. Clay minerals in cosmetic foundations and shampoos adsorb sebum and sweat. They are also used to remove sediments deposited at the bottom of wine barrels during the winemaking process and to filter organic impurities out of water. Clay minerals therefore have been benefitting us in many ways in everyday life.

Certain physicochemical properties of clay minerals played a particularly important role in the aftermath of the nuclear accident at the Fukushima Daiichi Nuclear Power Plant caused by the Great East Japan Earthquake in March 2011. Large amounts of radioactive cesium released from the accident site onto the ground were adsorbed by clay minerals in the soil. This is why the top soil layers have been removed in affected areas as a decontamination measure.

Mechanisms behind clay's excellent adsorption capacity

The ability of clay minerals to adsorb and retain substances from the surrounding environment is made possible by their structures.

The main chemical elements constituting clay minerals are silicon (Si), aluminum (Al), magnesium (Mg) and hydrogen (H). The basic building blocks of clay minerals—tetrahedral and octahedral units—are composed of these chemical elements and oxygen (O). These building blocks bind together to form tetrahedral and octahedral sheets. Many clay minerals have layered structures, with each layer composed of overlaying tetrahedral and octahedral sheets (Figure 1).

Clay mineral layering can be broadly classified into two types: 1:1 layer type, in which a single tetrahedral sheet is stacked onto a single octahedral sheet, and 2:1 layer type, in which an octahedral sheet is sandwiched between two tetrahedral layers (Figure 2). Layered clay minerals are basically composed of stacks of multiple 1:1 or 2:1 layers.

Various substances migrate into the interlayer spaces in clay minerals. Layers in naturally occurring clay minerals are often negatively charged. They tend to incorporate positively charged cations into their interlayer spaces to achieve an electrically stable neutral state. By the same token, clay minerals with positively charged layers tend to incorporate negatively charged anions into their interlayer spaces to neutralize themselves electrically.

Typical adsorption mechanisms in clay minerals are driven by ion exchanges in which ions in interlayer spaces are replaced with external ions with the same electrical charges (i.e., exchanges between different types of cations and anions).

In addition, various forces bind atoms, molecules and ions together (e.g., the Coulomb force and the van der Waals force) in the interlayer spaces. The types of substances clay minerals incorporate are also influenced by the strength of these forces.

Broader application through artificial synthesis

The basic structures of naturally occurring clay minerals are frequently altered by external factors, such as temperature, pressure and pH (e.g., partial changes in the stacking order of layers, introduction of impurities and replacement of Si in clay mineral crystalline structures with Al). Because of these alterations, even the same species of clay minerals have slightly different physical properties depending on the geographical areas in which they originate.

It is therefore vital to collect naturally occurring clay minerals from around the world and screen them for desirable characteristics to develop effective clay mineral-based materials. Using this approach, materials scientists first select promising clay minerals and then modify them chemically to enhance their performance. Some NIMS scientists have been using unique methods to chemically modify montmorillonite—a type of clay mineral—with the goal of developing a material capable of efficiently removing caffeine from coffee (see p. 6).

Certain naturally occurring clay minerals only exist in limited quantities, and their physical properties vary widely. Artificial synthesis can offer a more convenient alternative to the use of naturally occurring minerals. For example, clay minerals called layered double hydroxide (LDH) and magadiite are relatively easy to synthesize by mixing raw materials and solutions. In addition, the performance of artificial clay minerals can be regulated by modifying the synthesis conditions. Because of these advantages, artificial clay minerals have been used in the development of medical materials (see p. 10) and in the synthesis of plastic raw materials (p. 14). The applicability of clay minerals is expected to further expand.

(by NIMS NOW Editorial Desk and Kumi Yamada)

Mica

Mica is composed of thin, flaky, translucent layers. The petri dish in the background can be seen through the more transparent portion of the mineral, which consists of fewer layers.

Figure 1. Structural backbones of clay minerals

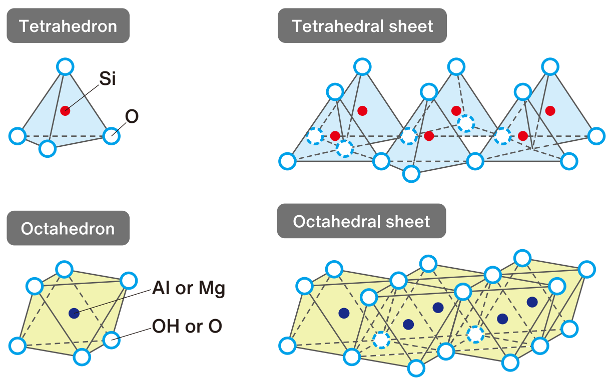
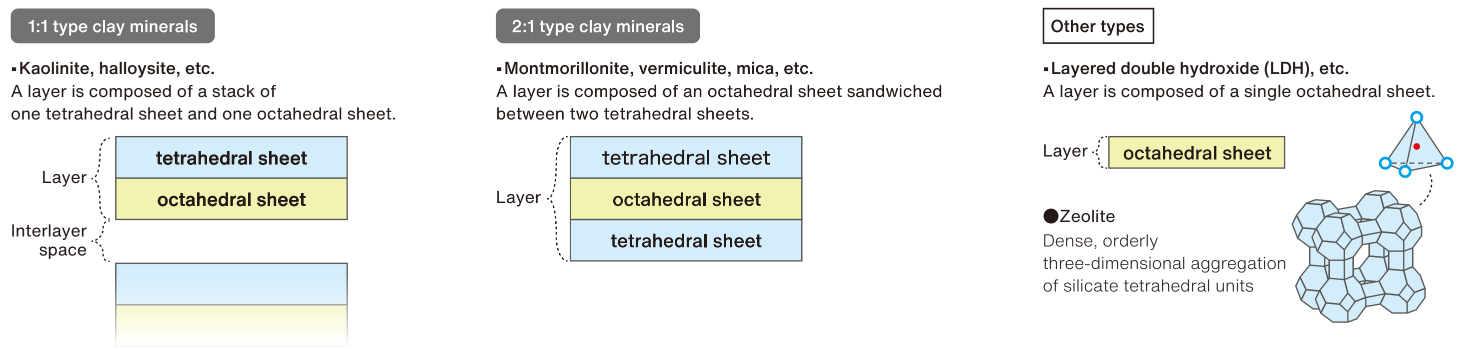


Figure 2. Major clay mineral structures



Research 1

Efficient decaffeination of coffee and tea without compromising taste

Demand for decaffeinated drinks has been growing in recent years for health reasons.
A research team led by Kenji Tamura and Hiroshi Sakuma made chemical modifications to naturally occurring clay materials, successfully developing an adsorbent capable of rapidly filtering approximately 99% of the caffeine out of a beverage.

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Request from food manufacturers

Clay mineral materials have been used in various industries. Kenji Tamura—a clay mineral research specialist—has a number of research achievements to his credit. One day, researchers from a food manufacturer approached Tamura to consult with him.

"The consultation was about caffeine in drinks," Tamura said. "These researchers had been attempting to decaffeinate beverages at the request of consumers concerned about the effects of caffeine on pregnancy and overall health. However, they were unable to do so using currently available techniques without removing other components that impart flavor. They came to me to ask whether it might be possible to efficiently remove caffeine alone using clay minerals."

The food manufacturer was keenly interested in clay minerals because they are naturally occurring. Food manufacturers believe food production should use naturally occurring materials to the extent possible to ensure consumer safety. Highly adsorbent clay minerals composed exclusively of non-toxic chemical elements are therefore ideal.

Designing clay minerals capable of adsorbing caffeine molecules

Tamura's research team launched an R&D project in response to the food manufacturer's request. The team selected montmorillonite (photo on p. 4) from among the many types of clay minerals available because of its inherent ability to adsorb caffeine. In addition, montmorillonite already has a proven record of compatibility with food products, ensuring reliability in the food industry, to which strict regulations (e.g., the Food Sanitation Act) apply. Tamura and Sakuma's first task was to make chemical modifications to montmorillonite to enhance its adsorption capabilities.

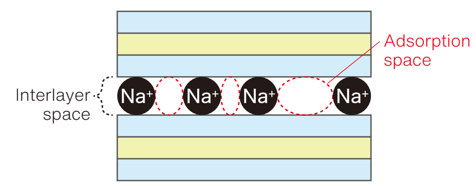


Figure. Unevenl space io "pillars (i.e., Na^+) distribut ed in the interlayer space of a naturally occurring montmorillonite. Tamura's research team has designed montmorillonite with evenly spaced ion pillars and wider adsorption spaces in order to achieve efficient adsorption of large, flat caffeine molecules.

Clay minerals are layered materials. Many clay minerals used as adsorbents have either positively or negatively charge surfaces. These naturally occurring clay minerals neutralize electric charge by incorporating cations or anions from the surrounding environment into their interlayer spaces. They subsequently exchange the incorporated ions with external ions with the same charge; a common ion adsorption mechanism. Some might jump to the conclusion that clay materials capable of incorporating molecules with the same electric charge as caffeine molecules would be the ideal materials to achieve caffeine adsorption. However, the task is not that simple because caffeine molecules are electrically neutral, and thus have no positive or negative charge.

"The adsorption mechanisms of naturally occurring montmorillonite are not yet understood," Tamura said. "Our initial approach was to widen the interlayer spaces in montmorillonite. Ions are distributed across an interlayer space like pillars. Because these 'pillars' are unevenly spaced, many interpillar spaces are inadequate to accommodate caffeine molecules. We wanted to have evenly spaced pillars and adequate interpillar spaces to increase montmorillonite's inherent caffeine adsorption capabilities." (Figure)

Ion valences* are an important factor when attempting to widen interlayer spaces. Montmorillonite often incorporates monovalent sodium ions (Na^+) into its interlayer spaces. If montmorillonite can incorporate ions with higher valences, fewer of these ions would occupy the interlayer spaces, widening the spaces between them and allowing them to

*The valence of an ion is the quantity of positive or negative charge acquired by an atom when it loses or gains electrons.

accommodate more caffeine molecules.

Naturally occurring montmorillonites also have another issue: their layers tend to separate when exposed to water, destroying the adsorption spaces. The presence of Na^+ in the interlayer spaces holds them together due to electrical attraction, but this force is weak. To address this issue, Tamura's research team began searching for more strongly electrically attractive multivalent cations and montmorillonites capable of incorporating them.

The physicochemical properties of montmorillonites vary depending on the geographical areas. Tamura's team first gathered about 20 montmorillonite samples from various locations and thoroughly analyzed their crystalline structures and chemical properties using X-ray diffraction, spectroscopy and chemical analyses. The team then carried out simplified tests to determine the samples' caffeine adsorption performance, narrowed the samples down to a few promising ones and experimentally added a variety of different cations to them.

As a result, the team was ultimately able to design a new montmorillonite equipped with stable caffeine adsorption spaces by replacing Na^+ in its interlayer spaces with multivalent cations (i.e., calcium and aluminum ions). The team then subjected this montmorillonite to the simplified tests again and found that its caffeine adsorption rate was approximately 99%, removing nearly all caffeine molecules. By comparison, the caffeine adsorption rate of currently available caffeine adsorbents is only approximately 60%.

Identifying adsorption mechanisms to better preserve the flavor of decaffeinated drinks

Although the montmorillonite was efficient in adsorbing caffeine, it also adsorbed small amounts of flavoring substances. Therefore, the technology is still imperfect in its ability to preserve the flavor of decaffeinated drinks as requested by the food manufacturer. To improve the montmorillonite, Sakuma has been leading the effort to understand its adsorption mechanisms using computer simulations and other methods.

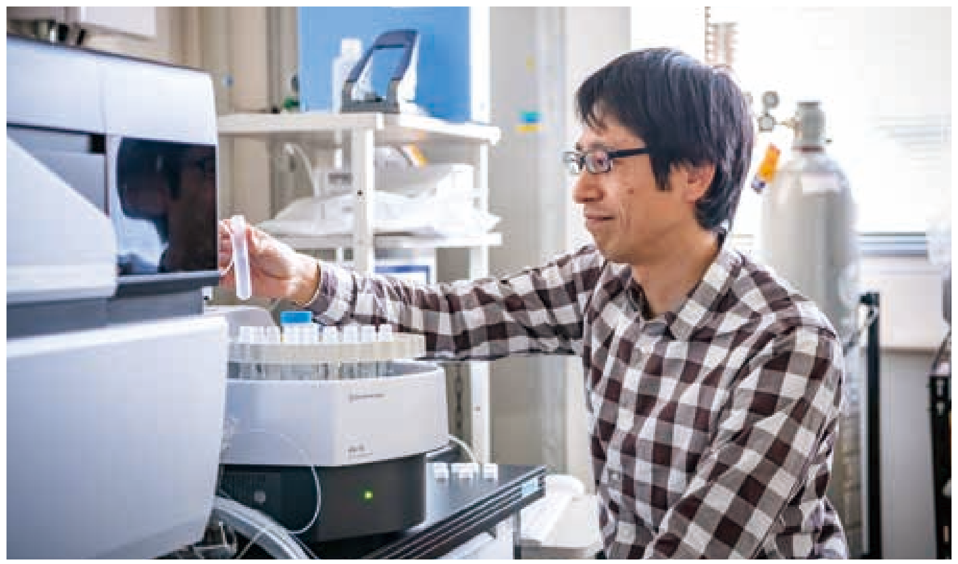
"Although our studies are still underway, we can now make some assumptions," Sakuma said. "We believe that efficient caffeine adsorption occurs through strong interactions between ions in the interlayer spaces and caffeine molecules in their surroundings. Caffeine molecules are electrically neutral as a whole, but they are actually polar molecules with internal electric charges. This characteristic of caffeine molecules allows ions in the interlayer spaces to interact with parts of them, causing the montmorillonite to absorb caffeine. This is the adsorption mechanism we think."

It might be assumed that the efficiency of caffeine adsorption would be directly related to the strength of the interaction between the ions in the interlayer spaces and caffeine molecules. However, this is not always the case, according to Sakuma.

"Even if strong interactions can be generated between interlayer space ions and caffeine molecules, this may weaken the interaction between the ions and the montmorillonite layers. When this interaction weakens, the interlayer space ions may easily leave the montmorillonite after binding to caffeine molecules, making them difficult to retrieve. Conversely, if the ions interact with the layers too strongly, their ability to bind with caffeine molecules weakens. Achieving the optimum balance between these two interactions is critical. We presume that the replacement of Na^+ with multivalent cations not only created adequate interlayer spaces to accommodate caffeine molecules but also optimized the balance between the two interactions. We will continue our investigation."

Increasing filtration efficiency by making particles uniform in size and shape

Once an effective adsorbent is created, processing it into a user-friendly form is vital. The adsorbent developed was a powder composed of fine particles less than 2 µm in diameter. The research team poured a liquid onto the adsorbent powder, but the pores between particles became clogged, preventing the liquid from passing through the pores. To address this practical issue, the team decided to make the particles uniform in size and shape, thereby increasing the filtration efficiency of the adsorbent.



A mass spectrometer, a vital tool in quantifying chemical elements adsorbed by clay minerals. A sample solution is prepared by dissolving a target clay mineral in a solvent. Plasma is then applied to the solution to ionize the chemical elements adsorbed by the clay mineral. Finally, the mass of the ionized chemical elements is measured at a part-per-trillion sensitivity.

"I decided to produce perfectly spherical particles 10 µm in diameter to increase filtration efficiency," Sakuma said.

To achieve this, Sakuma used a centrifugal atomizer (photo on p. 6) equipped with a cylindrical furnace containing a rotary disc. He sprayed a suspension of water and a montmorillonite adsorbent from the top of the atomizer onto the disc heated to 180°C and spinning at high speed. This produced a clay mineral-containing water film of uniform thickness over the spinning disc, which was subsequently thrown off by centrifugal force, forming particles.

"Suspending the montmorillonite in water causes its layers to exfoliate and become evenly distributed," Sakuma said. "Application of centrifugal force to the suspension produces particles uniform in size and shape."

Sakuma adjusted the experimental conditions a number of times, changing the rotational speed of the disc and the amount of the suspension sprayed, and finally obtained perfectly spherical particles 10 µm in diameter (photo on the right). He actually filtered coffee through the adsorbent powder developed and found that caffeine was successfully adsorbed without clogging the inter-particle pores.

"We should be able to achieve more rapid caffeine filtration by optimizing particle size and shape," Sakuma said. "I hope to determine optimum particle conditions and understand the adsorption mechanisms."

Caffeine adsorbent

Tamura also expressed his ambitions. "I would like to develop smart adsorbents capable of selectively removing molecules other than caffeine based on what I have learned from this project."

(by Kumi Yamada)

FOCUS

Searching for traces of extraterrestrial life in clay

Scientists have found clay minerals on other planets. The unmanned rover Curiosity discovered large amounts of clay minerals on Mars in May 2019 while conducting geological surveys in a giant crater. This news attracted a great deal of attention, as clay minerals had previously been found on the planet only in small quantities. Clay minerals are formed through chemical reactions between rocks and water. As such, their presence is proof that water once existed on what now appears to be an arid planet.

Studying these clay minerals may offer vital clues that may help solve a great mystery: does extraterrestrial life exist? Even if a planet has water, life is unlikely to exist there if the living environment is extremely acidic/alkaline or if nutrients essential to life are lacking. Clay minerals are capable of recording water quality. This is because clay minerals tend to adsorb and incorporate ions from the surrounding environment. In other words, analyzing the composition of clay minerals can reveal ancient water's characteristics.

This analysis was carried out by a research team organized for the Aqua planetology project[*1] launched in 2017. Sakuma was a member of the team led by Professors Keisuke Fukushi (Kanazawa University) and Yasuhito Sekine (Tokyo Institute of Technology).

The team analyzed sediment data collected by Curiosity. In-depth analysis of X-ray diffraction and other data determined the species of cations present in the interlayer spaces of the clay minerals. The team also analyzed data on salts and other minerals formed by the reaction of water in the areas in which the clay minerals were sampled. The team then studied the characteristics of the water from the perspectives of thermodynamics, chemical kinetics and other theoretical bases.

According to the research team's findings, published in October 2019[*2], ancient Martian water was saline, containing mainly sodium and chlorine. Its salt concentration was approximately one-third that of Earth's oceans and it was rich in minerals and neutral in pH, indicating that Martian water was life-friendly. The study has shed light on a new facet of Mars. Future projects to investigate the geographical extent of ancient water on Mars and water characterization surveys on other planets may someday provide convincing evidence for the existence of extraterrestrial life.

Photos provided by NASA

*1 Aqua planetology project: funded by the Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology

*2 Fukushi, Sekine, Sakuma, Morida & Wordsworth, Nat. Commun. 2019, 10, 4896.

Research 2

Improving medical gas usability: a “breathing” clay mineral with hot spring-like effects

Some gases (e.g., hydrogen sulfide (H_2S), nitric oxide (NO) and carbon monoxide (CO)) exhibit physiological benefits, generating a great deal of interest in their medical applications in recent years. However, these gases are not in widespread use due to their toxicity at high concentrations and difficulty in regulating their concentrations at low safe level.

To overcome these issues, a research team of Shinsuke Ishihara and Nobuo Iyi has developed a material capable of slowly releasing physiologically beneficial gases at low concentrations. The team accomplished this using a clay mineral with a “breathing” character.

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Medical gas use today: small amounts produce benefits

The Japanese people have been using hot springs for their therapeutic benefits since ancient times. Sulfur hot springs are particularly well known for their efficacy in treating dermatitis, chronic bronchitis and high blood pressure. One component of hot spring water contributing to these benefits is dissolved hydrogen sulfide (H_2S) gas, a source of the typical hot spring “rotten egg” smell.

Other gases also have positive physiological effects on humans. Nitric oxide (NO) can expand blood vessels, thereby lowering blood pressure. NO inhalers have been used to treat patients with severe pulmonary conditions. Carbon monoxide (CO) has also been found to play a part in various physiological functions, such as anti-inflammatory processes, cellular protection and neurotransmission.

However, these gases have medicinal effects only at very low concentrations. At higher concentrations (roughly 0.01% or higher), they are toxic to humans. Accidental deaths frequently occur in the vicinity of volcanic craters where H_2S has accumulated and in closed spaces filled with CO produced by incomplete combustion. In addition, NO inhalers need to have elaborate safety mechanisms, given that NO turns into harmful nitrogen dioxide (NO_2) when exposed to the air. For this reason, only a limited number of medical institutions are equipped with NO inhaler.

The research team of Ishihara and Iyi has been developing new clay materials that will make medical use of physiologically beneficial gases more convenient and accessible. [*1]

Inspired by a clay mineral that “breathes”

The team has developed a gas releasing material composed primarily of a clay mineral called a layered double hydroxide (LDH)—a layered inorganic compound composed of hydroxide layers of magnesium (Mg) and aluminum (Al). The naturally occurring mineral of LDH is known as hydrotalcite. LDH can also be artificially synthesized relatively easily.

Hydrogen sulfide (H_2S) releasing patches
LDH powder synthesized (right) releases H_2S when it is exposed to the air. Patches (left) are composed of LDH powder sandwiched between two filters.

Portable nitric oxide (NO) inhaler
A manual hand pump (far side) sends air into a column filled with water-soaked cotton for humidification. The air then passes through a column filled with LDH in which chemical reactions release NO. The NO gas then passes through a column filled with $Mg(OH)_2$ to filter out NO_2 from the gas. Finally, NO is mixed with air to optimize its concentration for safe inhalation by patients.

Ishihara and Iyi measuring the amount of H_2S released from LDH using a gas sensor. During the measurement, air is allowed to pass through LDH in a container.

Ishihara and Iyi discovered new interesting phenomenon about LDH in 2013. "Unlike many other clay minerals, LDH contains positively charged layers; therefore, it incorporates anions in the spaces between the layers (i.e., interlayer space). LDH also has a high ion exchange property: anions in interlayer spaces of LDH are exchanged when LDH is exposed to a solution containing anions. The carbonate ion (CO_3^{2-}) is a type of anion that LDH stably incorporates in its interlayer space. We discovered that the incorporated CO_3^{2-} is continuously replaced with atmospheric carbon dioxide (CO_2). LDH is therefore "breathing" in a manner similar to the way in which humans inhale O_2 and exhale CO_2." [*2]

Ishihara and Iyi tried to find ways of using this "breathing" mechanism, in more technical words gas-solid anion exchange mechanism, to allow LDH to release H_2S or NO. Their vision was to place the precursor anions of H_2S or NO gas in the interlayer spaces of LDH. LDH is then allowed to "breath" the air, triggering a slow release of H_2S or NO at low concentrations.

"Atmospheric CO_2 is nearly constant in concentration at approximately 400 ppm, and ambient CO_2 can enter the LDH interlayer spaces only at a limited rate. In addition, the number of anions that can be stored in the LDH interlayer spaces can be adjusted by modifying the synthesis method. These mechanisms eliminate the risk of LDH rapidly releasing large amounts of H_2S or NO into the ambient environment. We envisioned using LDH to develop simple, battery-free medical devices capable of safely supplying these gases," Iyi recalled.

H_2S patches: simple dermal application will produce hot-spring-like effects

Ishihara and Iyi first developed materials that release H_2S. They synthesized LDH with interlayer spaces containing chloride ions (Cl^-) as the starting material of H_2S-releasing LDH. This material is easy to synthesize and has a high anion exchangeability. When placed in a sodium hydrosulfide (NaHS) solution, the Cl^- ions in the interlayer of LDH are replaced with hydrosulfide ions (HS^-). Subsequent exposure to the air causes HS^- in LDH to react with carbonate ions (CO_3^{2-}) produced by a chemical reaction between atmospheric CO_2 and water, finally forming H_2S. Namely, HS^- serves as a precursor to H_2S gas.

The challenge Ishihara and Iyi faced was regulating the rate of the chemical reactions that lead to a slow release of H_2S. They attempted to control the rate at which reactants migrate within of the interlayer space by adjusting the size of the gaps between the layers. They accomplished this by changing the ratio of Mg and Al, the two LDH components. When the Mg-to-Al ratio was 2:1, rather than 3:1, the interlayer space was narrower, achieving a slower H_2S release.

"We eventually processed powdery LDH into a patch form," Ishihara said. "By placing the powder between two filters, making it easier to handle (photo at upper left on p. 12). The patch prototype is stored in sealed bags and activated by simply exposing it to the air, triggering a gradual H_2S release at low concentrations. It can be used safely and easily, like a disposable hand warmer."

Ishihara and Iyi stored the patches in a sealed bag at room temperature for more than six months and found that they were still able to release H_2S at the rate and concentration as designed.

Portable, battery-free NO inhaler: a revolutionary way to treat respiratory distress

Ishihara and Iyi have also developed an NO releasing material. Ishihara explained the significance of this effort.

"In utero, babies naturally maintain a high pulmonary blood pressure that spontaneously lowers at birth. However, this fails to occur in about 0.2% of newborns, causing them to develop severe respiratory problems. Infants with this condition urgently need to have their pulmonary blood vessels dilated to lower their blood pressure. Maternity wards equipped with artificial respirators capable of administering NO to babies are limited because the equipment is large and expensive. In the United States, administration of NO is more expensive than any other drug administered to newborns."

Ishihara and Iyi aimed to synthesize a NO-releasing LDH that would be more accessible to patients, but they encountered a problem: no anion could be found that could serve as a direct precursor to NO gas. Unlike acidic H_2S gas—which can be produced by association of HS^- ion and hydrogen ions (H^+)—neutral NO gas cannot be produced in the same straightforward manner, requiring a creative approach.

They subsequently focused on nitrite ions (NO_2^-). NO_2^- would react with atmospheric CO_2 to produce nitrous acid (HNO_2). They anticipated the thus produced unstable HNO_2 to self-decompose into NO.

Ishihara and Iyi actually synthesized LDH with interlayer spaces containing NO_2^- and exposed it to the air. As expected, the material released NO. They encountered another issue, however.

"The NO gas produced also contained toxic NO_2," Ishihara said. "We therefore filtered out acidic NO_2 gas by allowing it to pass through basic solid, $Mg(OH)_2$, thereby obtaining non-contaminated NO gas."

This success led to the development of a portable, battery-free NO inhaler prototype (photo at upper right on p. 12). This device is equipped with a manual hand pump which sends air into a series of three columns filled with a humidifying material, NO^-releasing clay and a NO_2 removing agent, respectively. The NO produced is then delivered to a patient via an artificial respirator.

"This device is expected to be effective in treating patients with severe respiratory conditions even in challenging situations, such as during power outages, during ground and air ambulance transportation and in remote areas and developing countries," Iyi said.

Ishihara and Iyi hope to put these technologies into practical use in collaboration with medical experts. They also plan to pursue further medical applications for LDH clay minerals by processing them into technologies capable of releasing CO and other unexplored physiologically beneficial gases.

(by Kumi Yamada)

[References]
*1 Ishihara & Iyi, Nat. Commun. 2020, 11, 453.
*2 Ishihara & Iyi et al., J. Am. Chem. Soc. 2013, 135, 18040.

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Ide is operating a hydrothermal synthesis oven used to synthesize various clay minerals. Silica gels, other raw materials and water are added to a sealed container, and the mixture is heated to approximately 150°C while being pressurized. Synthesis takes several hours to several days at a constant temperature.

Research 3

Cost-efficient synthesis of chemical product raw materials: Synergic combination of a clay mineral and a photocatalyst

The organic compounds benzoic acid and phenol are important raw materials for medical and plastic products. They are currently synthesized at high temperature under high pressure, requiring huge amounts of energy. Yusuke Ide has succeeded in developing techniques capable of significantly reducing the amount of energy needed to synthesize these compounds.

Clay minerals retrieve photocatalyst-oxidized compounds

Organic compounds are indispensable ingredients in various chemical products. For example, benzoic acid has been used as a food preservative, fungicide and mildew-proofing agent while phenol is a raw material in plastics.

Both benzoic acid and phenol need to be synthesized at high temperature under high pressure, requiring enormous amounts of energy. Global R&D efforts are underway to develop alternative, more energy-efficient methods of synthesizing these compounds using photocatalysts. Photocatalysts are materials capable of oxidizing (or reducing) compounds when activated by sunlight, fluorescent light or other light sources.

Benzoic acid can be prepared using titanium dioxide (TiO_2) as a photocatalyst. TiO_2 is capable of oxidizing toluene dissolved in an organic solvent into benzoic acid. Despite it proven efficiency, this photocatalyst has not been used for benzoic acid synthesis because the synthesized benzoic acid immediately decomposes into CO_2 and other compounds. Moreover, benzoic acid and intermediate compounds formed during its decomposition are deposited on the surface of TiO_2, interfering with its function. As a consequence, the use of TiO_2 can yield only small amounts of benzoic acid. Ide has been researching the combined use of photocatalysts with clay minerals to quickly retrieve synthesized compounds before they decompose.

Magadiite: a mysterious clay mineral

Ide focused on magadiite, a type of clay mineral. Magadiite is a layered compound in which each layer is composed of two-dimensionally extended silicon-oxygen tetrahedrons. Sodium ions (Na^+) are often incorporated into the spaces between the layers. Because magadiite has the ability to adsorb a wide variety of organic compounds and is relatively easy to synthesize, it may potentially be used as an effective adsorbent for many different purposes. Ide surmised that adding magadiite to a solvent containing toluene (a benzoic acid raw material) and TiO_2 would allow the magadiite to immediately adsorb benzoic acid as soon as it is synthesized before it decomposes or is deposited on and thereby disables the photocatalyst.

In its natural state, magadiite is almost completely incapable of adsorbing benzoic acid, but it can acquire moderate adsorption capabilities after being treated with acid to remove Na^+. The treated magadiite then needs to be chemically modified in order to further enhance its ability to adsorb benzoic acid. However, this proved difficult to accomplish as little was known about magadiite's crystal structure. Although x-ray techniques are commonly used to analyze crystal structures, they can only be used to analyze large crystals, and are therefore incompatible with magadiite, a powder composed of tiny crystals. Moreover, electron microscopic analysis was not possible because even weak electron beams would readily destroy magadiite's crystal structure.

To deal with these issues, Ide consulted with Satoshi Tominaka, an expert on so-called X-ray PDF (pair distribution function) analysis who was a colleague of the same group at the time. Ide asked Tominaka to conduct a precision analysis of magadiite. X-ray PDF measurements can be used to determine the local structures of tiny crystals, which can then be used to estimate crystal structures.

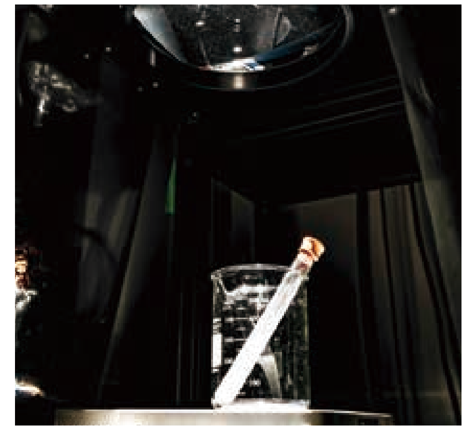
Tominaga's analysis revealed for the first time that magadiite layers contain many pores—called eight-membered ring channels—composed of eight oxygen atoms and eight silicon atoms alternating with each other (Figure).

"It had previously been assumed that benzoic acid adsorption in magadiite from which Na^+ has been removed occurs in the interlayer spaces," Ide said. "Acid treatment presumably removed the Na^+ and modified the layers' surface structures, thereby strengthening their adsorptive interactions with benzoic acid. However, the acid treatment was found to have an additional effect: it removes Na^+ and water molecules from the eight-membered ring channels, creating more space in them. This action presumably made the channels more conducive to incorporating benzoic acid than the narrow interlayer spaces. Based on this assumption, we investigated ways of completely removing Na^+ from magadiite while preserving its structural integrity and began searching for organic solvents that may potentially enhance the adsorption capabilities of magadiite."

Producing benzoic acid from toluene

After an extensive search, Ide found acetonitrile to be a promising organic solvent. He added acid-treated magadiite, toluene (a benzoic acid raw material) and TiO_2 to acetonitrile, which was then irradiated with simulated sunlight to activate the TiO_2 (photo at right). As a result, magadiite adsorbed benzoic acid as soon as it was synthesized, achieving a recovery rate greater than 20%.

"As intended, the amounts of benzoic acid incorporated into magadiite's eight-membered ring channels increased," Ide said. "I believe that the flexible frameworks of the eight-membered ring channels, with their broad oval cross-sections, were the key to this success. We are continuing our analysis in this area. Compounds with eight-membered ring channels are actually not uncommon; zeolite is a well-known example. However, the channels in zeolite have rigid frameworks with circular cross-sections narrower than the molecules of aromatic compounds, including benzoic acid, making it impossible for the channels to adsorb these compounds. The organic solvent acetonitrile is seemingly able to widen magadiite's flexible eight-membered ring channel frameworks, creating sufficient spaces to accommodate benzoic acid molecules. This is our current explanation."



Measuring the proportion of benzoic acid retrieved by magadiite. A test tube containing acid-treated magadiite, toluene, TiO_2 and acetonitrile is irradiated with simulated sunlight.

Producing phenol from benzene

In addition to the accomplishment above, Ide has succeeded in efficiently isolating and retrieving phenol using magadiite. Similar to benzoic acid, phenol is currently synthesized at high temperature under high pressure, although its photocatalytic synthesis is considered feasible. Benzene can be oxidatively broken down into CO_2 and other compounds using TiO_2. Phenol is formed as an intermediate product during this oxidation process.

Ide added acid-treated magadiite to an aqueous solution containing TiO_2 and benzene and then irradiated the mixture with simulated sunlight. Consequently, phenol was adsorbed by the magadiite as it was formed. The phenol recovery rate was approximately 80%, dramatically greater than the approximately 3% recovery rate achieved through the conventional high temperature, high pressure method.

"In contrast to the location of benzoic acid adsorption, phenol is probably adsorbed in the interlayer spaces of magadiite. In this project, we used water as a solvent, which was found to widen interlayer spaces. Adsorption spaces of magadiite can be altered depending on the types of solvents used. Magadiite is still a mysterious material whose versatility has yet to be fully understood. It is easy to synthesize and has a flexible framework despite the fact that it is an inorganic material. I hope to widen the applicability of this unique material beyond synthesis of organic compounds," said Ide with enthusiasm.

(by Kumi Yamada)

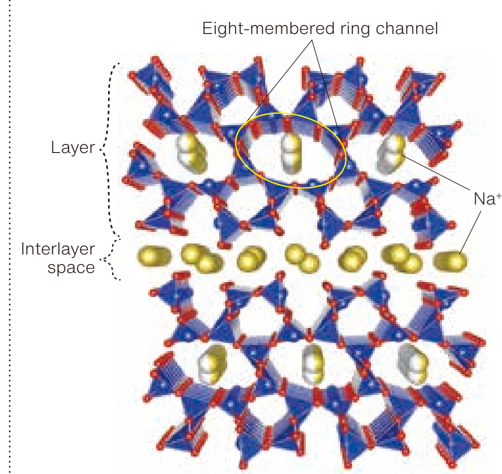


Figure. Basic magadiite structure

NIMS NEWS

NIMS sets a new Guinness World Record for the longest-running material creep test

NIMS carried out a creep test for 14,868 days from June 19, 1969 to March 14, 2011, setting a new Guinness World Record for the longest continuous testing.

The previous world record in this category had been held by Germany's Siemens AG, which conducted creep tests for 356,463 hours ending in 2000. NIMS has officially broken this record by collecting creep deformation data for 356,838 hours.

NIMS will continue full operation of its 500 creep testing machines for materials research and testing to ensure that high-temperature structural components used in power plants and other facilities will perform adequately and reliably.

Outline of the record-breaking NIMS creep test

Material tested	Carbon steel
Temperature	400°C
Applied stress	294 MPa
Test duration	356,838 hours
Deformation amount	5.6%

What is a creep test?

A creep test is designed to measure the time it takes for metal materials to undergo creep deformation or rupture by heating test pieces to a high temperate and applying a constant load to them. These constant stresses cause metal materials to experience slow plastic deformation (i.e., a creep process). Creep damage is a major concern in metal materials used in large, high-temperature equipment, such as boilers and turbines in thermal power plants and pressure vessels in petrochemical plants.

Array of creep testing machines at the NIMS Sengen Site facility

NIMS scientist chosen as a Mission Innovation Champion

Yoshiki Takagiwa (Independent Scientist at the NIMS Center for Green Research on Energy and Environmental Materials) has been selected as the 2020 Japanese winner by the 2nd cohort of Mission Innovation Champions Program, an international initiative to recognize exceptional individuals contributing to clean energy research and development.

This program honors one researcher or innovator who has made outstanding contributions to promoting the use of clean energy from each participating country. This year's winners have been invited to meet with national government ministers, business leaders and distinguished researchers advocating clean energy use at the Mission Innovation Ministerial Meeting.

Takagiwa was recognized for his joint research project with Aisin Seiki Co., Ltd. and Ibaraki University entitled "Autonomous Power Supply for IoT Devices Using Thermoelectric Power Generation" funded by the NEDO Advanced Research Program for Energy and Environmental Technologies.

Takagiwa's research: **https://www.nims.go.jp/eng/news/press/2019/08/201908210.html**
The Mission Innovation Champions Program: **https://www.michampions.net/**

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on the cover : a clay filter capable of removing only the pigment

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