



Fundamental and applied research on clay minerals: From climate and environment to nanotechnology

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ARTICLE INFO

Article history:

Received 11 January 2013

Accepted 21 February 2013

Keywords:

Clay minerals
Layered structure
Functionalization
Catalyst
Adsorbent
Biomaterial

ABSTRACT

This brief overview comments on recent trends in scientific research and development of clay minerals and was stimulated by the compilation of papers for this special issue to pay tribute to the 34th International Geological Congress held in 2012. The essentially geological context of the conference was a reminder that increased understanding of the genesis and evolution of clays and clay minerals provides insights that have applications in mining, environmental management, paleoclimate, Earth and extraterrestrial sciences. The requirement for multidisciplinary knowledge, including geology, mineralogy, chemistry and materials science, and modern instrumentation and analysis of clay minerals, is essential to a full understanding of the genesis, role and potential new uses for these fine-grained industrial minerals. Latest studies are typically focused on processing and modifying of clay minerals as adsorbents, catalysts, and biomaterials. The emphasis for future work is on advanced clay-based nanomaterials for use in new approaches to sustainable energy, green environment, and human health.

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1. Introduction

Clays and clay minerals are ubiquitous at or near the surface of the Earth. With advancements in X-ray diffraction, spectroscopy, electron microscopy and other instrumental analytic techniques, our understanding of the genesis, structure and chemistry of clay minerals has improved significantly, especially over the past few decades. Simultaneously, the use of clay minerals has expanded. Advances in scientific knowledge and technology on clay minerals have made substantial contribution to human society through the many uses of clay-based products from traditional ceramics to modern functional nanocomposites. Recently, the attention of clay scientists has been focused particularly on the properties of clay minerals as natural nano-sized particles with uses in adsorption, catalysis and biology, in line with the rapid growth in nanotechnology research on synthetic materials. Knowledge of clay minerals is essential to effective management of the environment and is also proving to be a useful tool for interpreting paleoclimates on Earth and possibly even the early state and evolution of extraterrestrial worlds (Pearson et al., 2002).

Aspects of the breadth of current research on clay minerals are reflected in the collection of papers in this special issue.

The terms clays and clay minerals are often used interchangeably yet have slightly different meanings, particularly when used across scientific disciplines (Bergaya et al., 2006). For example, “clay” is used by engineering geologists and sedimentologists to describe geological materials <4 µm in size, by soil scientists to denote the soil fraction containing particles <2 µm size, and colloidal scientists <1 µm. Mineralogists define ‘clay’ as naturally occurring material composed of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Guggenheim and Martin, 1995). Clays may therefore be mixtures of fine-grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. The term ‘clay minerals’ however is not restricted by particle size but refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing (Guggenheim and Martin, 1995). Phyllosilicates are a large family of minerals that commonly show layered structures and include kaolin, smectite, chlorite, mica and serpentine groups.

Based on their layered structure, clay minerals can be categorized as types 1:1 or 2:1. Each layer forming a clay mineral particle is fundamentally built of one or two tetrahedral silicate (Si–O) sheets and one octahedral metal oxide/hydroxide (M–O or M–OH) sheet. A 1:1-type clay mineral consists of one tetrahedral sheet and one octahedral sheet. Examples of 1:1-type clay are kaolinite, halloysite and serpentine. A 2:1-type clay mineral is composed of an octahedral

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sheet sandwiched between two tetrahedral silicate (Si–O) sheets, and examples of 2:1-type clay minerals include talc, vermiculite, montmorillonite, saponite, and sepiolite. Clay minerals are hydrous aluminum or magnesium phyllosilicates, often with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations present either in the interlayer space or in the lattice framework by isomorphous substitution. Variations consisting of mixed layers of different clay minerals also exist and are usually referred to as interstratified clay minerals. Moreover, the ordering of the assemblage of layer-to-layer can be random or regular. Examples of mixed layer clay minerals are corrensite with mixed chlorite–smectite layers and rectorite with mixed illite–smectite layers.

Human society has been using clays and clay minerals since the Stone Age, due primarily to the fact that clay minerals are common at the Earth's surface and are widely utilized for agriculture (soils), ceramics, and building materials, with a very long history. Our increased understanding of the mineralogy, structure and properties of clay minerals has been accompanied by rapid advances in processing and modification of clay minerals for many new commercial uses. The wide variety of applications include oil refining and absorbents, iron-ore pelletizing, animal feeds, pharmaceuticals, drilling fluids, waste water treatment, fillers in paint and plastic, and coating paper (for a detailed listing of uses see [Konta, 1995](#)).

As shown by papers in this special issue, the scientific study and the utilization of clay minerals continue to expand and develop new directions. Fundamental studies continue into the properties of clay minerals and the geological processes by which they are formed. Understanding how and where various clay minerals are formed provides industry and land-planning agencies with the information necessary to locate and plan future mineral extraction that takes account of social and environmental impacts. This knowledge also has broader application in, for example, providing new insights into the extent and impact of past climates ([Morton, 2005](#)) and the processes in organic–inorganic interactions leading to formation and modification of fossil fuels ([Wu et al., 2012](#)). For furthering the application of clay minerals, investigations are increasingly focused on how to make use of the chemical and structural characteristics of clay minerals (e.g. [Brigatta and Mottana, 2011](#)). Clay minerals have a wide range of particle size from tens of angstroms to millimeters. Many clay minerals form sheet-like particles or platelets. In particular, the thickness of each clay mineral layer is around one nanometer, for

example 0.96 nm thickness for montmorillonite. As natural nano-scale particles with a layered structure and interlayer space, clay minerals have the potential to play a significant role in manufacturing and environmental industries, through new processes and approaches arising from the present surge in nanotechnology research.

2. Clay mineral formation and implications for their use

2.1. Genesis

While clays are widespread and extensively exploited by industry, the trend in demand for clay minerals with specific chemical properties or physical characteristics for specialized uses is expected to continue. Greater understanding of the geological and environmental factors that control formation and growth of clay minerals will aid exploration for deposits to supply specialized markets and will assist also with planning for extraction and beneficiation. Clays are formed across a range of geological environments and throughout geological time ([Fig. 1](#)). They are commonly present as a major component of soil, continental and marine sediments, weathered rock and sediment, altered volcanic deposits, hydrothermal alteration systems, and fault gouge. Clay minerals often form by alteration of pre-existing minerals, including other clay minerals, in rocks or sediments which are in contact with water, air, or steam, or they can crystallize directly from solution ([Galan, 2006](#)).

Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits, or deposits that can be readily beneficiated, that are of economic interest. Clay minerals are typical weathering products of common silicate minerals including feldspar, mica, amphibole and olivine, which are altered to kaolin, smectite, illite or serpentine, depending on the environmental conditions. Similarly, sedimentary deposits containing quartz, feldspar, mica and transported clay minerals, or volcanic glass, carbonate and poorly crystalline iron oxide will be transformed *in situ* by diagenetic processes into more stable minerals, particularly clay minerals, mostly through dissolution and recrystallization. Also, erosion of earlier-formed continental and marine rocks or regolith containing abundant clay minerals can result in selective transport and deposition of clays to give sedimentary deposits suitable for mining. In this issue, [Li et al. \(2013\)](#) describe unusual deposits of black talc in sedimentary rocks from the late Neoproterozoic Dengying

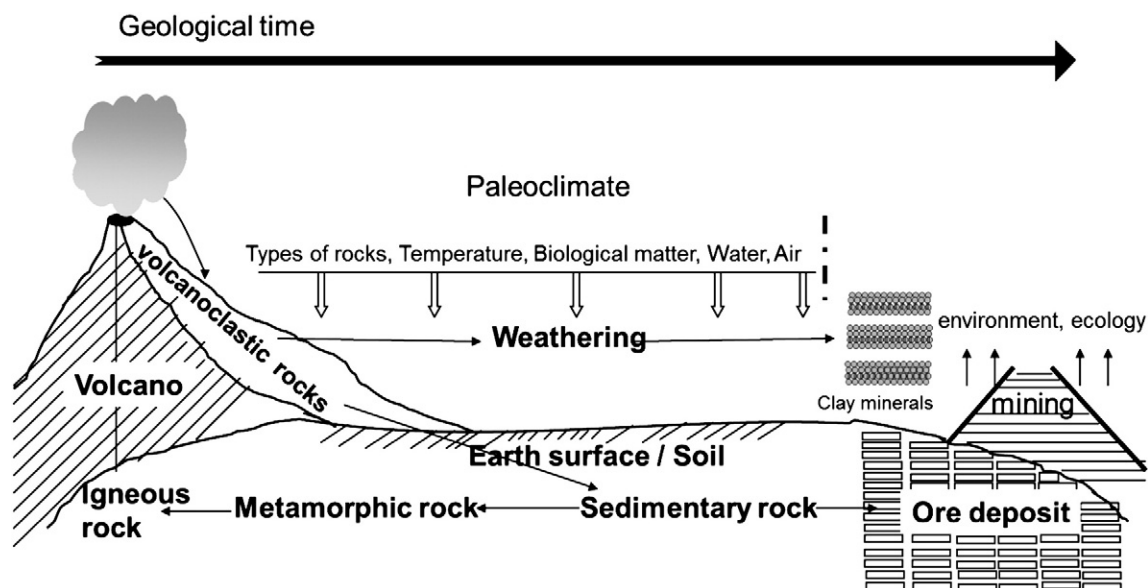


Fig. 1. Schematic depicting the inter-relationship of clay mineral formation with geology, climate, environment and ecology.

Formation, in Guangfeng County, Jiangxi Province, China. The resource was estimated to exceed 500 million tons. The mineralogical and geochemical characteristics of the deposits indicated that they formed primarily as impure sedimentary oolites, of probable carbonate and clay minerals, that were diagenetically altered to fine-grained talc (30–70%), with variable content of dolomite, quartz, and magnesite. An investigation of hydroxy-interlayered vermiculite (HIV) in Jiujiang (China) red earth sediments by Yin et al. (2013) concluded that the HIV clays in Jiujiang soils resulted from the weathering of illite. The soils were derived from loess deposits of kaolinite and illite, and the irregularly interstratified illite-HIV and HIV formed in response to climatic conditions of frequent wetting and drying.

The geochemical environment of clay formation may exert a strong control on the crystallinity and degree of order, thermal stability, morphology and surface characteristics of clay minerals (Fig. 1). For example, Hu and Yang (2013) reported that for soft kaolinites from different sources in China, the temperature of maximum dehydroxylation increased linearly with increasing crystallinity. Variation in crystallinity was also associated with morphological differences that were reflected in particle size distribution and surface area measurements. Keeling et al. (2012) described halloysite from different geological settings where the environment of formation appeared to be a significant factor controlling particle morphology and particle size distribution. This work was extended by Pasbakhsh et al. (2013) in which the properties of six halloysites from various deposits and geological settings were compared. Significant differences were found in physical properties including surface area, tube dimensions and pore size distribution that will affect how these clays perform in industrial applications, and also in the environment.

2.2. Implications in paleoclimate and extraterrestrial studies

While clay research is essential to development and mining of clay resources and can assist with exploration for metallic minerals and fossil fuels, studies on the mineralogy and formation of clay minerals can also provide useful information for interpreting paleoclimate (Fig. 1), and extraterrestrial environments.

For example, in this issue, Wang et al. (2013) investigated clay mineralogy throughout a sequence of early Cenozoic sedimentary rocks in the south-western portion of the Tarim basin, China. Change in the proportion of clay minerals and clay indices, as well as the proportion of non-clay minerals, gypsum, and morphology of the clays were used to correlate the stratigraphic interval when paleoclimate in the Tarim basin underwent a dramatic change from warm and humid to cold and dry. The interval occurred in sediments of late Eocene to early Oligocene age. This period of cooling and aridification in the Asian interior followed retreat of the Neo-Tethys Sea leading to reduced moisture supply to continental interiors, but was not a localized event. Rather the timing was consistent with changes observed in the geological record at various locations across the Earth and provides additional evidence of a more widespread response to the onset of global climatic cooling during the Eocene–Oligocene Transition. Wang and Yang (2013), examined the detrital clay mineralogy of sediments from two cores in the Changjiang delta to determine the origin of the clays and to test whether variation in monsoon climate during the Holocene could be reconstructed from the composite sedimentary record of this large catchment. The peak content for smectite occurring at ca. 13–11.5 ka was ascribed to the increased input of clays weathered from the upper Changjiang catchment under the impact of an enhanced Indian Summer Monsoon. Despite different sediment sources across the catchment and the complexities of interpreting clay origins in marginal marine sediments, regular variations in crystallographic indices and chemical index of illite were measured and shown to correspond with isotopic data from cave

stalagmites used to track the evolution of the Asian Summer Monsoon. The authors concluded that clay mineral indices were sufficiently sensitive to climate-induced chemical weathering that sediments from estuarine and deltaic deposits of large catchments were useful in reconstructing climate changes affecting the catchment.

A recent review by Ehlmann et al. (2011) of the significance of widespread clay minerals associated with 4.1–3.7 billion year old Noachian terrains on Mars highlighted the possibilities of using clay mineralogy to refine our understanding of the evolution of environments on extraterrestrial bodies. The presence of clays requires interaction between water and rock, which is not observed for current Martian atmospheric conditions where ice typically sublimates directly to the water-undersaturated atmosphere. The distribution and composition of clay minerals and the timing of clay formation were indicative of water interaction with rock over 1 billion years during the Noachian and Hesperian periods between 4.1 and 3.1 billion years ago. Widespread low-temperature hydrothermal groundwater circulation was interpreted by the authors as the most likely mechanism for the extensive formation of Fe,Mg-clays in Noachian rocks. This was followed by more restricted fluvial and lacustrine deposits of Fe,Mg clays, Al-clays and salts appearing in the late Noachian to early Hesperian period. Evidence of early aqueous activity during the formation of Earth has been largely obliterated. What is preserved in the Martian landscape may provide important insights about processes leading to potentially habitable environments capable of initiating and sustaining the development of organisms during the formation and evolution of planets.

3. Engineering clay minerals into functional materials

3.1. Properties for present uses and engineering clay minerals into functional materials

Though the traditional uses of clay minerals have seen continual increase in the past decade of the 21st century, engineering of clay minerals into functional materials has received particular attention and interest of many clay scientists. The inherent features of clay minerals that make them attractive for use in a wide variety of applications include: (a) very large surface area that arises from the layered structure, along with swellability and the potential for delamination; (b) small size of the particles in the range of micro- to nano-scale; and (c) naturally-charged particles leading to relatively strong electrostatic interactions. Based on their physical properties, clay minerals are often applied as fillers and gellants. For example, clay minerals are used by the paint industry to promote even dispersion of pigment and to reduce settling. A mixture of clay with a little water results in a mud that can be shaped and dried to form a relatively rigid solid body. This property is exploited by potters and the ceramics industry to produce plates, cups, bowls, pipes, and so on. The swelling and drying properties of montmorillonitic clays make them ideal for such diverse uses as drilling mud, foundry-sand bonding agent, and binder for pelletizing iron ore. Environmental industries use the properties of swelling and dispersion to produce homogeneous liners from montmorillonitic clays for containment of waste.

The inherent properties of clay minerals also make them chemically active and adsorptive, thereby leading to a variety of uses as absorbent and catalyst products. In clay minerals, the active sites may arise from (1) “broken edge” sites and exposed surface aluminol and silanol groups, (2) isomorphic substitutions, (3) exchangeable cations, (4) hydrophobic silanol surfaces, (5) hydration shell of exchangeable cations, and (6) hydrophobic sites on adsorbed organic molecules (Fig. 2). These peculiar chemical features combined with the nanometer scale layering and interlayer spacing, allows for a variety of approaches to engineer clay minerals into functional materials with potential applications in advanced technologies, in particular, nanotechnology.

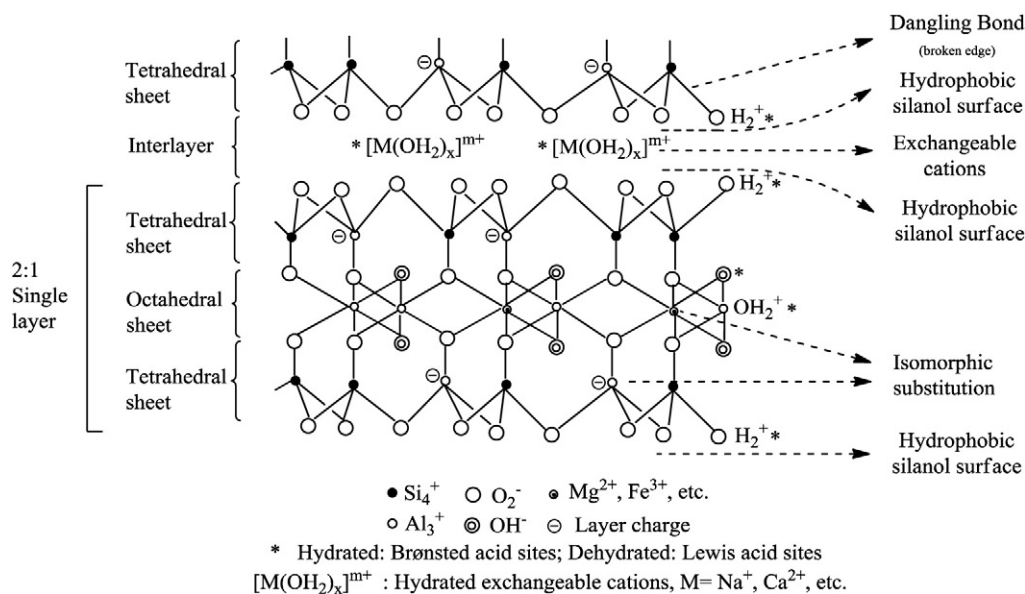


Fig. 2. Schematic drawing of 2:1-type clay mineral showing active sites.

3.2. Adsorptive composites

Most clay minerals have peculiar adsorption arising from their layered structure, charged layers and active edges. Layered structure provides interlayer space to host guest molecules and ions. Charged layers and “broken edge” sites attract species with opposite charges through van der Waals force. Such features allow clay minerals to be used as adsorbents for the removal of heavy metal ions from water. Clays can also be effective adsorbents/absorbents of oily pollutants and animal waste, and are used as carriers for the controlled release of pesticides and fertilizers. Montmorillonite is also used as a liner to restrict the leakage of radioactive elements that may arise from activities of the nuclear power industry. The charged layers and “broken edge” sites can be enhanced by chemical reactions. For many decades, acid-activated montmorillonitic clays have been used commercially for bleaching liquids (vegetable oil, grease, and wine, etc.).

As indicated above, the guest species adsorbed by clays is not limited to inorganic ions. Various interactions between organic molecules or ions and clay minerals have been observed over a long period. The studies of these interactions have not only improved our understanding of the formation and evolution of organic matter in soil, but have led also to practical products such as organoclays. Adsorption by clay minerals in soils is an important factor affecting the fate and transport of organic compounds in the environment. In this issue, Wu et al. (2013) describe the adsorption of nalidixic acid (NA), a quinolone antibiotic, on montmorillonite and kaolinite under different pH and initial concentration conditions. At pH conditions favoring NA^0 in solution, electrostatic interaction and the formation of a coordination bond between the keto oxygen in the pyridine ring or the C=N group in the pyridine ring and the exchangeable cation in the interlayer space was identified as a significant factor in the high level of NA adsorption on montmorillonite.

The capacity for adsorption, particularly of organics, by clay minerals in the natural state cannot, in many cases, meet the requirements of industry. To increase their absorption capacity or specificity, clay minerals often need to be modified in chemical composition and structure by organo-functionalization through intercalation and surface grafting of organic species. In this manner, organo-bentonite was produced, on comparatively large scale for more than two decades, for commercial use in paints (Cinku et al., 2000). Another

approach to enhance the adsorption capacity of clay minerals is to build porosity within them. This method usually involves 3D structural composites (e.g. pillared clay) or more complex hierarchical structures. These strategies and the resulting functional materials are illustrated by a few studies in this issue, as discussed below.

Fatimah and Huda (2012) report the intercalation of cetyl trimethylammonium ions (CTMA) into montmorillonite (from an Indonesia deposit) which then became adsorptive for toluene, a common pollutant in waterways. Using dimethyl sulphoxide as the solvent, cetyl trimethylammonium ions were also introduced into the interlayer of sericite (Liang et al., 2013). While intercalation offers a means of modifying electrostatic attraction, surface grafting can give rise to strong covalent bonds between host and guest. For example, Peng et al. (2013) used chitosan-modified palygorskite (CTS-modified PA) prepared by surface grafting to develop an effective adsorbent for the removal of reactive dye. The adsorption capacities of CTS-modified PA (71.3 mg g^{-1}) were comparable to equivalent weight of pure chitosan but required less than half the amount of the more expensive chitosan.

Through the judicious supermolecular assembly of clay minerals and their derived organo-functionalized solids, multifunctional hierarchical materials can be obtained. In this regard, Zhou's AMSC group (Zhou et al., 2012), recently developed a functional paper-like composite of biopolymer cellulose and clay minerals for the removal of chemical pollutants in waterways. The material is sustainable and environmentally benign and can be used in the form of paper scrolls, which can be deployed and recovered quickly and cleanly for subsequent disposal.

3.3. Catalysts

In the development of clay minerals as catalysts, their chemical functions generally need to be intensified to improve efficiency or effectiveness. Zhou (2011) summarized possible ways of making ‘catalytically active sites’ within and onto the matrix of clay minerals as follows. (1) the framework of clay minerals contains active species which can be made accessible; (2) the ions within the interlayer space are judiciously exchanged with active components for catalysis purpose; (3) functional nanoparticles (NPs) or clusters are forged onto or within the clay nanostructure; and (4) clay minerals or their derivatives are used as catalyst supports. The various approaches

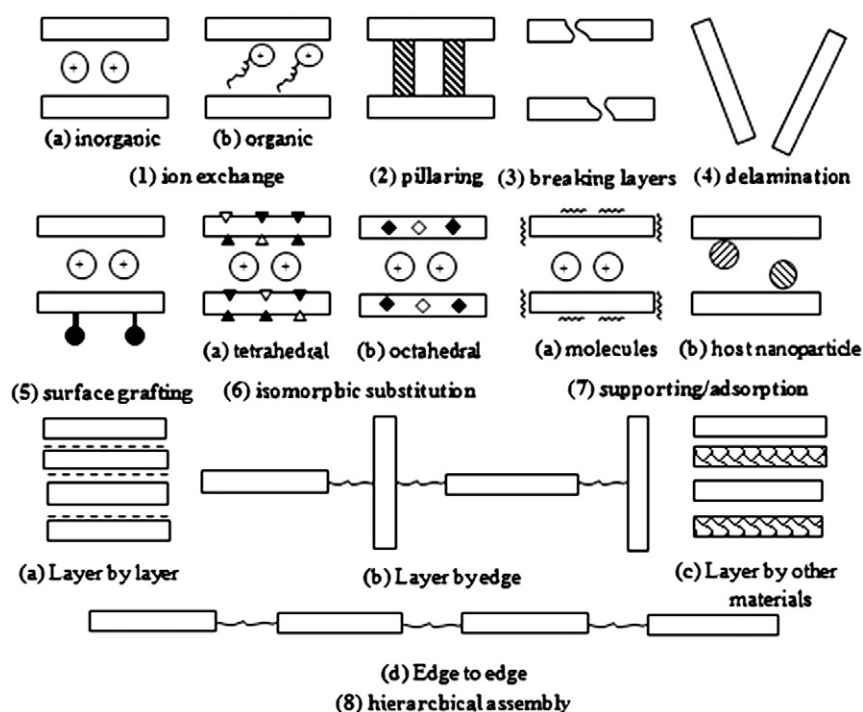


Fig. 3. Summary of possible approaches to making new functional material from clay minerals.

are summarized in Fig. 3 and are today often used for the preparation of clay-based catalysts, as illustrated by several papers in this issue.

In facing the challenges of achieving renewable fuels and chemicals, the engineering of clay minerals into catalysts for the conversion of biomaterials becomes increasingly attractive. For instance, in this issue, Zhou's research group report on the catalytic dehydration of glycerol to acrolein over sulfuric acid-activated montmorillonite catalysts (Zhao et al., 2013) and the hydrolysis of cellulose to reducing sugar in water solution over a series of acid-activated montmorillonite catalysts (Tong et al., 2013). Both glycerol and cellulose are abundant, bioavailable chemical feedstocks with sustainability. The choice of acids and the conditions of acidification for the treatment of montmorillonite have an important influence. However, to achieve highly active and selective catalysts, the processes of acid-activation, or ion exchange reaction of clay minerals need to be finely tuned. In many cases, clay minerals are natural acidic catalysts. Yet they can be made into basic catalysts through supporting techniques. For instance, Kusuma et al. (2013) used a natural occurring zeolite (from a deposit at Pacitan Indonesia) as the catalyst support to produce KOH/zeolite. The resulting catalyst showed good catalytic performances in the transesterification of palm oil to methyl esters (biodiesel). The catalyst made from the impregnation of zeolite with KOH concentration of 100 g/100 mL gave maximum yield of biodiesel. Zeolites are framework porous aluminosilicates and not members of the clay mineral family but they do have many similarities in the ways they can be modified to make high-performance catalysts.

The ability to exchange ions, related to the charged surface of clay minerals is an important property of the clay mineral. Various ions can be attracted to the surface of a clay particle or taken up within the structure of these minerals. The ion exchange reaction with other active metal ions and the addition of promoters have been employed to make catalysts from clay minerals to give enhanced performance. For example, Jha et al. (2013) describe solid acid catalysts that were prepared by exchanging metal cations such as Zn^{2+} , Fe^{3+} and Al^{3+} in montmorillonite clay for the hydroxyalkylation of p-cresol with formaldehyde to 2,2'-methylenebis (4-methyl phenol)

(DAM). The results indicated that the activity of the catalysts was related to the increase in acidity of parent montmorillonite after the exchange of cations, in the order of $\text{Zn}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}$. The selectivity was influenced by the type of exchanged cation.

A current trend is to use clay minerals to host nanoparticles. This strategy is a useful way to construct a stable platform for active nanocatalysts. In this issue, three studies provide examples of making this class of catalyst. Huo and Yang (2013) describe the preparation of silicate nanofibers (palygorskite, PAL) coated with CuO nanoparticles and subsequently modified with PVP-Pd solution. Both the CuO/PAL and Pd-CuO/PAL nanocomposites exhibited higher photocatalytic activities than pure CuO in the photodegradation of methyl orange under UV-light. The enhanced photocatalytic activity of CuO/PAL and Pd-CuO/PAL composites was ascribed to the surface adsorption and efficient electron-hole separation at the coupled interface. Also Liu et al. (2013) prepared Fe_3Ni_8 /palygorskite for catalytic cracking of benzene and Bineesh et al. (2013) reported the preparation of V_2O_5 supported on Al-pillared clay (V/Al-PILCs) for the catalytic oxidation of hydrogen sulfide. The nanoparticles are the active component essentially controlling the catalytic performance of these new materials and it has been shown that activity decreases with an increase in the size of the active component (ie. surface area is reduced). Adsorption onto the surface of clay minerals can result in more uniform dispersion of the active nanoparticles and reduce agglomeration. However other factors also come into play due to surface interactions between the clay support and the nanoparticle, so that it is not always straightforward to identify the exact cause of the enhanced catalytic performance of these new materials.

Significantly, the chemical modification and hybridization of clay minerals can be used to make the resultant materials electric, electronic and magnetic. For example, Xu et al. (2013) fabricated supercapacitors for electricity storage from transition metal-containing layered double hydroxides (LDHs). As-prepared LDHs showed a relatively high capacitance ($13\text{--}140 \text{ F g}^{-1}$) at the scanning rate of 1 mV s^{-1} and a current load of 20 mA g^{-1} using 6 M KOH as an electrolyte. Calcination of LDHs at 400°C (e.g. LDOs) enhanced the exposure of electrochemical active species, but can lead to a specific capacitance of $50\text{--}210 \text{ F g}^{-1}$.

Remarkably, the capacitance of both LDOs and LDHs remained stable after 100–500 cycles.

3.4. Biomaterials

The property of clay minerals that causes ions in solution to be fixed on clay surfaces or within internal sites applies to all types of ions, including organic biomolecules. In this context, more attention is being directed towards understanding the interaction between active biomolecules and clay minerals, particularly with regard to medical science and health. There is increasing interest in the use of clay minerals as agents on which drugs can be adsorbed and then delivered to target sites in the body in a manner which allows for controlled release of the drug. This has potential to be extended to the delivery of genes and vaccines. Similarly, the interaction of biomolecules and drugs with clay minerals can be used to assess the fate of pesticides and medicines in the environment and their effects on ecology. Through the interaction of fluorescent molecules and reversible ion exchange reactions, clay minerals can be developed as biomaterials for analytical tests. If the intercalated species in the interlayer of a clay mineral are elements responsive to magnetic resonance imaging (Ikeda et al., 2011), the resulting solids can be used as contrast media or contrast agents (Zhou, 2010). Montmorillonite has been considered as a catalyst for nucleotide dimer synthesis and even RNA formation, with implications for the potential role of clays in the origin of life on Earth (Joshi et al., 2012).

In environmental science, for example, Jiang et al. (2013) showed that the intercalation of ciprofloxacin (CIP) was accompanied by dehydration in rectorite. The uptake of CIP by rectorite was mainly via a cation exchange reaction between CIP and hydrated cations previously occupying the interlayer. The intercalated CIP was thermally more stable compared to crystalline CIP, suggesting that the presence of swelling clay minerals in soil and wastewater treatment systems may provide a place for contaminant accumulation and shelter that protect CIP from thermal degradation.

As a potential carrier for drug delivery, halloysite, the tubular form of kaolin, has comparatively large internal storage for nano-sized molecules. Pasbakhsh et al. (2013) characterized halloysites from various locations to compare internal pore volumes and surface areas. The results showed significant variation in the physical properties of tubular halloysite from different sources. Halloysites with low levels of impurities and regular, thin-walled tubes gave the highest pore volumes associated with the cylindrical cavity or lumen of the tube. The authors concluded that these physical aspects need to be considered in the selection of halloysite for particular uses and that tailoring the choice of clay to meet specific requirements should assist in optimizing the performance of new products.

4. Looking forward

The uses of clay minerals are based on their characteristics of chemical composition, electrical charge, layered structure, and size. In many cases, the investigations require the integration of multidisciplinary knowledge from geology, mineralogy, chemistry and materials science. Certainly more can be learned through a greater understanding of the genesis of clay minerals. The conditions of formation for specific clay minerals provide information useful for the discovery, mining and rehabilitation of clay resources but also provide information about the wider environmental factors operating at the time. This can assist with reconstructing past climates and the processes involved in the evolution of extraterrestrial bodies. In turn, this knowledge may lead to new approaches for clay mineral synthesis, and novel applications, including improved management of the ecology and environment. In particular, clay minerals offer real possibilities to contribute to new developments in the areas of sustainable

energy, biochemical process, and biomaterials. These developments will require the composition, micro- and nanostructure of clay minerals to be finely tuned and functionalized so as to yield selective catalytic activity, electro- and magnetic properties, and bioactivity. To these goals, further collaborative efforts should be encouraged and supported by scientists in the fields of clay geoscience, instrumentation and analysis of clay minerals, mineral extraction and processing, chemists and medical scientists.

Acknowledgements

Our thanks also go to Sa Xiao and Ling-Yun Wang for helping with drawing the Figures. CHZ wishes to acknowledge the Distinguished Young Scholar Grant from Zhejiang Provincial Natural Science Foundation of China (R4100436), and the Natural Scientific Foundation of Zhejiang Province (LQ12B03004), and the international cooperation project (2009C14G2020021/2010C14013) from the Science and Technology Department of Zhejiang Provincial Government for the efficient use of industrial minerals.

References

- Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), 2006. *Handbook of Clay Science: Developments in Clay Science*, vol. 1. Elsevier, Amsterdam.
- Bineesh, K.V., Kim, M.-I., Lee, G.-H., Selvaraj, M., Park, D.-W., 2013. Catalytic performance of vanadia-doped alumina-pillared clay for selective oxidation of H₂S. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.04.023>.
- Brigatta, M.F., Mottana, A. (Eds.), 2011. *Layered Mineral Structures and their Application in Advanced Technologies*. European Mineralogical Union and the Mineralogical Society of Great Britain & Ireland, London (370 pp.).
- Cinku, K., Ipekoglu, B., Bilge, Y., 2000. Production of rheological additives for solvent based paint from Turkish bentonite. *Developments in Mineral Processing* 13 (C5–16–C5–23).
- Ehlmann, B.L., Mustard, J.F., Murchie, S.L., Bibring, J.-P., Meunier, A., Fraeman, A.A., Langevin, Y., 2011. Subsurface water and clay mineral formation during the early history of Mars. *Nature* 479, 53–60.
- Fatimah, I., Huda, T., 2012. Preparation of cetyltrimethylammonium intercalated Indonesian montmorillonite for adsorption of toluene. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.05.002>.
- Galan, E., 2006. Chapter 14: Genesis of clay minerals. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), *Handbook of Clay Science, Developments in Clay Science*, vol. 1. Elsevier, Amsterdam, pp. 1129–1162.
- Guggenheim, S., Martin, R.T., 1995. Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and Clay Minerals* 43 (2), 255–256.
- Hu, P., Yang, H., 2013. Insight into the physicochemical aspects of kaolins with different morphologies. <http://dx.doi.org/10.1016/j.clay.2012.10.003>.
- Huo, C., Yang, H., 2013. Preparation and enhanced photocatalytic activity of Pd–CuO/palygorskite nanocomposites. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.07.001>.
- Ikeda, M., Yoshii, T., Matsui, T., Tanida, T., Komatsu, H., Hamachi, I., 2011. Montmorillonite-supramolecular hydrogel hybrid for fluorocolorimetric sensing of polyamines. *Journal of the American Chemical Society* 133 (6), 1670–1673.
- Jha, A., Garade, A.C., Shirai, M., Rode, C.V., 2013. Metal cations-exchanged montmorillonite clay as catalysts for hydroxyalkylation reaction. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.10.005>.
- Jiang, W.-T., Wang, C.-J., Li, Z., 2013. Intercalation of ciprofloxacin accompanied by dehydration in rectorite. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.07.009>.
- Joshi, P.C., Aldersley, M.F., Zagorevskii, D.V., Ferris, J.P., 2012. A nucleotide dimer synthesis without protecting groups using montmorillonite as catalyst. *Nucleosides, Nucleotides & Nucleic Acids* 31 (7), 536–566.
- Keeling, J.L., Pasbakhsh, P., Churchman, G.J., 2012. Halloysite from the Eucla Basin, South Australia – comparison of physical properties for potential new uses. In: Broekmans, M.A.T.M. (Ed.), *Proceedings of the 10th International Congress for Applied Mineralogy (ICAM)*. Springer, Berlin, Heidelberg, pp. 351–359.
- Konta, J., 1995. Clay and man: clay raw materials in the service of man. *Applied Clay Science* 10, 275–335.
- Kusuma, R.I., Hadinoto, J.P., Ayucitra, A., Soetaredjo, F.E., Ismadji, S., 2013. Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.04.021>.
- Li, C., Wang, R., Lu, X., Zhang, M., 2013. Mineralogical characteristics of unusual black talc ores in Guangfeng County, Jiangxi Province, southeastern China. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.12.004>.
- Liang, Y., Wang, Y., Ding, H., Liang, N., 2013. Intercalation and characterization of sericite by cetyltrimethylammonium bromide in dimethyl sulfoxide solvent. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2013.01.009>.
- Liu, H., Chen, T., Chang, D., Chen, D., He, H., Yuan, P., Xie, J., Frost, R.L., 2013. Characterization and catalytic performance of Fe₃Ni₂/palygorskite for catalytic cracking of benzene. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.04.005>.

- Morton, O., 2005. Major shifts in climate and life may rest on feats of clay. *Science* 26, 1320–1321.
- Pasbakhsh, P., Churchman, G.J., Keeling, J., 2013. Characterisation of properties of various halloysites relevant to their use as nanotubes and microfibre fillers. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.06.014>.
- Pearson, V.K., Sephton, M.A., Kearsley, A.T., Bland, P.A., Franchi, L.A., Gilmour, I., 2002. Clay mineral–organic matter relationships in the early solar system. *Meteoritics & Planetary Science* 37, 1829–1833.
- Peng, Y., Chen, D., Jia, J., Kong, Y., Wan, H., Yao, C., 2013. Chitosan-modified palygorskite: preparation, characterization and reactive dye removal. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.10.002>.
- Tong, D.S., Xi, X., Luo, X.P., Wu, L.M., Lin, C.X., Yu, W.H., Zhou, C.H., Zhong, Z.K., 2013. Catalytic hydrolysis of cellulose to reducing sugar over acid-activated montmorillonite catalysts. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.09.002>.
- Wang, C., Hong, H., Li, Z., Yin, K., Xie, J., Liang, G., Song, B., Song, E., Zhang, K., 2013. The Eocene–Oligocene climate transition in Tarim Basin, Northwest China: evidence from clay mineralogy. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.09.003>.
- Wang, Q., Yang, S., 2013. Clay mineralogy indicates the Holocene monsoon climate in the Changjiang (Yangtze River) Catchment, China. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.08.011>.
- Wu, Q., Li, Z., Hong, H., 2013. Adsorption of the quinolone antibiotic nalidixic acid onto montmorillonite and kaolinite. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.09.026>.
- Wu, L.M., Zhou, C.H., Keeling, J., Tong, D.S., Yu, W.H., 2012. Towards an understanding of the role of clay minerals in crude oil formation, migration and accumulation. *Earth-Science Reviews* 115 (4), 373–386.
- Xu, Z.P., Li, L., Cheng, C.-Y., Ding, R., Zhou, C.H., 2013. High capacitance electrode materials based on layered double hydroxides prepared by non-aqueous precipitation. <http://dx.doi.org/10.1016/j.clay.2012.06.015>.
- Yin, K., Hong, H., Churchman, G.J., Li, R., Li, Z., Wang, C., Han, W., 2013. Hydroxy-interlayered vermiculite genesis in Jiujiang late-Pleistocene red earth sediments and significance to climate. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.09.017>.
- Zhao, H., Zhou, C.H., Wu, L.M., Lou, J.Y., Li, N., Yang, H.M., Tong, D.S., Yu, W.H., 2013. Catalytic dehydration of glycerol to acrolein over sulfuric acid-activated montmorillonite catalysts. *Applied Clay Science*. <http://dx.doi.org/10.1016/j.clay.2012.09.011>.
- Zhou, C.H., 2010. Emerging trends and challenges in synthetic clay-based materials and layered double hydroxides. *Applied Clay Science* 48 (1–2), 1–4.
- Zhou, C.H., 2011. An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis. *Applied Clay Science* 53, 87–96.
- Zhou, C.H., Zhang, D., Tong, D.S., Wu, L.M., Yu, W.H., Ismadji, S., 2012. Paper-like composites of cellulose acetate–organo-montmorillonite for removal of hazardous anionic dye in water. *Chemical Engineering Journal* 209, 223–234.