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Review article

Current fundamental and applied research into clay minerals in China

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ABSTRACT

This paper briefly examines current fundamental and applied research into clay minerals in China. A collection of studies from Chinese clay scientists and as a special issue suggests that investigations into the genesis and mineralogy of clay minerals for geology and geochemistry, synthetic clay minerals, the modification of clay minerals for advanced materials, comprehensive and reutilization of clay minerals are important aspects of fundamental and applied clay science within China. Effort is being made to increase the understanding of the genesis and evolution of clay minerals and such knowledge is believed to have scientific implication for paleogeographical, paleoecological, and paleoclimatic conditions and to have applications in mining and processing clay minerals and related environmental and ecological management. Studies on the modification of clay minerals by Chinese clay scientists aim predominantly to make functional clay mineral-polymer nanocomposites, adsorbents, catalysts, and biomaterials. In China, increasingly strict management of natural resources and environment, and an increasing demand for value-added clay-based products, along with the requirements for the sustainability of using clay mineral resources, offer opportunities and challenges to Chinese clay scientists and clay community.

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1. Introduction

Clay minerals are ubiquitous on Earth. The utilization of clay minerals by human beings has an extremely long history; clay science and technology covers a very wide range of topics (Bergaya and Lagaly, 2013; Zhou and Keeling, 2013). So does clay research in China. In the context of clay minerals, to China and Chinese, historically there are at least several remarkable things. Firstly, rocks that are rich in kaolinite, one of the most commonly used clay minerals in industry and daily life, are known as kaolin or China clay (Bergaya and Lagaly, 2006). The name is derived from a Chinese site called Kao-Ling (In Chinese, the two-character means 'High Ridge') (Bergaya et al., 2006), a name of a village near Jingdezhen, Jiangxi province, China. Secondly, China, particularly Yellow River valley, is one of cradles of ancient human civilization. Since prehistoric time, Chinese has been using clay minerals to make pottery and later has ever been famous for ceramics, nicknamed china, in the world. Thirdly, some 1000 years ago, early in the Northern Song Dynasty (A.D. 960–1127), Chinese as the pioneering creator of movable-type system for printing used clay minerals to make movable characters.

Those wonderful clay mineral-related crafts, skills and products, of course, are just some among many Chinese achievements listed in the history. Clay scientists in China are now endeavoring to make a new innovative picture of clay science and technology. With the rapid development of Chinese economy and society, nowadays, the research interests and activities in China have evidently been growing and broadening along with fast-growing demands for and large consumption of clay minerals in industry. The papers in this special issue of Applied Clay Science are a collection of some current fundamental and applied research into clay minerals conducted by Chinese clay scientists. All these studies are conducted within China, with the exception of two papers contributed by work from international collaboration. Without doubt, the present collection would merely provide a glimpse into some current activities in clay research within China. Such collection could hardly be expected to offer a panorama of current research of clay scientists within China, still less reflect their past contributions in the field of clay minerals. But the papers in this issue, to some extent, do suggest that studies on the genesis and mineralogy of clay minerals,

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synthetic clay minerals, the modification of clay minerals, properties, and applications capture much more attention and are important aspects of fundamental and applied clay science in China.

2. Genesis and mineralogy of clay minerals

In China there are many deposits with clay minerals of economic interest. Somewhat abundant are kaolinite (the ideal chemical composition: $Al_4Si_4O_{10}(OH)_8$), pyrophyllite ($Al_4Si_8O_{20}(OH)_4$), montmorillonite ($Na_{0.50-1.20}[(Al_{3.50-2.80}Mg_{0.50-1.20})(Si)_8O_{20}(OH)_4]$), illite ($K_{0.50-1.50}[(Al_{4.00})(Si_{7.50-6.50}Al_{0.50-1.50})O_{20}(OH)_4]$), sepiolite ($(Mg_4(Si_6O_{15})(OH)_2 \cdot 6H_2O)$ and palygorskite ($(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$)). Knowledge about the occurrence of these clay minerals in China certainly aids the efficient exploitation of the deposits to satisfy the demand from specialized markets (Zhou and Keeling, 2013). Beyond that, the study on the genesis and mineralogy of clay minerals is of great scientific significance. For example, the information on the formation and alternation of clay minerals has much implication for paleogeographical, paleoecological, and paleoclimatic conditions (Zhou and Keeling, 2013) and even extraterrestrial exploration (Ehlmann et al., 2011). Moreover, clay minerals could play a significant role in crude oil formation, migration and accumulation (Wu et al., 2012). A study from Hu et al. (2016-in this issue) shows that the genetic characteristics of clay minerals and K–Ar dating of illite from pelitic rocks could be used to determine the metamorphic pressure–temperature conditions and the timing of metamorphism for the upper permian Linxi formation, southern Da Xing'an Mountains, China. Lu et al. (Zuo et al., 2016a–in this issue), by characterizing the samples of chromium-sericite collected from eight gold deposits hosted in granite in Jiaodong Peninsula, China, reveal that the strong intensity of hydrothermal alteration led to the chromium-sericite with a high content of Si and a low content of K in it. Wang et al. (Lu et al., 2016-in this issue) describe the formation of halloysite ($Al_4Si_4O_{10}(OH)_8 \cdot 4H_2O$) on weathered muscovite plates from a granite outcrop near Gaoling village, Jingdezhen, China and propose that the halloysite was derived from the surface leaching of muscovite possibly by two mechanisms: dissolution-precipitation or local dissolution-rearrangement of residue structure. As seen from the formation of clay minerals, it is common that clay minerals co-occurred with other minerals which are often regarded as impurities in industry. Hence, the extraction of clay minerals from the mixture is a commonplace in industry. But it is certainly a good thing to use all components. In this connection, Chen's Group (Xie et al., 2016–in this issue) of Hefei University of Technology describes the microstructural characteristics and thermochemical reactivity of dolomite-palygorskite. Such scientific information could help the comprehensive utilization of dolomite–palygorskite deposits.

3. Synthetic clay minerals

Natural clay minerals are usually inhomogeneous in composition and particle size. For increasing commercial value of such natural clay minerals and using them to produce advanced materials, an existing challenge is to establish an economic, green and efficient way of separating clay minerals from other co-occurring minerals. For example, to achieve montmorillonite of high purity in an economical way is still a tough issue at an industrial scale in China. On the one hand, innovating extraction and separation technology are a way out, but on the other, to use synthetic clay minerals offers a viable alternative (Zhang et al., 2010). Successful examples of synthetic clay minerals commercially produced in China are synthetic hectorite (the ideal chemical composition: $Na_{0.50-1.20}[(Mg_{5.50-4.80}Li_{0.50-1.20})(Si_{8.00})O_{20}(OH)_4]$) (Zhou et al., 2005; Zhang et al., 2010), synthetic saponite (Zhang et al., 2010: $Na_{0.50-1.20}[(Mg_{6.00})(Si_{7.50-6.80}Al_{0.50-1.20})O_{20}(OH)_4]$) (Jiang et al., 2010) and synthetic mica (Chen and Peng, 1990). These synthetic clay minerals with well-designed chemical composition, structure and morphology under controllable synthetic conditions possess much improved properties in comparison with their natural counterparts and have practical applications, and thereby they have good marketplace in China.

New high-tech products derived from these synthetic clay minerals are being developed in China. A key issue in this aspect could be on how to take advantage of the two dimensional (2-D) layered nanostructure. Besides, supramolecular assembly of the layered nanoparticles is worth being used to manufacture advanced materials. Zhou's group (AMSC) of Zhejiang University of Technology has successfully commercialized a series of processes of synthetic clay minerals and has demonstrated that the structure of 'house-of cards' from delaminated platelets of synthetic clay minerals can be used as superhydrogels and films (Zhou et al., 2005; Jiang et al., 2010; Zhang et al., 2010; Zhou, 2011; Zhou et al., 2011a) and as space-confined reactors for tailoring the nucleation and growth of crystalline solids, for example zeolitic titanosilicate-1 materials (Xia et al., 2011). In this regard, an interesting study reported in this issue suggests that the synthetic layered double hydroxide (LDH) and natural clay minerals can be combined together to form a novel multifunctional material (Li et al., 2016–in this issue).

4. Intercalation and exfoliation of clay minerals

It is well-documented that the surface and the interlayer space of clay minerals can be modified. In particular, the interlayer space of smectites (e.g. montmorillonite, saponite, and hectorite) can be intercalated with 'new' guest cations through an ion exchange reaction or other physical and chemical interactions. For example, Liao et al. (2015, in this issue) describe that cationic, anionic and non-ionic species from organic surfactants were able to be sequentially introduced into the interlayer space of montmorillonite. It is worth noting that the modification of montmorillonite by cationic quaternary ammonium ions to yield 'organoclay' is already a commercial process in China for more than fifteen years and a few large leading producers are located in Zhejiang, China. For such mature 'organoclay' products, however, there are still rooms to improve the process so as to make it to become an exact green one and to improve the performances of the products. For instance, Zhou's group of Zhejiang University of Technology has recently revealed a clean way to produce 'organoclay' and proposed possible mechanism of the swelling in xylene of the organoclay (Yu et al., 2014).

Accurate characterization and theoretical calculation and simulation (Dong et al., 2016–in this issue), in particular at an atomic and electronic level, are essential and helpful to understand the structure, to acquire methods to modify clay minerals properly and to fine tune the properties of resultant products. In this context, He's group of Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, has shown good examples in which the status of atoms in the octahedral and tetrahedral sites in montmorillonite and saponite is well probed (Zhu et al., 2011; Ma et al., 2015; Zhou et al., 2015). Based on such in-depth knowledge, He's group has successfully prepared a class of novel organoclays from montmorillonite and zwitterionic surfactants. In addition, it is worth noting that many other functional organic compounds and biomolecules can also be intercalated into or adsorbed onto clay minerals (Yu et al., 2013; An et al., 2015). Furthermore, the interlayer space of clay minerals can also act as a confined nanoreactor for in situ interlayer reaction and a nanoscale 'container' for confined nucleation, growth, or clustering of nanoparticles and nanoaggregate. For instance, the work from Peng et al. (Sun et al., 2015, in this issue) reports the introduction of TiO_2 nanoparticles into montmorillonite by an in-situ reaction in the interlayer space of montmorillonite, thereby leading to the homogeneous dispersion of TiO_2 nanoparticles within the interlayer space of montmorillonite.

Yet, to make layered clay minerals, especially smectite, to be exact nanomaterials faces a significant challenge in completely exfoliating the minerals to form individual nanolayers (Nicolosi et al., 2013).

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