Clays and Clay Minerals, Vol. 36, No. 2, 97–101, 1988.

1986 GEORGE W. BRINDLEY LECTURE

The third George W. Brindley lecture was delivered at the 23rd annual meeting of The Clay Minerals Society in Jackson, Mississippi, on October 13, 1986, by R. E. Grim, a Distinguished Member of the Society. The following review of the development of clay mineralogy is based on that lecture.—Editor

THE HISTORY OF THE DEVELOPMENT OF CLAY MINERALOGY

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Key Words—Bentonite, Catalysis, Correns, Differential thermal analysis, Endell, Geotechnical properties, Hendricks, Hofmann, Jordan, Kaolinite, Montmorillonite, Organoclays, Ross, X-ray powder diffraction.

It is an honor to have been invited to give the George W. Brindley Lecture for 1986. I first met George Brindley in 1948 before he came to the United States. We were good friends through the years, and I have wonderful memories of visits with George and of our discussions of the structure and properties of clay minerals. The following report chronicles the beginning of modern clay mineralogy and points out what I consider to be the major events that have led clay mineralogy to its present position as an important part of geologic activities.

DEVELOPMENT OF THE "CLAY MINERALS" CONCEPT

Prior to the 1920s, geologists making analyses of sediments listed the finest particles as clay, with no consideration of what this material actually was. Occasionally, a chemical analysis was made, but the significance of the analysis was rarely considered. Studies of soils by agronomists followed the same pattern, but, in general, they gave more consideration to the structure and mineral identity of these finest particles. Chemical analyses of many clay materials had shown that two clays may have about the same chemical composition, but different properties, or about the same properties, but different chemical compositions. There was no generally accepted concept of the nature, identity, or structure of the fundamental components of clays, primarily because there were no adequate techniques for studying the extremely small particles making up the clays.

Professor Heinrich Ries of Cornell University was perhaps the first American geologist to specialize in the study of clays. He studied clays from many of the eastern states and published reports on their clay resources, as illustrated by *Clays and Shales of Virginia, West of the Blue Ridge* (Ries, 1920). This report described the clays of this region on the basis of their ceramic properties, such as plasticity, shrinkage, and firing characteristics. He used the standard petrographic microscope to identify the minerals in the clays as kaolinite and hydromica, but stated that "little attention is now paid to chemical analyses . . . it gives little information regarding the physical properties of the material".

About 1924, C. S. Ross and colleagues (Ross and Shannon, 1925) of the U.S. Geological Survey began a study of the mineral composition of clays that led to a series of monumental papers on the clay minerals (Ross and Kerr, 1930, 1931). They investigated a variety of clays and soils by painstaking optical microscopy, supplemented by excellent chemical data. They showed that the components of clay materials were essentially crystalline and limited to several distinct crystalline components to which the name "clay minerals" was applied.

Simultaneous with Ross and Kerr, scientists in Europe began to study the small clay particles by means of X-ray powder diffraction. In 1923, Hadding in Sweden and in 1924, Rinne in Germany, working quite independently, published the first X-ray powder diffraction analyses of clays. They reported that the smallest particles of clay were indeed crystalline and that the several samples studied seemed to be composed of the same small group of minerals. Ross and his colleagues later added X-ray powder diffraction to their investigations. In 1930, Hendricks and Fry and in 1931,

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https://doi.org/10.1346/CCMN.1988.0360201 Published online by Cambridge University Press

Kelly *et al.* independently presented results showing that on the basis of X-ray powder diffraction, soil materials, even in their finest fractions, are composed of crystalline particles of a limited number of minerals.

With the publication of *The Mineralogy of Clays* by Ross in 1923 and of *The Clay Minerals and Their Identity* by Ross and Kerr in 1931, the concept of clay mineralogy was firmly established. In Germany in 1933, the publication of K. Endell, U. Hofmann, and D. Wilm entitled "Über die Natur der Keramische Tone" (Endell *et al.*, 1933) established the clay mineral concept in Europe. This was not a totally new concept, for LeChatelier as early as 1887 arrived at a similar concept, but had no specific evidence to prove it.

The classic investigation of the atomic structure of layer silicates by Linus Pauling (1930) provided basic ideas that permitted the elaboration of the structure of many clay minerals. Following Pauling's original ideas, Gruner (1932) worked out a structure for kaolinite. Hendricks and Teller (1942) later presented the theory of X-ray powder diffraction for interstratified minerals, which permitted their detailed study and evaluation.

In Germany, beginning about 1931, several groups of investigators began studying the clay minerals. At the Technische Hochschule in Berlin, Hofmann *et al.* (1933) suggested an atomic arrangement for montmorillonite that featured an expanding structure. Variable numbers of layers of water molecules were possible between the silicate sheets, thereby providing a variable *c*-axis dimension. Consequences of this concept for the first time provided plausible explanations for many properties of clays hitherto not understood. C. W. Correns and his associates (e.g., Correns and Mehmel, 1936) at the University of Rostock published valuable data on the X-ray powder diffraction, optical, and chemical properties of the various clay minerals. Mehmel (1935) was the first to indicate clearly that two forms of halloysite existed. The work by Ardenne *et al.* (1940) showed the electron microscope to be another powerful tool for the investigation of clay minerals. It provided precise information on the shape and morphology of the extremely small particles making up these materials.

Studies of the dehydration characteristics of clays and the changes in their physical properties on heating to elevated temperatures had been made by ceramists and others for many years (LeChatelier, 1887), but the development of differential thermal analyses (DTA) allowed a better understanding of these changes. Beginning about 1930, several laboratories began to investigate clays using this technique. Smothers and Chiang (1966) and Mackenzie (1970) have summarized these beginnings. With the development of X-ray powder diffraction techniques, the precise identification of the new phases developed on heating could be made. In the 1930s, improvements in DTA procedures and instrumentation were forthcoming, and as a result, DTA provided an additional fingerprint for the identification of clay mineral components of soils and clays (Grim and Rowland, 1942).

DEVELOPMENT OF APPLICATIONS OF CLAY MINERALS

Ceramics and refractories

About the same time that DTA was developing, a great change occurred in the way ceramic ware was fired. The old procedure was to stack the ware in a periodic kiln, fire it, allow the kiln to cool, remove the ware, and then fill and fire it again. Continuous kilns supplanted this procedure. In these new type kilns, the ware entered one end and moved continuously through the kiln where it was exposed to gradually increasing temperatures. DTA data indicated the temperature intervals at which changes in the ware took place and temperatures at which nothing happened. These data permitted optimum heating schedules to be designed, and in at least one case shortened the time through the kiln by about 25%, thereby saving fuel costs and increasing the capacity of the kiln.

The following example shows the close connection between research and industry in the development of applications of clay materials. About 1937, the Illinois Geological Survey, as part of an ongoing research program, began a systematic collection of samples from all operating plants producing clay products in the state. At the pit of the Illinois Clay Products Company near Joliet, samples were collected not only from the underclay used to produce refractory brick, but also from a greenish clay in the overburden. This overburden was generally discarded because it was not refractory. The greenish clay was a thoroughly weathered shale, and mineral analyses showed that it was a mixture of an expandable clay mineral and illite. It was extremely plastic, and a foundry molding test proved it to be an excellent bonding clay for molding sands (Grim and Bradley, 1939). The company subsequently marketed the material for this purpose with definite success.

Bentonites

Studies of bentonite and the development of a bentonite industry have played major roles in the growth of clay mineralogy. Knight (1898) suggested the name "bentonite" for a peculiar clay-like material having soapy properties occurring in the Fort Benton unit of a Cretaceous formation in Wyoming. Hewitt (1917) and Wherry (1917) established that this particular clay was an alteration product of volcanic ash. Ross and Shannon (1926) found that the dominant component of bentonite is usually montmorillonite. At the present time, bentonite is defined as a clay composed dominantly of a smectite clay mineral and whose properties are a consequence of this mineral component regardless of its mode of origin (Grim and Güven, 1978).

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Some bentonites are hydrothermal alteration products of igneous rocks, rather than altered ash.

Commercial production of bentonite began in the United States in the 1920s. The unique physical properties of this clay and its widespread use were powerful incentives for much clay mineral research. The two men primarily responsible for the commercial development of bentonites and the research efforts to explain the unique properties of these clays were Paul Bechtner and George Ratcliff. Bechtner, owner of American Colloid Company, expanded the use of bentonites in foundry molding sands and in water-impedence, cosmetics, pharmaceutical, and other applications. Ratcliff, who started the Baroid Company, now part of NL Industries, promoted the use of bentonite in oil-well drilling muds. For a considerable time, the major bentonite production was from Wyoming deposits, but production soon spread to Mississippi, Texas, Arizona, and other western states.

Bentonites were not recognized and developed in Europe until the 1930s, some years after the development of the Wyoming deposits. Kurt Endell was a leader in the development of the Bavarian deposits in Germany. The widespread commercial use of bentonite has caused a world-wide search for this clay, and today, it is extensively mined in many countries, including the United Kingdom, Germany, Italy, Greece, India, Japan, and the Soviet Union (Grim and Güven, 1978).

Organoclays

In 1942, as part of the celebration of the fiftieth anniversary of its founding, the University of Chicago sponsored a number of symposia on various frontiers of science. The symposia were well attended and widely publicized. One of these organized by the Department of Geology was concerned with clay mineralogy. Papers were presented by mineralogists, chemists, ceramists, engineers, and others and published in Volume 50 of the *Journal of Geology* in 1942. The symposia did more than any other single event to establish clay mineralogy as a significant part of geology.

George Ratcliff attended the meeting and concluded that other uses must exist for bentonite than making mud out of it for drilling oil wells or for use as a bonding agent for molding sands. He pursued his idea by establishing a fellowship at Mellon Institute in Pittsburgh and setting up a technical committee to guide and direct the fellowship. Meanwhile, the military, responding to the onset of World War II, needed to find a way to harden loose soil material so that landing strips could be built quickly. Work commenced at Cornell University, Massachusetts Institute of Technology, and elsewhere. Ernst Hauser (see Hauser, 1941) of MIT had been involved in this research and had tried various compounds to stabilize soils. He was a member of the Mellon fellowship committee and recommended that the reaction of bentonite with various organic reagents be the subject of the first Fellow's research.

John W. Jordan, the first Mellon Fellow, started his work visiting laboratories where clay studies were in progress, including the clay laboratory at the Illinois Geological Survey. He then visited deposits where various types of clay were being mined. All of this gave him a background in clays before he began his laboratory studies. After several years, Jordan developed a group of organo-montmorillonites dubbed "Bentones" (Jordan, 1949). These products immediately found widespread use in paints, greases, drilling fluids, and other materials needing sophisticated rheological control. They became successful items in the clay product line of NL Industries. The work of Jordan and the success of Bentone was the most important factor in opening the door to a flood of research on the reaction of clay minerals with various types of organic compounds—research that persists today.

Catalysts

Until the 1920s, distillation was used almost exclusively to refine crude oil to gasoline and other products. Then, chiefly due to French research (e.g., Houdry *et al.,* 1938) the industry changed to the use of catalytic converters, which efficiently convert a higher percentage of crude oil to gasoline and result in gasoline having higher octane numbers. The initial catalysts were various synthetic types of aluminosilicates. In the early years of World War II, Wright W. Gary, working in a federal agency responsible for aviation supervision, conceived the idea that commercial catalysts, especially those used to produce aviation fuel, could be made from bentonite. Acid-activated bentonite was known to possess some catalytic properties; the problem, however, was to channel these catalytic properties to changes in petroleum. The goal was to develop a catalyst that produced an acceptable percentage of gasoline having an acceptable octane number from crude oil. The catalyst also had to be hard enough to resist abrasion in the converter. After about two years, a successful catalyst was developed from bentonite and a plant was built at Vernon, California, to produce it.

A few years later, David Lilienthal assembled Minerals and Chemicals Corporation from the Attapulgus Clay Company, Edger Kaolin Company, a flotation research laboratory in Lakeland, Florida, and several limestone operations, with Gary as president. Gary attempted to use kaolins as the feed stock for the manufacture of catalysts because they contained no iron to poison catalytic activity. After a few years, a successful commercial product was developed which is now manufactured in Georgia. The process consisted essentially of attacking the kaolinite structure with sulfuric acid and then, at elevated temperature and pressure, reforming it into a different structure that possessed desirable catalytic properties.

https://doi.org/10.1346/CCMN.1988.0360201 Published online by Cambridge University Press

In more recent years, other types of catalysts have been produced from kaolin. These catalysts are the well-known zeolites A and X and are made by reacting kaolin or metakaolin with caustic soda. Such catalysts have essentially "taken over" the petroleum catalyst industry.

The literature now contains a tremendous fund of data on the catalytic properties of clay minerals in all sorts of organic reactions. Clay minerals have even been suggested as catalysts that produced the first living organic compounds on the Earth.

Engineering

Many large cities such as Chicago, London, Paris, São Paulo, and Mexico City, are built on relatively soft soil materials. Preliminary to building structures on and excavating tunnels in these materials, the engineer first obtains undisturbed core samples with the natural moisture content retained, and determines their strength under compaction and shearing stress, their plasticity, their moisture content, and many other properties. Based on these data the foundations and structures are then designed. Prior to about 1940, clay mineral analyses were not part of the data sought by engineers engaged in such activities. Few people realized that such analyses could indicate the fundamental factors controlling the properties measured and possibly indicate how such properties might be changed during and following construction, when the environment in which the soil existed was changed.

In 1937, as I returned from Europe by ship, I discussed these ideas with a fellow passenger, a famed engineer from an eastern university. He was not interested, claiming that all he needed were the laboratory data. He no longer thinks so—what changed his mind was what happened in Chicago in the early 1940s. Much of downtown Chicago, the "Loop," rests on soft lake sediments. Engineers had long considered that subways could not be built under streets in the Loop area without great potential danger to the foundations and structures lining the street. In the late 1930s, a plan was conceived, however, in which the subways would be built by sinking shafts down from the surface. Outward from the shafts, tunnels would be cut in the clay of the exact size of the subway tunnel. The tunnels would be lined as they were cut with a concrete and steel shell. The shell would fit exactly; there would be no opening around the shell, and the remaining clay would not be disturbed.

Unexpectedly, however, shortly after the subways were completed, the streets above the subways gradually sank by two feet or more. One could walk down State Street in front of the Palmer Hotel and look out over the top of the tram cars. At places where the subway came close to the curb, the engineers placed huge timbers to provide support for the buildings. Eventually State Street was filled to bring the surface to its previous level, but at tremendous cost.

The significant point of the story is that although the engineers performed every test they could think of on the clay, the data did not predict settlement. It was a clear case of settlement without any load on the clay. In this soft clay, having a high liquidity index, the rigid water which bound together the clay mineral particles liquified and drained out, causing the surface above the subway to sink. The problems surrounding the construction of the Chicago subway more than anything else convinced engineers that information on clay mineralogy is vital to the success of a project. Since then, large construction firms place considerable importance on geological and clay mineral studies. In major universities, clay mineralogists now appear on the faculty of engineering departments.

DEVELOPMENT OF THE CLAY MINERALS SOCIETY

About 1945, the U.S. National Research Council established a Committee on Clay Minerals. Members appointed were from a variety of disciplines, such as geology, mineralogy, ceramics, chemistry, engineering, and agronomy. The function of the Committee was to keep abreast of clay research in the various disciplines and to make the activities known by annual publications. The Committee's activities continued until the annual Clay Minerals Conferences were well established.

In 1951, A. F. Frederickson of Washington University in St. Louis organized a symposium on clays and bauxites as part of an annual meeting in St. Louis of the American Institute of Mining and Metallurgical Engineers (see Frederickson, 1952). The symposium was well attended, and the presentation of papers was followed by a lively discussion of current clay research. At the close of the symposium, those attending decided that "We should do this again; let's have annual meetings of this sort". After considerable discussion on how such annual meetings should come about, who should sponsor them (inasmuch as many disciplines were involved, no single society should sponsor such annual conferences), I was asked to explore the possibility of the National Research Council, through its Clay Minerals Committee, sponsoring such annual meetings. The National Research Council agreed, and the Annual Clay Minerals Conferences came into being, the first being held in 1952 at the University of California in Berkeley. The National Research Council published the Proceedings after the first conference and sponsored the annual conferences until The Clay Mineral Society was formed.

Clay mineral research was developing as rapidly in many European countries in the 1940s as it was in the United States. Meetings of clay mineral groups were being held in various countries, notably Great Britain,

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France, Belgium, and Germany. At the International Geological Congress in London in 1948, clay mineralogists from several countries met informally and set up a committee to explore the formation of an international association of the various national clay mineral groups. They also planned the first meeting sponsored by this international association for the next International Geological Congress in Algeria in 1952. Hénin and Caillérè of France agreed to head the activities for this initial meeting. The meeting held in Algiers resulted in the formal organization of Association International pour l'Etudes des Argiles, otherwise known as AIPEA. Some twenty national clay mineral groups have now been organized, and International Clay Conferences are held every three years.

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(Received 18 October 1986; accepted 27 October 1987; Ms. 1616)

https://doi.org/10.1346/CCMN.1988.0360201 Published online by Cambridge University Press