History and Perspectives of Clay Science

The first Latin-American Clay Conference (LACC) was held in Funchal, Madeira, in 2000 (p. 76). The high scientific level represented in two large conference volumes corresponded to a very pleasant social programme. A fortunate detail was the invitation of Faiza Bergaya to give an introductory lecture on the history and perspectives of clay science entitled “Clay Science studies in the world”. However, time is very valuable and seldom available in large amounts, and this lecture could not be published in the conference volumes. This was a further fortunate fact as we can present an extended version of this lecture in this Newsletter. We try out a new avenue to figure this presentation and show the most important results in the following pages.

The presentation is divided into three parts:

- Birth and Development of Clay Research
- Clay Science Perspectives
- Clay Meetings and Conferences.
Birth and Development of Clay Research

Clays minerals: names, first locality, structural identification, and literature

Allophane (Stromeyer, 1816)

“The name allophane was first applied by Stromeyer and Hausmann in 1816 to material lining cavities in marl (Balingen). The term is derived from Greek words meaning “to appear” and “other”, in allusion to its frequent change, on outstanding, from a glassy material to one with an earthy appearance because of the loss of water. Since the work of Stromeyer and Hausmann a considerable number of materials have been described as allophane or classed with it. In general all such material was thought to be amorphous, and hence the name allophane came to be associated with amorphous constituents of clay“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 34-35).

F. Stromeyer: (Allophan, named and analyzed by Stromeyer but reported by J. F. L. Hausmann). Göttingische Gelehrte Anzeigen 2 (1816) 251-253

Structural identification:

Attapulgite (De Lapparent, 1935)

“The name attapulgite was first applied by De Lapparent in 1935 to a clay he encountered in fuller’s earth from Attapulgus, Georgia, Quincy, Florida, and Mormoiron, France. Bradley determined the structure of the mineral, showing silica chains similar to those in amphibole to be essential components of its structure....Much material described as palygorskite is clearly the same as attapulgite. However, the descriptions of palygorskite are frequently vague, and the exact relation of the material to either sepiolite or attapulgite cannot be determined“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 44).

J. De Lapparent: Formula and structure of attapulgite. Compt rend 202 (1936) 1728-1731

Structural identification:

Detailed structure:
W. F. Bradley: The structural scheme of attapulgite. Amer Mineral 25 (1940) 405-410

**Beidellite** (Larson and Wherry, 1925)

“Beidellite was first used by Larson and Wherry in 1925 for a clay mineral occurring in a gouge clay in a mine at Beidell, Colorado. These authors first described this material as leverrierite in 1917 but in their later work suggested that it was a distinct species... Leverrierite was first described by Termier in 1890 from material in black carbonaceous shales near St. Etienne, France. It was named after the mining engineer Le Verrier“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 47).

E. S. Larsen, E. T. Wherry: Leverrierite from Colorado. J Wash Acad Sci 7 (1917) 208-217

Structural identification:

**Bentonite** (Knight, 1898)

The first name Taylorite was in honor of William Taylor who first focused attention to the deposits in USA. The name Bentonite was given by Knight in 1898 according to the first site of discovery near Fort Benton in Montana. Hewett showed that this clay was formed by alteration of volcanic ash in situ.

W. C. Knight: Bentonite. Eng Min J (1898) 66: 491
D. F. Hewett: The origin of bentonite. J Wash Acad Sci 7 (1917) 196-198

Structural identification:
U. Hofmann, K. Endell, D. Wilm: Kristallstruktur und Quellung von Montmorillonit. (Das Tonmineral der Bentonittone.) Z Kristallogr 86 (1933) 340-348

**Brammallite** (Bannister, 1943; also structural identification)

Named after the british mineralogist A. Brammall.
Celadonite (Glocker, 1847)

Named after the grey-green dress of the shepherd Céladon in the novel “L’Astrée“ of H. D’Urfé (1568 - 1625).

“Celadonite was proposed in 1847 by Glocker for a soft gray-green mineral that is a hydrous silicate of iron, magnesium, and potassium. The name, meaning „sea-green“ in French, refers to the color of the mineral. Similar material appears to have described earlier as “terra verti“ by DeLish in 1783 and as “Grünerde“ by Hofmann in 1788. Hendricks and Ross in 1941 showed that celadonite and glauconite have a very similar structure. The original celadonite came from amygdaloidal fillings, and Kerr and Hamilton suggested that it might be desirable to retain the name celadonite because of its different origin from that of glauconite“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 49).

E. F. Glocker: Generum et Specierum Mineralium Secundum ordines Naturales Digestorium Synopsis. Halle (1847) 195
C. Hofmann: Bergmännisches J (1788) 519

Structural identification:

Chlorites (Werner, 1789)

“Werner appears to have first used the name chlorite in 1799. It has been used for a group of green hydrous silicates in which ferrous iron is prominent and which are closely related to the micas. A large variety of materials have been described as chlorites, and there has been much confusion regarding the identity and validity of species belonging to the group“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 43).

Structural identification:
L. Pauling: The structure of chlorites. Proc Natl Acad Sci U.S.A. 16 (1930) 578-582

**Corrensite** (Lippmann, 1954)
The mineral was named in honor of Carl Wilhelm Correns (1893 - 1980).


Structural identification:
Stephen, D. M. C. MacEwan: Swelling chlorite. Géotechnique 2 (1950) 82-83

**Dickite** (Dick, 1908)

“Dick in 1908 described a mineral from the island of Anglesey in Wales, without giving it any specific name, which was referred to with other clay minerals as a “mineral of kaolin“. Ross and Kerr showed that the “Dick mineral“ was a distinct species and first applied the name dickite“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 43).


Structural identification and name:

**Fuller’s earth** (before 3000 BC in Mesopotamia, Egypt and Greece)

“The English word fuller, as foulon in French or fullone in Italian, derives from the Latin term fullo, indicating a person whose job was that of degreasing and thickening clothes. In Romans’ times, pieces of cloth were first steeped into old urine (very rich in ammonia) or other alkaline solutions. Then they were heavily tread upon in a large bowl or a basin containing mud, the so called „fuller’s earth, or „creta fullonia“ in Latin. Several rinses were needed with fresh water in order to remove the fuller’s earth, which took away with it the main part of grease and dirt present into the fleece. The Greeks, Egyptians and Romans worked after this method“ (G. Novelli: La bentonite - una argilla nei secoli. Lecture presented 1999 during the institution of the prize „Giovanni Novelli“ on
Glauconite (Keferstein, 1827)

From Greek “glaukos“ (bluish shining).

C. Keferstein: (Glaukonit) Teutschland geognostisch-geologisch dargestellt und mit Charten und Durchschnittszeichnungen erläutert. Im Verlage des Landes - Industrie - Comptoirs, Veimar 5 (1827) 508-511

Structural identification:

Halloysite (Berthier, 1826)

“The name halloysite was given by Berthier in 1826 for material found in pockets in Carboniferous limestone near Liège, Belgium, in a district of old zinc and iron mines. It was named in honor of Omalius d’Halloy, who had observed the mineral several years previously. In the years prior to the development of X-ray-diffraction technique many materials were described as halloysite. Dana listed under halloysite 16 mineral names that be considered to be synonymous with it. Ross and Kerr studied much of this material by modern methods and in addition obtained samples from the mineralogical collections of the University of Liège which are probably as nearly representative of the type material as can be obtained at the present time. They showed that halloysite is crystalline and stated that it is closely related to but distinct from kaolinite“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 37-38).

J. D. Dana: System of Mineralogy. 6th edition, Wiley, New York (1914)

Structural identification:
U. Hofmann, K. Endell, D. Wilm: Röntgenographische und kolloidchemische Untersuchungen über Ton. Angew Chem 47 (1934) 539-547

**Hectorite** (Strese and Hofmann, 1941; also structural identification)

The name Hectorite was applied to material from Hector in California.


**Illite** (Grim, Bray and Bradley, 1937)

“*The term illite was proposed by Grim, Bray, and Bradley in 1937 as a general term, not as a specific clay-name, for the mica-like clay minerals. The name was derived from the abbreviation for the state of Illinois. Prior to 1937 the widespread occurence of a mica-like clay mineral had been suggested, e. g., potash-bearing clay mineral, sericite-like mineral, and Glimmerton. Grim et al. pointed out objections to these earlier names, and their term illite has now been widely accepted for a mica-type clay mineral with a 10 Å c-axis spacing which shows substantially no expanding-lattice characteristics....Sarospatite has been suggested by Hofman, Endell and Mägdefrau as a substitute for illite, but the same objection can be raised, namely, that the type material from Sárospatak, Hungyary, is a mixture of clay materials. It is believed that experience has shown the desirability of using a new name for this clay-mineral group rather than attempting a redefinition of an old name, particulary if the old name originally described a mixture of minerals*“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 42-43).


Structural identification:

R. E. Grim: Relation of the composition to the properties of clay. J Amer Ceram Soc 22 (1939) 141-151

**Imogolite** (Yoshinaga and Aomine, 1962a)

The name Imogolite was first used by Yoshinaga and Aomine in 1962 for a component present in the clay fractions of the soil (“Imogo“) derived from glassy volcanic ash.
N. Yoshinaga, S. Aomine: Imogolite in some Ando soils. Soil Sci Plant Nutr (Tokyo) 8 (3) (1962a) 22-29
N. Yoshinaga, S. Aomine: Allophane in some Ando soils. Soil Sci Plant Nutr (Tokyo) 8 (2) (1962b) 6-13

Structural identification:

**Kaolinite** (Johnson and Blake, 1867)

“The name kaolin is a corruption of the Chinese ,,kauling“ meaning ,,high ridge“, the name is a hill near Jauchau Fu, China, where the material was obtained centuries ago. Occurrences in many parts of the world are well known today. Johnson and Blake in 1867 appear to have first clearly intended the name kaolinite for the ,,mineral of kaolin“. Ross an Kerr showed that the kaolin minerals cannot be assigned to a single species, i. e., clays of this character are not composed of a single mineral species, and minerals of that composition also are not all the same samples. They concluded that three distinct species are represented, namely, kaolinite, nacrite, and dickite“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 35-36).


Structural identification:

**Montmorillonite** (Cronstedt, 1788; Damour and Salvetat, 1847)

Mauduyt named in 1847 the mineral Montmorillonniste after Montmorillon in France. Damour and Salvetat proposed the name Montmorillonite in 1847 for a mineral also from Montmorillon, France.

Mauduyt: Un mot sur un morceau de quartz d’une variété particulière, ainsi que sur une substance minérale trouvée dans le department de la Vienne. Bull Soc Géol France 4 (1847) 168-170

“The name montmorillonite is used currently both as a group name for all clay minerals with an expanding lattice, except vermiculite, and also as specific mineral name. Specifically it indicates a high-aluminia end member of the montmorillonite group with some slight replacement of Al$^{3+}$ by Mg$^{2+}$ and
substantially no replacement of Si$^{4+}$ by Al$^{3+}$. MacEwan suggested the term montmorillonoid for the group name to avoid confusion with montmorillonite as a specific mineral name, and Correns suggested Montmorin as the group name. Neither of these names has found favor. The name smectite suggested as a group name by the Clay Minerals Group of the Mineralogical Society of Great Britain at the outset met strong opposition, particularly by many American mineralogists, but it is becoming widely accepted“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 41).


Structural identification:
U. Hofmann, K. Endell, D. Wilm: Kristallstruktur und Quellung von Montmorillonit. (Das Tonmineral der Bentonittone.) Z Kristallogr 86 (1933) 340-348

**Morencite** (Lindgren and Hillebrand, 1904)

"Morencite was first described from Morenci, Arizona, by Lindgren and Hillebrand in 1904 as a brownish-yellow hydrous silicate of ferric iron with magnesium, calcium, and aluminium. Gruner showed the mineral to be structurally the same as nontronite“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 49).


Structural identification:

**Nacrite** (Brongniart, 1807)

From French “nacre“ (nacreous).
"Nacrite was proposed by Brongniart in 1807. Later Des Cloizeaux, and much later Dick, described a mineral called nacrite from mines in Saxony with sufficient analytical data to differentiate it from the "Dick material" but not from the "mineral of kaolin". Mellor accepted nacrite as a distinct mineral, and Ross and Kerr finally established its identity" (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 36).

A. Brongniart: [Nacrite] Traité élémentaire de minéralogie, avec des aplications aux arts, etc. Paris (2 vols.) 1 (1807) 505
J. W. Mellor: Do fireclays contain halloysite or clayite? Trans Ceram Soc (England) 16 (1916) 83

Structural identification:

Nontronite (Berthier, 1827)

"Berthier proposed the name nontronite for a material associated with manganese ore in the arrondissement of Nontron near a village of Saint Pardoux in France. A chemical analysis given by Berthier shows the mineral to be a hydrous ferric iron silicate. Collins in 1847 appears to have been the first to recognize the association between nontronite and montmorillonite. The similarity of nontronite and montmorillonite was established by Larsen and Steiger, Ross and Kerr, and Gruner. Nontronite is now the name generally applied to the iron-rich end member of the montmorillonite group" (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 40-41).

E. S. Larsen, G. Steiger: Dehydration and optical studies of Alunogen, Nontronite, and Griffithite. Amer J Sci ser 5 15 (1928) 1
Structural identification:
G. Nagelschmidt: On the atomic arrangement and variability of the members of montmorillonite group. Mineral Mag 25 (1938) 140-155

**Palygorskite** (Ssaftschenkow, 1862)

Named after Palygorsk in the Ural.

"Much material described as palygorskite is clearly the same as attapulgite. However, the descriptions of palygorskite are frequently vague, and the exact relation of the material to either sepiolite or attapulgite cannot be determined“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 45).


Structural identification:
W. F. Bradley: The structure scheme of attapulgite. Amer Mineral 25 (1940) 405-410

**Pyrophyllite** (Hermann, 1829)

From Greek “pýr“ (fire) and “phýllon“ (leaf).


Structural identification:

**Saponite** (Svanberg, 1840)

"The earliest use of the name saponite is difficult to establish. The name, derived from “sapo“, meaning soap, was used by Svanberg in 1840, and 1842 he published chemical analysis showing the material to be essentially a hydrous magnesium silicate. As in the case of many of the other clay minerals, prior to the development of modern analytical techniques, the mineral could not well characterized, and the early literature includes a considerable variety of materials under this name. Ross and Kerr in 1931 identified saponite as a member of the montmorillonite group with a high content of MgO. Ross and Hendricks in 1945 defined saponite as a member of the montmorillonite group in which the replacement of Al$^{3+}$ by Mg$^{++}$ is essentially complete and with some

Structural identification:

Sauconite (Roeper and Genth, 1875)

Structural identification:
C. S. Ross: Sauconite - a clay mineral of the montmorillonite group. Amer Mineral 31 (1946) 411-424

Sepiolite (Glocker, 1847)

“Sepiolite and Meerschaum have long been considered as synonymous by mineralogist. The name Meerschaum appears to have been first applied by Werner in 1789 and is German for “sea froth“, alluding to the lightness and color of the material. The term sepiolite was first applied in 1847 by Glocker and is derived from the Greek for “cuttlefish“, the bone of which is light and porous.... Much material described as palygorskite is clearly the same as attapulgite. However, the descriptions of palygorskite are frequently vague, and the exact relation of the material to either sepiolite or attapulgite cannot be determined“ (R. E. Grim: Clay Mineralogy 2nd edition, McGraw-Hill Book Company, New York (1968) 44-45).

E. F. Glocker: Generum et Specierum Mineralium Secundum Ordines Naturales Digestorium Synopsis. Halle (1847) 195
Structural identification:
G. Migeon: Contribution à l´étude de la définition des sépiolites. Bull Soc Française de Minéralogie 59 (1936) 6-133
Detailed structure:

**Stevensite** (Leeds, 1873)


Structural identification:
G. T. Faust, K. J. Murata: Stevensite redefined as a member of the montmorillonite group. Amer Mineral 38 (1953) 973-987

**Vermiculite** (Webb, 1824)

The name Vermiculite from the Latin „vermiculari, to breed worms“ was first used by Webb in 1824 for a platy mineral from Millbury near Worcester in Massachusetts. This mineral exfoliates when heated and wriggles like a worm.


Structural identification:
J. W. Gruner: Vermiculite and hydrobiotite structures. Amer Mineral 19 (1934) 557-575

**Volkonskoite** (Anonymous, 1830; Kämmerer, 1831)

Anonymous: Description of the occurrence of a green-coloured mineral discovered on a certain estate in the Province of Perm and named in honour of Mr. Minister of the Imperial Court Volkonskoite (i.e. Prince Volkonskoi). Gorn Zh Mosk, Part IV (1830) 261-267; see R. C. Mackenzie: Discovery of volkonskoite. Mineral Mag 48 (1984) 297-298

Structural identification:
Clay science since about one century

Clays were used since the early history but Clay Science studies go back only about one century

Commercial production of bentonite played a major role in the growth of clay science

1898 Knight suggested the name "bentonite" for clay-like materials with soapy properties, occurring in Fort Benton in Montana

1917 It was established independently by two authors (Hewitt and Wherry) that this clay is an alteration product of volcanic ash.

> 1920 Commercial exploitation of the Wyoming deposits starts in USA: Betcher owner of the American Colloid Ratcliff started the Baroid Company (actually part of N. L. Ind.)

Bentonites were recognized in Europe only 10 years later with widespread commercial uses of the Bavarian deposits in Germany. Bentonite deposits are now extensively mined in many other European countries and also in India, Japan, North Africa, etc...

This leads to the world-wide search for bentonite until today
Le Chatelier in 1887 suggested the concept "argile" with no specific evidence to prove what it is.

Le Chatelier studied clay minerals with his method of thermal dehydration. He observed that dehydration of the fine clayey materials occurs within certain temperature regions. He concluded that constitutional water is desorbed, which, at the knowledge in this time, only occurs with minerals. He stated that the clay must be crystalline.

H. Le Chatelier: De l’action de la chaleur sur les argiles. Bull Soc France Min 10 (1887) 204-207

Geologists recognized finest particles of sediments as clays without consideration of what this material is.

Theodor Schlözing the Elder (1824-1919) investigated clays by sedimentation techniques and in 1903 described different fractions: below diameters of 0,0005 mm clayey sands followed by the (also in the microscope) invisible sands which remain dispersed in pure water for unlimited time periods and represent colloidal particles.

Th. Schlözing: Compt rend 137 (1903) 369

The swedish soil scientist Albert Mauritz Atterberg (1846 - 1916) studied plasticity of soils. He investigated the flocculation of different soil fractions which he obtained by sedimentation. The Atterberg sedimentation technique is still an important method for separating clays and clay minerals into fractions. Atterberg recommended the following notation:

- clay < 0,02 mm (in diameter), sand 0.02 - 2 mm, gravel >2mm.
A. Atterberg: Die rationelle Klassifikation der Sande und Kiese. Chemiker Zeitung 29 (1905) 4
A. Atterberg: Die Plastizität und Kohärenz der Tone und Lehme. Chemiker Ztg (1910) 42: 369

Agronomists studying soils used the criterium of particle size but considered also the identity of the samples (first chemical analysis). Way in 1852 focussed attention on the “base exchange capacity“ of soils, which, at this time, was considered to arise from amorphous materials only. Lemberg (1876) assumed that very fine zeolitic complexes are newly formed which are responsible for the base exchange. Van Bemmelen (1830 - 1910) proved in 1888 that the gel-like silicates provide the adsorption sites in the soils.

J. Lemberg: Über Silicatumwandlungen. Z Dtsch Geol Ges 28 (1876) 519-526
J. M. van Bemmelen: Über die Absorptionsverbindungen und das Absorptionsvermögen der Ackererde. Landw Versuchs Stat 35 (1888) 69

1920 1st report on clay resources from Ries in USA
Identification of some clays by a petrographic microscope and with identification of some physical (ceramic) properties like plasticity, shrinkage and firing characteristics

H. Ries: Clays and shales of Virginia, west of the Blue Ridge. Virginia Geol Surv Bull 20 (1920) 118
many groups started investigations using
- optical microscopy
- chemical analysis
- XRD

1923 Hadding in Sweden; 1924 Rinne in Germany, and 1925 Ross in USA

Hadding (1923) in Upsala (Sweden) and Rinne (1924) in Leipzig (Germany) are the first who used the Debye-Scherrer technique for clay mineral studies. Ross and co-workers in USA studied clay minerals with X-ray techniques, chemical and optical methods.

F. Rinne: Röntgenographische Untersuchungen an einigen feinzerteilten Mineralien, Kunstprodukten und dichten Gesteinen. Z Kristallogr 60 (1924) 55-69
C. S. Ross, E. V. Shannon: The chemical composition and optical properties of beidellite. J Wash Acad Sci 15 (1925) 467-468

Carl Wilhelm Correns in Rostock (Germany) studied the clay minerals in sediments.

C. W. Correns: Über die Bestandteile der Tone. Z Dtsch Geol Ges 85 (1933) 706-712
XRD: unavoidable tool for clay research

Wilhelm Conrad Röntgen (1845 - 1923)
detection of X-rays, 1895 1st Nobel Prize (Physics) 1901

W. C. Röntgen: Über eine neue Art von Strahlen (in several languages) Nature 53 (1896) 274 (23.01.1896); L’Eclair Electr 7 (1896) 354 (08.02.1896); Science 3 (1896) 227 (14.02.1896)

Röntgen’s experimental equipment in 1895: B Rühmkorff induction coil,
C photographic plate, T Hittorf-Crookes evacuated tube
Max von Laue (1879 - 1960)
X-ray diffraction, 1912
Nobel Prize (Physics) 1914

W. Friedrich, P. Knipping, M. Laue: Interferenzer-
scheinungen bei Röntgenstrahlen. Sitzungsberichte
der königlichen Bayerischen Akademie der Wissen-
schaften, Mathe.-Phys. Klasse (08.06. 1912) (1912)
303-322 [auch Ann Physik 4. Folge 41 (1913) 971]

Linus Carl Pauling (1901 - 1994)
atomic structure of micas, 1930
Nobel Prize (Chemistry) 1954
Nobel Prize (Peace) 1962

(1930) 123-129

1930 Determination of the structure of micas by Pauling provided the
basis for the elaboration of many other clay mineral structures.

> 1930 Several groups began studying clay minerals:

1932 Gruner: structure of kaolinite

J. W. Gruner: The crystal structure of kaolinite. Z Kristallogr 83 (1932) 75-88
1933 Hofmann, Endell and Wilm (Berlin): structure of montmorillonite

Hofmann, Endell and Wilm proposed the structure of montmorillonite consisting of a central octahedral layer and two tetrahedral layers, now accepted. They also explained the swelling of clay minerals on the basis of this structure. In 1934 they identified Bolus and Walkererden (fuller’s earths) - which before were considered as “highly concentrated allophane“ - as crystalline clay minerals.

U. Hofmann, K. Endell, D. Wilm: Kristallstruktur und Quellung von Montmorillonit (Das Tonmineral der Bentonittone.) Z Kristallogr 86 (1933) 340-348
U. Hofmann, K. Endell, D. Wilm: Röntgenographische und kolloidchemische Untersuchungen über Ton. Angew Chem 47 (1934) 539-558

1935 Mehmel (Rostock): structure of halloysite and metahalloysite


1936 Correns and Mehmel (Rostock): identification of clay minerals


1942 Hendricks and Teller: theory of XRD for interstratified minerals (mixed-layer minerals)

Other techniques for clay research

Besides XRD other techniques were also developed around 1930

DTA

- provided additional fingerprints of clay minerals in soils
- better understanding of the physical properties and thermal changes observed by ceramists
- identification (XRD) of the new phases developed by heating

Electron microscopy

- a powerful tool for investigation of clay minerals, information on shape and morphology
- investigation of the finest fraction of bentonites and soil clays

In 1940, von Ardenne, Endell und Hofmann first studied clays minerals by electron microscopy.


Manfred von Ardenne at the electron microscope
Flood of research in three domains of clay applications

1. Bleaching earth

Ancient times - 1906/07

Fuller’s earths (p. 9) were used in ancient times for degreasing and thickening cloths. During a travel in the Middle East an American observed that olive oil is shaken with clay to get a light color. This observation started the use of fuller’s earth for bleaching oils (details will be reported in the Newsletter 2002).

1906 Pfirslinger Mineralwerke Gebr. Wildhagen and Falk, Kitzingen/Main (Germany) produced bleaching earths by reacting clays with acids. The product was called “Frankonite“. Probably at the same time, the Tonwerke Moosburg A. and M. Osterrieder in Moosburg/Germany (now Süd-Chemie) reacted bentonites with hydrochloric acid and marked this product with the name “Tonsil“.


Fuller’s Earth Cream
2. Clays as catalysts

- Until the 1920s crude oil was refined by distillation. Catalytic conversion (cracking) was introduced on the basis of research results in France: "Houdry Process" in 1938
- acid-activated bentonite was first used as catalyst
- acid-activated kaolinite was used a few years later
- base-activated kaolinite was used in the 1950s


- Introduction of the synthetic zeolites A and X killed the use of clays in the refining processes.
- Interest on clays as catalysts raised again with the development of Pillared Clays in the 1970s
- Clays in raw or activated form are used as heterogeneous catalysts in many organic reactions.
- Clay minerals were considered as catalysts that produced the first living on the earth. Research on clays and the origin of the life, already suggested in the religious books, is still of actuality.

Martin Vivaldi Award selection committee appointed in 1999 (Euroclay 1999) the contribution of Bujdak on "Clay catalysis and their possible role in prebiotic formation of peptides" (p. 68).

3. Clays in engineering

- geotechnical problems during the Chicago subway construction (1940) convinced engineers (who performed many tests but could not predict the settlement) that information on clay minerals is vital to the success of building structures.
- This concerned also other large cities like London, Paris, Sao Paulo or Mexico City which are built on soft soil materials.
- In the building industry the use of sealing walls (subterraneous curtains, now with depths of 100 m) became very important:
The procedure goes back to the middle of the 19th century when it was found that watery bentonite suspensions can be used to support unlined borehole walls. However, slurry walling was first broadly noticed in 1967 in the context of the “Stachus“ (Karlsplatz) conversion in Munich.

4. Organoclays

- Importance of interdisciplinarity was already pointed out
- During the 5th anniversary of its founding (1942), the University of Chicago sponsored symposia on various frontiers of science.
- The symposium organized by the department of geology was concerned with clay mineralogy, and clay papers were presented by scientists of different disciplines.
- This established clay mineralogy as significant part of geology.
- Ratcliff concluded from this meeting that bentonite can be used for various applications and established a fellowship with a technical guide committee.
- Jordan, the first fellow, developed a research group on organophilic bentonites (today known as bentones) (1949).


Clay research from 1948 - 1966

About 20 years after the second world war, Grim noted five important orientations:

1. studies of the atomic structure of clay minerals
2. the IR technique as a fundamental method of clay mineral investigation, not only as fingerprint tool
3. the intercalation and adsorption of organic molecules and ions by clay minerals, initiated by Jordan in 1949

4. studying the phases and the structural reorganization of the phases during the thermal treatment of clay minerals

5. studying the various types of clay minerals in soils and sediments and the fundamental factors which control their origin

The fundamental advances in clay mineralogy (atomic structure and surface properties) greatly promoted clay mineral technology.

Clay research from 1966 - 2000

Techniques

1. The use of old but improved techniques (revisted techniques) allows to obtain more information on the clay properties. The application of several techniques within the same apparatus to study the same sample in the same state gives precious informations on the texture and physico-chemical properties of the clays and clay minerals.

2. New techniques were developed and increased our knowledge on the small and not well crystallized particles: NMR, Raman, Mössbauer spectroscopy, Neutron diffraction, CRTA (controlled rate thermal analysis), AFM, ESEM, Plasma etc..

3. Alkylammonium method for layer charge determination


4. Computer modelling as a new useful tool (if the starting parameters are correctly chosen)
Pluridisciplinary and multiscale approach

5. Coupling micro- or mesoscopic properties to macroscopic behavior of clay minerals is more and more taken into account, particularly in civil engineering studies, where the molecular level is no longer neglected.

6. Interdisciplinary research around Clay Science.
   This is not a new idea, but more attention is given to the crossing with Biological Sciences, particularly at the end of the century.

New Clay Materials

7. New clay materials for environment protection and technology:
   Modified clays, pillared clay minerals, and porous clay heterostructures as adsorbents of different kinds of pollutants, for slow release formulations of drugs, pesticides..., and new types of catalysts


8. Nanocomposites of clay minerals (raw or modified) and polymers to improve polymer properties or as conducting polymer membranes for electrochemical devices


Introduction of new layered materials:

9. Layered double hydroxides (LDH) ("anionic clays")

   W. Feitknecht: Über die α-Form der Hydroxyde zweiwertiger Metalle. Helv Chim Acta 21 (1938) 766-784
   R. Allmann: Doppelschichtstrukturen mit brucitähnlichen Schichtionen: [Me(II)_{x}Me(III)_{x}(OH)_{2}]^{x+}. Chimia 24 (1970) 99-108
   H. P. Böhm, J. Steinle, C. Vieweger: [Zn_{2}Cr(OH)_{6}]X · H_{2}O, neue Schichtverbindungen mit Anionenaustausch- und Quellvermögen. Angew Chem 89 (1977) 259-260
10. Alkali silicates and crystalline silicic acids

Magadiite (Eugster, 1967)

Named in 1967 after the first locality Lake Magadi (Kenya).


Synthesis

Kenyaite (Eugster, 1977)

Named in 1977 after the first locality (Lake Magadi) in Kenya.


Synthesis

Makatite (Sheppard and Gude III, 1970)

Makatite is named for the Masai (Kenya) word, emakat, which means soda, in allusion to the high sodium content of the mineral.


Synthetic Magadiite (K. Beneke)

Structural identification:
Synthesis


Kanemite (Johan and Maglione, 1972)

Kanemite was first found in the interdunary depression of Andjia, Kanem, on the north-eastern edge of Chad Lake. The name is taken from Kanem, the region where the salina is located.

Z. Johan, G. Maglione: La kanemite, nouveau silicate de sodium hydraté de néoformation.

Bull Soc France Minéral Cristallogr 95 (1972) 371-382

Synthesis


Silinaite (Chao, Grice and Gault, 1991)

The name alludes to the composition (Si-Li-Na).


Structural identification

J. D. Grice: The crystal structure of silinaite, NaLiSi$_2$O$_5$ · 2 H$_2$O. A monophyllosilicate. Can Mineral 29 (1991) 359-362

Synthesis

Silhydrite (Gude III and Sheppard, 1972)

Silhydrite is named for its composition. It is the first natural crystalline silicic acid, found in Trinity County, California.

J. Gude III, R. A. Sheppard: Silhydrite, 3 SiO$_2$ · H$_2$O, a new mineral from Trinity County, California. Amer Mineral 57 (1972) 1053-1065


Lake Magadi (Kenya)
Clay Science Perspectives

Clay minerals are **nanostructured porous materials** with confined interlamellar spaces which cover unlimited fields of investigations.

Clays and clay minerals must be considered as "respectable", not only for geologists but also for other scientists.

Clay Science plays an important role in basic geological research but advanced fundamental knowledge about clay minerals is strongly needed for the hudge diversity of industrial and applied technologies.

**Clay Science must become more important in physics, chemistry and biology fundamental research, particularly in colloid science and under pharmaceutical and medical aspects**

to communicate more easily between all clay scientists and scientists and clay users, it is necessary to homogenize our clay vocabulary in the world

**Fundamental questions in progress**

1. on clay mineral genesis
2. on the extended fields of clays and clay minerals and
   - water
   - different types of inorganic and organic compounds
   - pollutants
   - polymers
   - other colloids
   - biology
3. on clay minerals and nanotechnology
4. on the colloidal behavior of clays and clay minerals
5. on redox reactions (particularly Fe$^{3+}$/Fe$^{2+}$) and the practical consequences
6. on solid state reaction studies and thermal processes
7. on clay fabric texture and porosity evolution of internal/external surface area and geometry of the pores
8. on multiscale approach analysis with techniques to link "eye observation" of clay mineral behavior and experimental data at the microscopic scale, for several properties and consequently for several applications
9. on purification processes
   • The different types of impurities in raw clays, kaolins, and bentonites present a great inconvenience for fundamental studies and industrial applications.
   • Purification processes need economic methods of separation of the solid materials from the aqueous colloidal dispersions.
10. on synthesis of large amounts of clay minerals
    • In contrast to the synthesis of many types of zeolites, synthesis of clay minerals is very limited. First syntheses of clay minerals were reported by Noll in Hannover (Germany).

W. Noll: Hydrothermale Synthese des Kaolins. Mineral Petrogr Mitt 45 (1934) 175-190

“Card-house“ structure of synthetic fluoro hectorite (from melts, K. Beneke)
Factors promoting advanced clay applications

1. **Scientific factor**

   Development of techniques and progress of fundamental knowledge in geology, physics, colloid science, inorganic and organic chemistry, biology

2. **Economic factor**

   - Nature gives us clays in all continents.
   - Clays are abundant and usually not expensive.
   - Clays are used in a large diversity of industrial processes as cheap products.
   - Clays are starting materials in several synthesis of zeolites, classical oxide ceramics, technical ceramics like SIALONs, mesoporous materials and...

3. **Human factor**

   Recent environmental wake up of our society toward the cleaning of our planet and to take care on pollution produced by human activity, fits perfectly well the benefit of clay applications.

   National and international concerns and directives increase the interests to search new solutions for depollution, and clays are more and more used for decontamination:

   - clays are not risky when used as industrial materials,
   - clays are used by many people as a natural harmless drugs,
   - clays are used in pharmaceutical products,
   - they help to solve environmental problems in agriculture,
   - clays and clay minerals in raw or modified form are effective adsorbents of pollutants.
Teaching Clay Science or Argillology?

Finally, but necessary

We cannot make efficient work in Clay Science without setting up an ambitious and great scientific and technical program in High Schools and Universities, in each country.

It is our role to convince our colleagues, departments, politics on the need for teaching Clay Science on international standard.

International nomenclature in Clay Science

What is a clay for each clay scientist and clay user?

with some questions among others

- Differentiation between "clay mineral" and "clay"
- Can we consider layered double hydroxides (LDH) or iron oxides, ...as "Clay"?

and many other questions ...

The nomenclature committee of AIPEA has in charge this work.
A great work has already been done
However...

Why not to collect opinions of all the clay community members on this question?
Clay Meetings and Conferences

<table>
<thead>
<tr>
<th>Year</th>
<th>Event/Location</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1963</td>
<td>1st ICC Stockholm</td>
<td>CIPEA decision to establish an International Association affiliated to UISG. In 1964, 22nd IGC (India) ratified this decision. In 1966, UISG executive committee agreed with this affiliation.</td>
</tr>
<tr>
<td>1966</td>
<td>2nd ICC Jerusalem</td>
<td>General Assembly: creation of ICC. AIPEA became independent of geology. 1st AIPEA Newsletter as an international link between clay scientist (this term is defined in three languages, p. 41). 36th AIPEA newsletter appeared in 2000 with a message from Schoonheydt on &quot;Clay Minerals and Material Science. Where are we going to?&quot;</td>
</tr>
</tbody>
</table>
Jacques Merin (1904 - 1973) was Director of CRSOCI that he created in 1969 (CNRS, Orleans), one of the founders of GFA (Groupe Francais des Argiles) ans of CIPEA. (F. Bergaya started her thesis with him in 1971).

<table>
<thead>
<tr>
<th>Year</th>
<th>Event Description</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1969</td>
<td>3rd ICC</td>
<td>Tokyo</td>
</tr>
<tr>
<td>1970</td>
<td>1st Hispano-Belge preparative meeting</td>
<td>Madrid</td>
</tr>
<tr>
<td></td>
<td>initiated by J. M. Serratosa and J. J. Fripiat</td>
<td></td>
</tr>
<tr>
<td>1971</td>
<td>1st informal Colloquium Hispano-Belge</td>
<td>Leuven</td>
</tr>
<tr>
<td></td>
<td>+ France + Great Britain</td>
<td></td>
</tr>
<tr>
<td>1972</td>
<td>4th ICC</td>
<td>Madrid</td>
</tr>
<tr>
<td></td>
<td>1st meeting of 12 European national groups + clay scientists of Switzerland</td>
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<tr>
<td></td>
<td>considered as</td>
<td>1st ECG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Madrid</td>
</tr>
<tr>
<td>1974*</td>
<td></td>
<td>2nd ECG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strasbourg</td>
</tr>
<tr>
<td>1975</td>
<td>5th ICC</td>
<td>Mexico</td>
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<tr>
<td>1977</td>
<td></td>
<td>Oslo</td>
</tr>
<tr>
<td>1978</td>
<td>6th ICC</td>
<td>Oxford</td>
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<tr>
<td>1980</td>
<td></td>
<td>Freising</td>
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<tr>
<td>1981</td>
<td>7th ICC</td>
<td>Bologne-Pavia</td>
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<tr>
<td>1983**</td>
<td></td>
<td>Prague</td>
</tr>
<tr>
<td>1984</td>
<td>1st Italo-Spanish Congress in Italy</td>
<td>Seiano di Vico Equense and Amalfi</td>
</tr>
<tr>
<td>1985</td>
<td>8th ICC</td>
<td>Denver</td>
</tr>
</tbody>
</table>

* since 1974 meetings of ECG every three years, like for ICC meetings

** since 1983 meetings of ECG and ICC every four years
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>6th Euroclay</td>
<td>Sevilla</td>
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<tr>
<td></td>
<td><strong>Foundation of ECGA to stimulate clay science and technology among European scientists</strong></td>
<td></td>
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<tr>
<td></td>
<td>1(^{st}) ECGA Newsletter appeared in 1997</td>
<td></td>
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<tr>
<td></td>
<td>3(^{rd}) ECGA Newsletter appeared in 2000</td>
<td></td>
</tr>
<tr>
<td>1989</td>
<td>9(^{th}) ICC</td>
<td>Strasbourg</td>
</tr>
<tr>
<td></td>
<td>7(^{th}) Euroclay</td>
<td>Dresden</td>
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<tr>
<td>1991</td>
<td>10(^{th}) ICC</td>
<td>Adelaide</td>
</tr>
<tr>
<td>1995</td>
<td>8(^{th}) Euroclay</td>
<td>Leuven</td>
</tr>
<tr>
<td>1996</td>
<td>2nd Italo-Spanish Meeting</td>
<td>Granada</td>
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<tr>
<td></td>
<td>+ France, Great Britain, Norway, clay scientists of Switzerland and USA</td>
<td></td>
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<tr>
<td></td>
<td>considered as 1(^{st}) MCM (Mediterranean Clay Meeting)</td>
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<tr>
<td>1997</td>
<td>11(^{th}) ICC</td>
<td>Ottawa</td>
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<tr>
<td>1998</td>
<td>2(^{nd}) MCM</td>
<td>Aveiro</td>
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<tr>
<td>1999</td>
<td>9(^{th}) Euroclay</td>
<td>Krakow</td>
</tr>
<tr>
<td>2000</td>
<td>1(^{st}) Latin-American Clay Conference, LACC</td>
<td>Madeira</td>
</tr>
<tr>
<td>2001</td>
<td>12(^{th}) ICC</td>
<td>Bahia Blanca</td>
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<tr>
<td></td>
<td>1(^{st}) Mid-European Clay Conference, MECC</td>
<td>Stará Lesná</td>
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<tr>
<td>2002</td>
<td>3(^{rd}) MCM</td>
<td>Jerusalem</td>
</tr>
<tr>
<td>2003</td>
<td>10(^{th}) Euroclay</td>
<td>Modena</td>
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</tbody>
</table>

**Conclusion**

Participation on Clay Conferences is very important and necessary but clay scientists should have the time to do their work in the laboratory and on the field.

**Note:**
The lack of clay groups is noticed in some (developing) countries, particularly in Africa. It is the role of the AIPEA members to increase the interest of these people in Clay Science.
Definition of "Clay Scientist"

in three languages in the first AIPEA Newsletter (1966):

The term ‘clay scientist’ is used in its widest sense as it covers a very large and varied group, with representatives in the cement industry, ceramics industry, civil engineering, cosmetic industry, crystallography, foundry technology, geology, geotechnics, medicine, mineralogy, paint industry, paper industry, pedology, petroleum industry, rubber industry, et cetera.

Le terme ‘spécialiste qui s’intéresse aux argiles’ est employé dans sa signification la plus vaste et couvre un groupe très varié et grand, qui a des représentants dans l’industrie de la céramique, l’industrie du ciment, l’industrie du caoutchouc, l’industrie de la cosmetique, la crystallographie, la technologie des fonderies, la géologie, la géotechnique, les ingénieurs civils, la médecine, la minéralogie, l’industrie du papier, la pédiologie, l’industrie de la peinture, l’industrie du pétrole, et cetera.

Der Term ‘Tonspezialist’ wird hier sehr weit gefaßt und deckt eine große und vielfältige Gruppe, deren Repräsentanten in vielen verschiedenen Zweigen der Forschung und Industrie tätig sind: Bauingenieur, Wissenschaft, Bodenkunde, Farbindustrie, Geologie, Geotechnik, Gießereitechnik, Gummiindustrie, Keramische Industrie, Kosmetikindustrie, Kristallographie, Medizin, Mineralogie, Papierindustrie, Petroleumindustrie u. a. m.

Legends

IGC  International Geological Congress
CIPEA Comité International pour l’Etude des Argiles
ICC  International Clay Conference
UISG Union Internationale des Sciences Géologiques
AIPEA Association Internationale pour l’Etude des Argiles
ECG  European Clay Groups
ECGA European Clay Groups Association
MCM Mediterranean Clay Meeting
LACC Latin-American Clay Conference
MEC Mid-European Clay Conference
MECC Mid-European Clay Conference