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CLAY MINERALS INCLUDING RELATED PHYLLOSILICATES: INTERDISCIPLINARY RESEARCH AND INWARD INTEGRATION

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ABSTRACT

More than 110 species of clay minerals and related phyllosilicates were discovered mostly in the 20th and 19th centuries, including 13 regular interstratifications (R1 range) naturally occurring or synthesized and referred to between 1950-2003. This contribution to theoretical and applied clay science, whose evolution is based on mineralogical roots, stresses interdisciplinary research among clay science, basic sciences (physics, chemistry, mathematics, geometry), earth-, biological-, applied- and related sciences and engineering technologies as a basis for substantial past and future discoveries. Not only a novel desirable cooperation with other theoretical and applied disciplines, but also a close inward integration among the six major research regions of clay science is necessary for its further development. Two diagrammatic presentations show: 1) a desirable multidisciplinary cooperation and mutual influence among sciences and technologies affecting the development and progress of clay science; 2) a view of desirable integration among the six major research regions within clay science in the near future.

KEYWORDS: theoretical and applied clay science, history, names of clay mineral species and related phyllosilicates (more than 110), research regions and subregions, interdisciplinary cooperation, desirable inward integration

1. INTRODUCTION

Clay minerals are essential constituents of argillaceous sediments and accompanying argillized volcanoclastics, weathering crusts, soils and hydrothermal clay accumulations. Most of these genetically different mineral accumulations contain important clay raw materials used by man through millennia. Argillaceous accumulations are typical of the surface region of the Earth. This means that many clay raw materials are easily accessible and extractable anywhere in the world. At present, clay raw materials are used in numerous industrial branches, especially in ceramics, paper, rubber, plastics, chemical, agrochemical, dyes, foundry, and cement industries and as silicate binding materials, in pharmaceutic, cosmetic, food, petroleum industries, and in civil engineering and ecological projects (Grim, 1962; Konta, 1995). Soil science and agriculture have applied theoretical clay science and its methodology for a long time (Gjems, 1967; Jackson, 1969; Gieseking, 1975; Stucki and Banwart, 1980; Smart and Tovey, 1981, 1982; Bolt, 1982; Sposito, 1984; Kodama, 1985; Dixon and Weed, 1989; Mackenzie, 1990). The knowledge of electrochemical properties of clay minerals occurring in the oil-bearing strata has been of great utility (Wyllie, 1955). The diagenetic transformations of clay minerals in sediments of different geological formations and ages are closely connected with the genesis and extraction of earth oil and gas (from Weaver, 1956; Burst, 1969; Shutov *et al.*, 1969; up to Drits *et al.*, 1997; Sakharov *et al.*, 1999a, b; Niu *et al.,* 2000; or Plançon and Drits, 2000; and others quoted by Konta, 2000).

No wonder that clay minerals, clay raw materials, many different argillaceous accumulations, and soils are intensively studied by mineralogists, petrologists, geologists, clay- and soil scientists, chemists, physicists and engineers of engaged technological branches. The results of their investigation may fall in one or more of the six major research regions of clay science: 1) crystal structures (including chemistry); 2) research methods (including modelling); 3) investigation of natural accumulations and genetic conditions of clay and related minerals; 4) physical and physicochemical properties of clay minerals and argillaceous rocks; 5) modified clays (by chemical or physical treatments); 6) applied clay science including exploitation and beneficiation of clay raw materials and ecological projects.

Although clay science has mineralogical roots in the 18th and especially 19th century, it emerged as an authentic scientific discipline in the mid-20th-century (Konta, 2000). The primary merit lies in the use of X-ray diffraction method and wide interdisciplinary cooperation of mineralogy, petrology, chemistry (inorganic, organic, analytical, physical chemistry and especially colloid chemistry), physics, mathematics, soil science and engineering technologies. Each of these disciplines has contributed to the development of clay science either by its theory, or research methods, experimental materials and research results.

2. MINERALOGICAL ROOTS OF CLAY SCIENCE

First mineralogical descriptions and chemical characterization of clay minerals and related phyllosilicates, including their macrocrystalline equivalents denoting mineral species or giving group and series names, go back to the 18th century: chlorite /a group name/, lepidolite /a series name/, mica /a group name/, montmorillonite, talc; terms mica, kaolinite (or kaolin), talc, similarly as "clay" or fuller's earth (Robertson, 1986), being still much older. Mineralogists of the 19th century were much more successful in the description of new layer hydrosilicates: allophane, amesite, antigorite, aspidolite, batavite, biotite /a series name/, celadonite, chamosite, chrysotile /a series name/, clinochlore, corundophyllite, cronstedtite, delessite, diabantite, ephesite, glauconite /a series name/, halloysite, kaolinite, muscovite, nacrite /a polytype/, nontronite, palygorskite, paragonite, penninite /or pennine/, phengite /a series name/, phlogopite, polylithionite, pyrophyllite, ripidolite, roscoelite, saponite, sauconite, sepiolite, serpentine, siderophyllite, stevensite, tainiolite, thuringite, vermiculite /trioctahedral and dioctahedral, distinguished in the 20th century/, volkonskoite, zinnwaldite /a series name/. Mineralogical research during the 20th century discovered further clay mineral species and related phyllosilicates: aluminoceladonite, annite, attapulgite, baumite, beidellite, berthierine /"kaolinite-type chamosite"/, boromuscovite, brammalite /a series name/, brindleyite, brunsvigite, cardenite, caryopilite, chromophyllite, clinochrysotile, cookeite, dickite /a polytype/, donbassite, eastonite, ferroaluminoceladonite, ferroantigorite, ferroceladonite, ferrocorundophyllite, garnierite, greenalite, griffithite, hectorite, hendricksite, illite /a series name, or hydromica/, imogolite, lepidomelane, lizardite /Mg and Al species/, loughlinite, masutomilite, medmontite, metahalloysite, minnesotaite, montdorite, nanpingite, nepouite, nickelian lizardite /nepouite series/, nickel vermiculite, norrishite, orthochrysotile, pimelite, preiswerkite, sheridanite, sudoite, tetra-ferriannite, tetra-ferriphlogopite, tobelite, willemseite, wonesite. The primary literature regarding some of these names and their first locality has been quoted by Bergaya *et al.* (2001). The priority authors with the years of the first publications about nearly all phyllosilicate species known prior to 1954 are referred to in the *Chemical Index of Minerals* (Hey, 1955). Many useful data can be found in the book, *Mineraly ilaste,* by Stoch (1974). The original discoveries of regular phyllosilicate interstratifications occurring or synthesized in the 1:1 ratio, i.e. R1 range, and published in the period between 1950-2000 (here until 2003) are referred by Konta (2000). They have been named as mineral species: rectorite (di Mi-di Mo, Bradley, 1950), corrensite (Ch-Ve or Ch-Sm, Lippmann, 1954, 1956), aliettite (Ta-Sa, Alietti, 1956; Veniale and v.d. Marel, 1968), tosudite (di Ch-di Mo, Sudo and Kodama, 1957; Frank-Kamenetsky *et al.,* 1965), Ka-Mo (not named, Altschuler *et al.,* 1963), hydrobiotite (Bi-Ve, Veniale and v.d. Marel, 1969), kulkeite (Ta-Ch, Schreyer *et al.*, 1982), Bi-Ch (not yet named, Olives and Amouric, 1984), Bd-Mo (synthetic, Yamada and Nakasawa, 1993), dozyite (Sp-Ch, Bailey *et al.,* 1995), trioctahedral rectorite (Mi-Sa, synthetic, Yamada *et al.,* 1999), Ch-Sa (synthetic, Yamada *et al.,* 1999), brinrobertsite (Pyph-Sm, Dong *et al.*, 2002). Abbreviations used: Bd = beidellite, Bi = biotite, Ch = chlorite, di = dioctahedral, Ka = kaolinite, Mi = mica, Mo = montmorillonite, Pyph = pyrophyllite, Sa = saponite, Sm = smectite, Sp = serpentine, Ta = talc, Ve = vermiculite.

Nomenclature of the micas according to Rieder *et al.* (1998) has been respected. For chlorites, the nomenclature by Foster (1962) has been adopted. Other names of chlorite species according to several diverse classification schemes (cf. Brindley, 1961) are not applied here. Polymorphs, but exceptionally polytypes, are taken as mineral species. Group names and series names are indicated.

More than 110 clay mineral species together with series names and related phyllosilicates including their macrocrystalline structural equivalents together with the named regular interstratifications are known up to the year 2003. Numerous varieties and polytypes would substantially exceed this number. Random interstratifications of phyllosilicates are common in nature, occurring in hundreds of possible combinations (see literature evaluated by Konta, 2000).

New methods of the 20th century, especially X-ray diffraction, and later IR spectrometry, TEM, SEM, HRTEM and EDAX together with other chemical and physical methods (see Konta, 2000) enabled not only discoveries of new phyllosilicates and their OD diversities, but to remove many superfluous names of "mineral species" from the system of phyllosilicates. Names like "picrolite, baltimorite, marmolite, williamsite, antillite, aphrodite" and others in the chrysotile-antigorite series of minerals are disregarded (Nagy and Faust, 1956). All serpentine minerals, *i.e.* 1:1 trioctahedral phyllosilicates, belong either to chrysotile (ortho- and clinochrysotile) or antigorite or lizardite (Whittaker and Zussman, 1956). "Anauxite" having excess silica compared to kaolinite is not more mineral species of the 1:1 dioctahedral phyllosilicates. "Anauxite" and kaolinite structures are identical (Bailey and Langston, 1969; Allen *et al.,* 1969). Opal particles associated with the kaolinite plates in the "anauxite" from Bilina were observed first under polarizing microscope and determined by index of refraction (Konta, 1957). Further superfluous names of "mineral species" disappeared in the course of modern investigation from the mineralogical system of chlorites, micas and other phyllosilicate groups.

The real clay minerals belong to the following groups: *mica* (the dominating mineral having the mica structure in clays is *illite* /a series name/ and its interstratifications with other clay minerals are common), *vermiculite, smectite, serpentine-kaolinite, talc-pyrophyllite, chlorite, pseudophyllosilicates or hormites (sepiolite-palygorskite)* and *allophane*. Micas as macroscopic equivalents of illite are taken in the system because their investigation helped much in the recognition of 2:1 clay/grade phyllosilicates. Micas without or with extremely small amount of molecular water (H_2O or H_3O^+) in the interlayer space are typical of mineral assemblages other than clays or they occur in clays as clastic remnants from other non-clay assemblages. Similarly, brittle micas (margarite, chernykhite, clintonite, bityite, anandite, kinoshitalite) having also the phyllosilicate structure, do not occur in natural assemblages typical of clay minerals. They belong to the system of phyllosilicates but are usually ignored by experts working with clays.

Bergaya *et al.* (2001) quoted some authors who introduced new layered materials, namely layered double hydroxides (LDH). Their general formula can be written as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$. The layer crystal structure of LDH is similar to that of brucite, $Mg(OH)_2$. When combined with one of anions, they are called "anionic clays". Hydrotalcites are "hydrotalcite-type anionic compounds" or more descriptively "layered double hydroxides of divalent and trivalent metals combined with carbonate anion". For example, a common hydrated hydroxycarbonate of M^{2+}, M^{3+} has a formula $[Mg_3Al(OH)_8]_2CO_3.nH_2O$. Divalent metals M^{2+} can be e.g. Mg^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}. Trivalent metals M^{3+} in these compounds are Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}. Hydrotalcite-like compounds have a general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}mH_2O$, where A^{n-} means anion, e.g. F^-, Cl^-, ClO_4^-, OH^-, NO_3^-, CO_3^{2-}, SO_4^{2-} or organic or complex anion, and x is atomic ratio of $M^{3+}/(M^{2+}+M^{3+})$ (Moroz *et al.,* 2001).

Due to the layered structure, LDH, hydrotalcites and hydrotalcite-like compounds reveal some properties related to the behaviour of clay minerals. They found use in practice, e.g. for their excellent catalytic, or sorptive capacities and simple, easy synthesis. LDH, however, are not hydrosilicates with alternating tetrahedral and octahedral sheets, which is primary a diagnostic condition for clay minerals. Similarly, although not layered hydrosilicates, zeolites with their catalytic, sorptive and ion exchange properties are widely used in practical applications close to those of natural or modified clay minerals.

The above shortly mentioned inorganic compounds cannot be included in the system of clay minerals or phyllosilicates, because they do not correspond the definition of clay minerals. Due to some of their properties resembling clay minerals, the research results on LDH, hydrotalcites, hydrotalcite-like compounds and zeolites are welcomed in journals specialized in clay science or become symposial parts of clay conferences.

Some alkali hydrated silicates, mentioned by Bergaya *et al.* (2001), discovered in the second half of the 20th century deserve more attention of mineralogists, crystallographers and engineers of potential technological branches. These silicates are distinguished according to their different Na_2O (or Li_2O):SiO_2:H_2O ratios (kanemite, kenyaite, magadiite, makatite, silinaite; see Eugster, 1967; Lagaly *et al.,* 1972). They occur together with layered crystalline silicic acid (silhydrite) in salina environments or can be easily synthesized. It seems, however, that they are not consistent with clay minerals having phyllosilicate structure and alternating tetrahedral and octahedral sheets (Annehed *et al.,* 1981).

3. RAPID PROGRESS DUE TO INTERDISCIPLINARY RESEARCH

The investigation of clay minerals, clay raw materials or soils lies not only in the recognition of clay mineral species, their order-disorder states, and genetic conditions. The understanding of such phenomena or properties as ion exchange, ion exchange capacity, swelling and shrinkage, thermal dehydration and rehydration, adsorption, absorption, desorption, sorption selectivity of phyllosilicates, acidity of clays, catalytic activity, plasticity, particle size distribution, dispersion in water or other liquids and the effect of electrolytes, flocculation and deflocculation of clay particles, differences in surface area, sealing properties, porosity, permeability, hydraulic conductivity, transport of chemicals through clays, ion diffusion, thixotropy and quasiviscosity of clay suspensions necessitated cooperation of mineralogy or sedimentary petrology with other science disciplines and experts of different production technologies (Konta, 2001). The research beginnings of the majority of these phenomena or properties preceded the era of the determination of crystal structure of clay minerals by X-ray diffraction. Some of the initial research reports, for example, on the absorption and desorption (Thompson, 1850; Way, 1850, 1852, 1854; van Bemmelen, 1878), on thermal dehydration and rehydration (Le Chatelier, 1887), plasticity and cohesion (Atterberg, 1910), ion exchange (Wiegner, 1912), particle size distribution (see references by Andreasen, 1929), the acidity of colloidal clay in soils (see references by Bradfield, 1923) or on thixotropy (Freundlich, 1928; Buzagh, 1929; Hauser and Reed, 1937) go back even more than 100 to 150 years ago. It was quite natural that the recognition of the above-mentioned properties or behaviour of clay matter attracted attention and cooperation of the basic sciences and experts of various production technologies. Ceramic technology, for example, still is in need of more information, namely about green and dry strength, dilatancy of dense suspensions, sintering temperature, sintering range, fusion temperature, thermal dilatation of prepared bodies, firing colour and others. The research of these and related phenomena and properties of clay matter above all, needed the support of the basic sciences, namely mathematics, physics and chemistry.

Similar interdisciplinary cooperation took place later in the research of the crystal structure and crystal chemistry of phyllosilicates (from 1928 till the present). Especially the intense entry of chemists and physicists into the mineralogical research and the application of the X-ray diffraction method brought about the first determination of atomic structure and crystal chemistry of some common clay minerals (Mauguin, 1928; Pauling, 1930a, b; Gruner, 1932a, b, 1933, 1934 a, b, 1935a, b; Hofmann *et al.,* 1933; Kazantsev, 1934; and others, see literature by Konta, 2000). The discovery of polytypism, first in the kaolinite minerals (Hendricks, 1939) and later in micas (Heinrich and Levinson, 1955), and the following refinement of crystal structures in all groups of phyllosilicates and their polytypes was a result of a cooperation among physicists, crystallographers, chemists and mineralogists in later decades (see literature compiled by Konta, 2000). Physicist Zvyagin with Pinsker (1949) introduced electron diffraction analysis into the investigation of clay grade crystals. Physicist Brindley with Robinson (1946, 1948) are first credited with the discovery of structural order-disorder states in a whole series of kaolinites. Ten years later, Brindley and Nakahira (1958) opened a new topic in the structural mineralogy by the first explanation of the nature of the interlayer hydrogen bonds in kaolinite minerals. A strong influence of physical chemistry and physics upon the research of order-disorder states of phyllosilicates is evident. This extensive research topic is connected with the investigation and the role of defects in solid state physical chemistry followed in literature for about 70 years (Lidiard, 2003). The phenomenon of different disorder states is proper to any crystalline material.

Radoslovich (1959, 1960, 1962, 1963a, b) and his coworkers (Radoslovich and Norrish, 1962; Veitch and Radoslovich, 1963) discovered further irregularities in the atomic structure of muscovite and later in the structure of other phyllosilicates. They measured cell dimensions, composition limits, interatomic forces, symmetry and distortion of octahedra and tetrahedra in phyllosilicates. They found that actual layer structures depart from the ideal hexagonal arrangement. Twists and tilts of the tetrahedral TO_4 groups in the mica structure have been documented in detail in their studies. They showed that 1*M*, 2*M* and 3*T* polytypes are common in nature. The trigonal form of the tetrahedral network accommodates the interlayer K^+ ions more satisfactorily in the observed mica polytypes than in the unobserved or rare forms. Basal oxygens are no longer coplanar but form corrugated surfaces. “Local balance of forces” in layer structures may provide a means of structural control over polytypism.

The application of spectroscopic methods and modernized electron microscopy with the theoretical basis in physics or physical chemistry helped a lot in the investigation of different structural and chemical inconformities commonly occurring in the crystals of phyllosilicates. First simple infrared studies of phyllosilicates fall into the mid-20th-century (Adler, 1950; Hunt, 1950; Keller and Pickett, 1950). Later, chemists Farmer (1968) specialized in the research of soils, and Parker (1969) specialized in ceramic clays successfully applied infrared spectroscopy to the investigation of the stacking relationships in phyllosilicates. Other spectroscopic methods (Mössbauer, Raman, electron spin resonance, neutron scattering method, diffuse reflectance spectroscopy, ultraviolet and visible light spectroscopy) and different magnetic resonance methods highly contributed to the knowledge of phyllosilicates and their modified derivatives (Bailey, 1975 and other authors; Fripiat, 1981; see literature evaluated by Konta, 2000).

Crystal chemistry of clay minerals encountered new horizons by the discovery of different chemical domains and cationic order-disorder states in individual structural sheets (Gatineau, 1964) and interlayer space (Besson *et al.,* 1974; Stul and Mortier, 1974; Lagaly and Weiss, 1976).

Geologists and sedimentary petrologists Weaver (1956), Kossovskaya and Shutov (1955, 1958, 1963), Burst (1969), Shutov *et al.* (1969), Dunoyer de Segonzac (1969), Weaver and Beck (1971) were the first to recognize the genetic importance and practical use of mixed-layer clay minerals, namely, their postsedimentary transformations in the sedimentary lithosphere.

Since 1940 electron microscopy, the domain of physicists, successfully applied by mineralogists, has enabled to study the shape variability of clay and related minerals (von Ardenne *et al.,* 1940). Later, it has been adopted as transmission (TEM or STEM) and scanning (SEM) electron microscopy, both methods simultaneously used e.g. for the investigation of morphological changes in a continuous smectite-to-illite conversion series (Ahn and Peacor, 1986; Inoue, 1986). Page and Wenk (1979) using TEM were the first to observe fine-scale intergrowths of micas with other clay minerals including chlorite in fine-grained alteration products of plagioclase. Veblen and Buseck (1979) used TEM for the study of mixed layering in serpentine minerals. However, the fine intergrowths, mixed-layering defects and different clay mineral interstratifications were still more effectively studied using high resolution transmission electron microscope (HRTEM), as shown by McKee and Buseck (1978), Buseck and Veblen (1981) or Veblen (1983). HRTEM helped much in the study of diagenetic transformation of phyllosilicates, e.g. mixed-layer Il-Sm (Guthrie and Veblen, 1989), or illitisation of smectite (Amouric and Olives, 1991). Środoń *et al.* (1990) used the HRTEM for measurement of the expandability of mixed-layer Il-Sm. HRTEM has been used for the investigation of some inconformities in the order-disorder states up to the position of individual atoms (literature quoted by Konta, 2000).

Specialized physicists and crystallographers applying the necessary mathematics developed and later refined the modelling as well as the simulation of crystal structures. This included the defects and the dynamics of structural transformations using computer technology (Reynolds, 1967, 1985; Bookin *et al.,* 1978; see more literature collected by Konta, 2000). Towards the end of the 20th century, the great contributions of physicists and crystallographers working in clay science led to the modular analysis of crystal structures (Zvyagin, 1997, 2001). Modular crystallography involves consideration, description, and derivation of modular structures, i.e. to simultaneously detect components, polymorphism, polytypism and order-disorder (OD) diversity. According to Zvyagin (2001), electron diffraction texture patterns are especially effective for the investigation of delicate inconformities in layer structures. They display separately the features of structural layers and how the layers are stacked. Electron diffraction applications have produced refinements or even a revision of results obtained from other techniques, which have imported to change ideas and conclusions in areas of polymorphism, polytypism and OD structures. The modular crystallographic analysis requires an experienced crystallographer indeed.

The strong influence of chemistry, physics and engaged technologies led to the preparation and investigation of modified clays. They comprise hydrophilic monocationic clays (e.g. with Na^+ or Ca^{2+} or other inorganic interlayer cation), organoclays, pillared clays (mostly with RIII and RIV oligomeric inorganic cations), acid activated clays, specifically calcined clays and systematically milled or ground clays.

In summary, chemistry, physics together with applied mathematics, and clay mineralogy influenced all research regions of clay science. The greatest progress, however, has been attained in the investigation of crystal structures and crystal chemistry of clay minerals.

The investigation of clay minerals and argillaceous accumulations, and the current state of clay science, have been and will continue to be the result of an interdisciplinary and multidisciplinary cooperation. It is done by nature, and still more by extensive and multilateral use of clay matter. The historical, existing, and future interdisciplinary integration of scientific disciplines and technologies for a better recognition and use of clay materials can be illustrated by a simple diagram (Fig. 1) showing their mutual influence. Such a desirable interaction of numerous scientific disciplines and technologies is not a privilege of the clay science alone, but of any science or technology.

4. EXISTING AND DESIRABLE CLOSE INTEGRATION OF SIX MAJOR RESEARCH REGIONS WITHIN CLAY SCIENCE

In clay science, the continuing and strenghtening influence of basic sciences for over more than seventy years led, first of all, to a strong progress in the recognition of crystal structures and crystal chemistry of individual phyllosilicates (the 1st research region). The successful development and application of the research methods is closely connected with the impressive crystal structure research region including crystal chemistry. Today, we can say that the knowledge in these two major research regions, i.e. 1) crystal structures and 2) research methods, has got ahead of the other four major research regions of clay science. The progress in the remaining four research regions of clay science depends now on the transmission of the attained structural discoveries, their effective integration, and the use of the most modern methods.

The 2nd research region of clay science, “Research methods”, comprises nearly 100 different methods for the investigation of clay minerals and argillaceous rocks (Konta, 2000). Each of these methods can be an individual research subregion. I don’t know any scientist who has mastered all these methods. I don’t know any laboratory or institution which uses half or more of these research methods. But this is not important. Much more significant for any research project is to know how to establish an effective cooperation among the institutions and individuals mastering the right methods.

The 3rd research region of clay science, i.e. “Investigation of natural accumulations and genetic conditions of clay and related minerals”, can be thematically divided into nine subregions: a) weathering processes, the behaviour of parent constituents (minerals and volcanic glass) and newly formed clay minerals in the weathering crusts and soils; b) hydrothermal clay minerals and their transformations; c) clay minerals in muds, clays and sedimentary rocks deposited in rivers, lakes, seas and oceans, and eolian deposits; d) erosion, transport, and sedimentation of clay particles, basin analysis; e) burial diagenesis; f) isotopes (O, H) and temperature history of clay minerals, and Rb-Sr, K-Ar or other isotope dating; g) synthesis of clay minerals; h) kinetic and thermodynamic approach, phase equilibria diagrams; i) medium- and high-temperature crystalline phases of clay minerals, notably in the SiO_2-Al_2O_3-H_2O system, but also in other chemical systems. The subregion “burial diagenesis” seems to be the most deeply and the most widely examined theme. The paper on the distribution, methods of identification and petrological importance of mixed-layer clay minerals in sedimentary lithosphere by Weaver (1956)

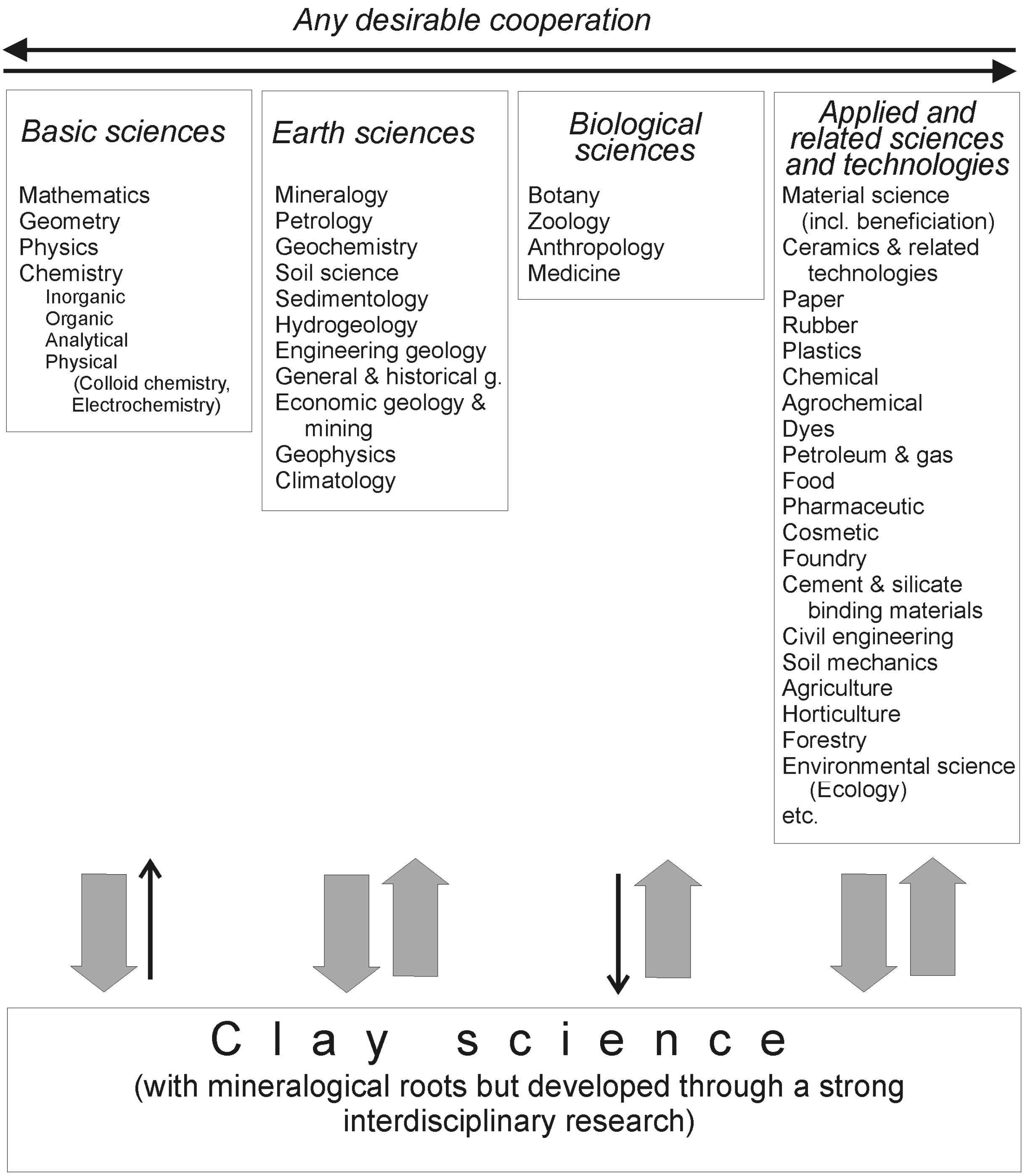

Fig. 1 Existing and desirable cooperation of clay science with the most influential theoretical, applied and related sciences, and respective technologies. The mutual influence is illustrated by arrows of varying strength.

was an initial work based on statistically large experimental material. His study of more than 6,000 sedimentary rock samples has shown that mixed-layer clay minerals are abundant in sedimentary basins, being present in approximately 70 % of the rocks. The investigation was supported by Shell Development Company, Houston, Texas. Weaver stated that random interstratifications Il-Mo with ratio ranging from 9:1 to 1:9, and Il-Ch-Mo are most abundant. Ch-Mo and Ch-Ve are common but relatively less abundant. Three different regular Ch-Ve interstratifications have been found. Similarly important have been the independently obtained data on the depth mineral zonality with well defined phyllosilicate, zeolite and other mineral associations in North Siberian sediments of different geological ages published by Kossovskaya and Shutov (1955, 1958, 1963), and Shutov *et al.* (1969). Burst (1969) studying the diagenesis of Gulf Coast clayey sediments finally dared to state its possible relation to petroleum migration. Burst was the first who referred that during the transformation of smectite to illite, a dehydration process takes place, which is strongly correlated with the production of hydrocarbons and primary oil migration. Dunoyer de Segonzac (1969) published further remarkable results on the diagenetic transformations of clay minerals and the parallel changes of organic combustible substance from the bore holes of the Douala Basin, Cameroon. The Cretaceous and Tertiary strata of pelites and lutites of the thickness of about 4 000 m contain, with increasing depth, gradually transformed phyllosilicates in two different rows. Montmorillonite transforms in the following sequences: 1) in the Mg-rich environment Mo → Ch-Mo or Ch-Ve → corrensite → chlorite, while 2) in the K-rich environment Mo → Il-Mo or Il-Ve → rectorite → illite. The nonvolatile organic C to total organic C ratio increases with depth from 0.1 to about 0.5-0.8. Later on, other authors of numerous papers measured the reflectance of vitrinite, one form of the solid organic combustible substance, which increases with the depth and the carbon content (e.g. Barker and Elders, 1981; Price, 1983; Sweeney and Burnham, 1990; Barker, 1991; Velde and Lanson, 1993; and many others; see also an excellent monograph by Degens, 1967).

The great progress in the investigation of diagenetic transformations of clay minerals in sedimentary basins of different geological ages, although mostly achieved in laboratories of dozens of universities, has occurred thanks to wide financial support granted by oil production companies, and geological or exploration surveys or the bureaus of economic geology of rich countries interested in hydrocarbon research programs. Good evidence of such concentrated research activities can be found in five specialized issues of the *Clay Minerals* journal published between 1984-2000. Vol. 19 (No. 3), June 1984, is devoted to "Patterns of mineral diagenesis on the NW European continental shelf and their relations to facies and hydrocarbon accumulation". Vol. 21 (No. 4), October 1986, contains 21 papers on "Features of mineral diagenesis in hydrocarbon reservoirs". Vol. 24 (No. 2), June 1989, with 17 papers, is oriented to "Clay diagenesis in hydrocarbon reservoirs and shales". Vol. 29 (No. 4), October 1994, contains 21 papers devoted to "Diagenesis, overpressure and reservoir quality". The last issue Vol. 24 (No. 1), March 2000, contains 25 papers on 322 pages and is entitled "Mineral diagenesis and reservoir quality – the way forward" (papers from Jeans, 2000, to Macaulay *et al.,* 2000). Similar issue appeared in *Clays and Clay Minerals*, 1993, Vol. 41 (No. 2), with 12 papers, p. 117-267, on the theme "Geothermometry and geochronology using clay minerals". It is not known that another genetic process would be as much financially supported and as deeply and widely studied as "burial diagenesis" of clay minerals or argillaceous rocks.

Close integration of geology with clay mineralogy, crystallography and crystal chemistry over the past three decades has enabled some mineralogical generalizations in burial diagenesis. From numerous published results, let us quote the latest views important for geological interpretations. Meunier *et al.* (1998) deduced several possible reactions that may occur during the diagenetic transformations of clay minerals: 1) low-charge montmorillonite + K^+(mica) → high-charge montmorillonite + illite + quartz; 2) high-charge montmorillonite layers → illite + chlorite + quartz; 3) low-charge montmorillonite → high-charge beidellite + saponite + quartz; 4) high-charge beidellite + saponite + K^+ → ordered Il-Sm + chlorite + quartz. Lanson *et al.* (1998) also showed that diagenetic history of the Tet:Oct 2:1 phyllosilicates in different sedimentary basins varied as a function of the geothermal gradient and its duration. They quoted numerous authors who systematically studied and reported on smectite illitization in argillaceous diagenetic series of different basins during the past thirty years. Their common diagenetic evolution scheme depending on the time-temperature conditions experienced by the sediments can be expressed by the following reaction sequence: smectite → randomly interstratified Il-Sm → ordered Il-Sm → illite. Well crystallized illite is the ultimate reaction product for the illitization of both Il-Sm precursors and kaolinite-group minerals. Kaolinite can be diagenetically transformed into smectite under higher activity of Mg^{2+} and Ca^{2+}, e.g. from the dolomite source, as experimentally proved by Nadeau (1998). Transformation of kaolinite to dickite in several buried oil-bearing sandstone reservoirs proceeds with increasing depth and temperature in the following sequence (Beaufort *et al.*, 1998): disordered kaolinite (600 m) → kaolinite ± disordered dickite → disordered dickite ± ordered dickite → ordered dickite + disordered dickite → ordered dickite (5,000 m). The dissolution of clastic feldspar accelerates the crystallization of ordered dickite starting from a depth about 3,000 m. Drits *et al.* (1998) investigated the changes in the crystal structure of 2:1 layers in diagenetic or hydrothermal illites and illite-smectites still into greater details. The determined amounts of *cis* (w_{cv}) and *trans* (w_{tv}) vacant 2:1 layers using both WILDFIRE simulation program and calculations based on some X-ray reflections enable an evaluation of the mechanism of illitization in various geological environments. Significant changes in w_{cv} and w_{tv} during illitization are likely due to a dissolution-precipitation, whereas almost constant values indicate a solid-state transformation.

The historical monograph by Konta (2000) reports upon a number of further papers on the progressive burial diagenesis and clay mineral transformations. They include formation of crystallites, dissolution/crystallization, precipitation and crystal growing, solid state transformation, changes in tetrahedral and octahedral sheets and interlayer space, Ostwald ripening, ion exchange, changes in layer charge, NH_4^+ ion in Il-Sm interstratifications, changes in particle morphology, TEM, SEM and HRTEM imaging, the role of water in the Sm-to-Il reaction, oxidation/reduction, compaction, dehydration, participation of non-clay materials, changes in the orientation of the anisometric components (by SEM), clay minerals in different microenvironment of the pore space, determination of Il-Sm and other structures using multispecimen X-ray diffraction profile fitting, determination of reliable and detailed structural models for mixed-layer minerals (MPFP = multi-specimen profile), oxygen isotope systematics, laboratory synthesis of clay mineral inter-stratifications, and on other themes.

The activities of major clay-mineral-forming elements, i.e. Al, Mg, Fe, Si shielded by oxygens ±hydroxyls, and Ca, Mg, Na, K, NH_4 hydrated with interlayer water, and the thermal gradients with time control the resulting mineral assemblage in any argillaceous accumulation. This is valid not only for the burial diagenesis of argillaceous sediments or hydrothermal assemblages but also for weathering crusts and soils. The argillization of primary rockforming minerals and volcanic glass has been expressed in literature by many stoichiometric equations in the mineral(volcanic glass)-water-(acid) systems (Keller, 1957; Loughnan, 1969 and many others). Thermodynamic or kinetic reaction diagrams may help a lot in the interpretation of genetic conditions and solubility of clay minerals (e.g. Zen, 1962; Helgeson *et al.*, 1969; Lippmann, 1981;Tardy and Fritz, 1981; Aagaard and Helgeson, 1983; Garrels, 1984).

Can we expect such great results as in the "burial diagenesis" in the investigation of clay minerals of weathering crusts or hydrothermal accumulations? The suitable samples are at one's disposal in many sites. This has been also the cause why clay mineral assemblages from weathering crusts and soils formed from various types of rock under varying conditions in the whole world were distinguished relatively early in the 20th century (see books by Grim, 1953; Chukhrov, 1955; Keller, 1957; Loughnan, 1969; Stoch, 1974). Similar knowledge has been attained in the investigation of hydrothermal clay associations. Now, can the most promissing discoveries using modern methods, and under the influence of all the recognized order-disorder states of clay minerals, be expected in the investigation of clay pseudomorphs after known rockforming silicates and volcanic glasses. It has been shown by several authors (see quotations and authors' results by Proust and Velde, 1978; Konta, 1981) that clay pseudomorphs, after rockforming silicates in weathering crusts, preserve the chemical micromilieu of original primary minerals not only in the root parts but also in the completely argillized upper parts of the profiles. The movement of aqueous solutions is initially controlled by the capillary system of the original cleavage and by the crystal structure of individual primary silicates. But later, the flow is combined with ion diffusion in the very dense capillary system within the clay mass. The narrow capillary and interlayer ways, the tortuosity of pathways and large specific surface area of newly formed clay matter retard any big scale equilibrium. The individual chemical and microstructural micromilieu in each clay pseudomorph plays a big role during the whole argillization. It influences not only the resultant chemical composition but also the order-disorder states of newly formed clay minerals. Volcanic glass in contact with water is less stable and its argillization proceeds more rapidly compared with the crystalline primary silicates of the corresponding chemical composition. The removal of dissolved components from glass, however, is retarded due to limited system of cracks and no cleavage system typical for most crystalline minerals. This is the reason why volcanic glasses still better preserve their geochemical milieu than crystalline primary silicates (compare the results by Gilg *et al.,* 2003).

What still lies before us is the investigation of clay minerals in the accessible universe. Are the astronomers and the seekers of life in outer space aware that the planets or moons without clay minerals or some clay remnants never possessed hydrosphere and thus life on their surfaces?

The 4th research region of clay science focuses on „Physical and physicochemical properties of clay minerals" related to the structure, crystal chemistry, layer charge, charge density, adsorbed ions, interlayer bondings, and properties of their aggregates including size distribution (Konta, 2000). It comprises the following research subregions: a) clay-water system, colloidal properties and surface chemistry; b) dispersion in water and the effect of electrolytes; c) flocculation and deflocculation; d) stability of suspensions in various liquids; e) swelling and shrinkage; f) adsorption of water and corresponding technological properties; g) sorption selectivity of phyllosilicates; h) organo-clay systems; i) transport of chemicals through clays; j) true density of clay minerals and argillaceous rocks; k) bulk density; l) porosity, preferred particle orientation and tortuosity of pathways; m) stability of clay minerals and other rockforming silicates in various environments; n) optical properties; o) magnetic properties. Modern investigation in any of these subregions requires knowledge of modern discoveries in the crystal structure and crystal chemistry of phyllosilicates.

The 5th research region "Modified clays" covers at least eleven theoretical and simultaneously widely applied subregions: a) homoionic clays with one of common hydrophilic inorganic interlayer cations (Na^+ or Ca^{2+} or others); b) clay minerals with one polar organic molecule adsorbed (e.g. pyridine, quinoline, ethylene glycol); c) expansible phyllosilicates with organic cation changing the original hydrophilic clay (with Na^+, Ca^{2+} and other cations) to an organophilic clay of desired microporosity (organo-clay molecular sieve); d) expansible clay minerals with negatively charged organic polymer (polyanion); e) clay minerals with non-ionic organic polymer; f) expansible phyllosilicates pillared with various oligomeric inorganic oxycations, mostly /III/- and /IV/-valent cations, which can be widely used as sorbents and catalysts; g) pillared inorgano-organo-clays; h) pillared and delaminated hydroxy-R/III/ interlayered smectites; i) H^+-smectites and acid activated clays; j) thermally treated (calcined) clays; k) milled or ground clays, delaminated but sometimes altered up to short-range structures ('amorphous state'). These research subregions are under strong influence of chemistry, physics and the demands of industrial technologies. The preparation and investigation of differently modified clays required great effort of many experts. One good example of the continual research endeavour has been referred by Komadel (2003) in his critical review of results obtained on: a) H^+-saturated smectites where exchangeable cations are replaced with protons; b) acid activated smectites; c) smectites with reduced structural Fe(III) to Fe(II) causing the increase of negative charge on the 2:1 layers; d) Li^+-saturated montmorillonites; e) interaction of smectites with methylene blue which is a very sensitive method to probe layer charge density of natural and chemically modified smectites. According to Madejová *et al.* (1998), IR spectra of a smectite treated in 6 M HCl at 80 °C for 0, 3, 4 and 8 hours show a gradual decrease of the Si-O-Al bending vibration near 520 cm^{-1}, which is the most sensitive band to the presence of residual Al in the octahedral sheet. They simultaneously showed an increase of the Si-O vibrations near 1100 cm^{-1} assigned to amorphous silica with a three-dimensional framework. Novak and Gregor (1969) found that the maximum surface area and the highest decolorizing ability is attained for some acid treated dioctahedral smectites after removal of 0.5, but for the others after removal of 2 up to 2.5 cations per unit cell containing 4 octahedral cations. Suquet *et al.* (1991) prepared similar porous material by a mild attack of a macrocrystalline vermiculite using 1 M HCl at 80 °C for 2 hours. By electron microscopy, infrared spectrometry, X-ray powder diffraction and thermal analysis, it has been shown that the leached vermiculite is composed of more or less attacked layers retaining their original platy morphology, and non-crystalline hydrated silica. The all hitherto published results testify that acid activation leading to an effective sorbent (bleaching earth) must be a partial dissolution of expanding phyllosilicates in inorganic acids. The final product must not be solely three-dimensional amorphous silica. We have to admit, however, that we don't know yet the structure and morphology of remanent silica after the optimum acid treatment.

A very promising field in the preparation of clay sorbents and quick inorganic reactants is the investigation of precisely reproducible grinding or milling leading to a product of constant properties. First, it is necessary to study the optimum energetical procedure and the optimum time length of the used mechanical treatment. There is a fundamental difference between dry and wet grinding or milling. The structural phenomena "finite crystal size as a lattice disorder" and "mechanically disordered structures" (Brindley, 1980) play a decisive role during grinding or milling of clay raw materials. The mechanically disordered structures and received short-range ordering attracted attention of scientists for more than fifty years (Bloch, 1950; Gregg *et al.*, 1953; Mackenzie and Milne, 1953; Robertson, 1953; Takahashi, 1959; Miller and Oulton, 1970; Petkof, 1975; Čičel and Kranz, 1981; Papirer and Roland, 1981; Cornejo and Hermosin, 1988; Pérez-Rodríguez *et al.*, 1988; Suquet, 1989; Drief and Nieto, 1999; Reynolds and Bish, 2002). We still don't know the temperature evolved on the surface of clay minerals during grinding or milling. The point-evolved temperature during dry treatment is probably high. Can it cause partial dehydroxylation and support local molecule or ion migration? Can a mere delamination during wet grinding in the presence of water or another suitable liquid be advantageous for the preparation of novel chemically modified clays? Do the defined mechanical treatments accelerate chemical reactions between dry or slightly wet clays and chemicals? These and many other questions pertaining to the remaining subregions of the 5th research region of clay science need, above all, a support from the 1st and 2nd research regions. More information about the research of other modified clays can be found in the monograph by Konta (2001).

The 6th research region "Applied clay science including the exploitation and beneficiation of raw materials focusing on the application in various industrial branches, soil science and agriculture, civil engineering and ecological projects", needs still a

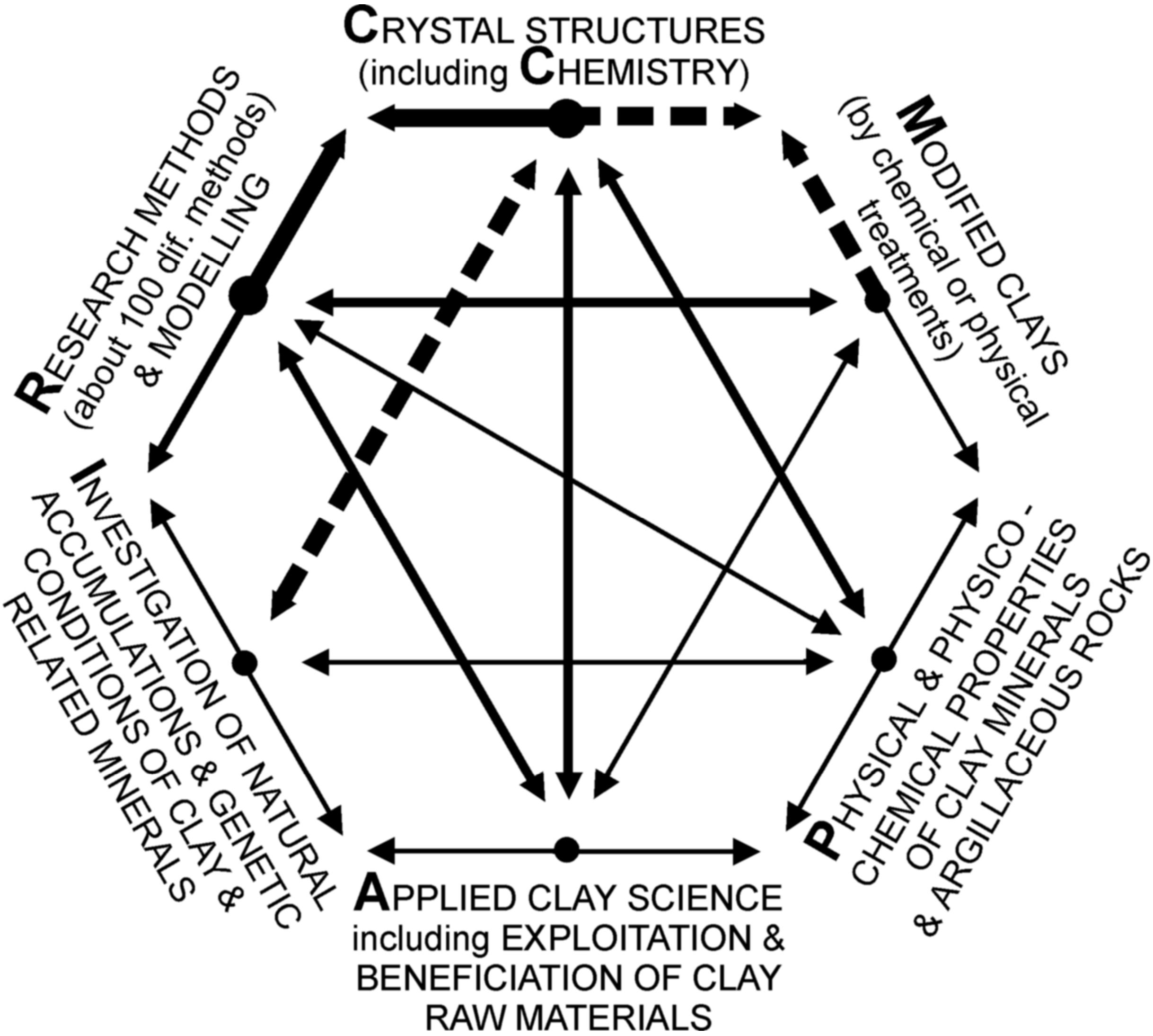

Fig. 2 A suggested view of the existing as well as desirable interaction among the six major research regions of clay science significant for their further development and practical applications. This view accentuates the expected development of clay mineralogy, petrology of argillaceous accumulations, soil science, and practical applications. Thin arrows: a mutual weak impact; thicker arrows: a mutual more intense impact; the heaviest arrows: the most successful integration and the most developed research between the first two research regions; the bold-hyphenated arrows: a desirable more intense integration.

stronger integration with the remaining five research regions. The applied research is usually oriented according to some immediate demands of the practice. Fig. 1 shows the existing and desirable cooperation of clay science with the most important theoretical, applied and related sciences and respective technologies. The special journal *Applied Clay Science,* edited by Elsevier in Amsterdam is one of the commendable initiatives supporting the 6th research region of clay science. Further development of applied clay science needs, however, much stronger support of interested industrial companies. Also it is necessary to ask: Do the present-day clay scientists sufficiently know the demands of modern industry and technologies? There is no doubt that great results have been achieved in theoretical clay science. The effective integration of research regions, 1 to 5 with the 6th region, needs also to organize modern conferences, e.g. on the theme, “Order-disorder states in the crystal structures and crystal chemistry of clay minerals and their application in technologies”. Such and similar topics can bring more support to clay science from industry.

Fig. 2 is an attempt to summarize partly the existing, and partly the desirable interaction among the six major research regions of clay science. Thin arrows indicate a mutually weak impact, which is perhaps common but insufficient. The thicker arrows indicate a more intense impact of the results radiating from one to another region. The heaviest arrows express the most successful integration and most developed research between the two first research regions. These also are marked by the heaviest points.

The strong dashed arrows show a desirable more intense integration between a) the crystal structure (including chemistry) research and the investigation of natural accumulations and genetic conditions of clay and related minerals; b) the crystal structure (including chemistry) and modified clays research regions. The integration sub a) reached some remarkable discoveries in the recognition of the diagenetic and epigenetic transformations of buried clay minerals, depending on the geothermal gradient and its duration in different geological formations.

5. CONCLUSION

Clay minerals as hydrous phyllosilicates with alternating tetrahedral (Tet) and octahedral (Oct) structural sheets (where Tet:Oct = 2:1 or Tet:Oct:Oct = 2:1:1 or Tet:Oct = 1:1) are the most common crystalline reaction products between the surface lithosphere and the hydrosphere. They occur ordinarily in soils, different argillaceous rocks, and clay raw materials of continental and marine environments formed through the geological history of the Earth. Due to their admirable physical and chemical properties, clay minerals are used in many industrial branches and are important in agriculture and forestry, civil engineering, and ecology.

Interdisciplinary research among clay science, basic sciences (physics, chemistry, mathematics, and geometry), earth sciences (mineralogy, petrology, geochemistry, soil science, sedimentology, hydrogeology, engineering geology, general and historical geology, economic geology and mining, geophysics, and climatology), biological sciences (botany, zoology, anthropology, and medicine), applied and related sciences and technologies (material science, ceramics and related technologies, paper, rubber, plastics, chemical, agrochemical, dyes, petroleum and gas, food, pharmaceutic, foundry, cement and silicate-binding materials industry, civil engineering, soil mechanics, agriculture, horticulture, forestry, and environmental science) had a great influence upon the development and advancement of clay science. The mutual cooperation introduced new research methods and opened new horizons in the investigation of clay matter during the 20th century.

Modern clay science needs still a broader interdisciplinary cooperation. However, it also needs a closer integration among the six major research regions within clay science and the numerous existing research subregions. The diagrammatic presentations show the attained interdisciplinary cooperation and desirable research integration within clay science. The cooperation and integration potential of clay science is great. It will bring further progress to clay science itself, as well as to all earth sciences and other cooperating scientific and engineering disciplines. More intense integration among the six research regions of clay science opens new horizons in both the theory and application.

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