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PHYLLOSILICATES IN THE SEDIMENT-FORMING PROCESSES: WEATHERING, EROSION, TRANSPORTATION, AND DEPOSITION

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ABSTRACT

Phyllosilicates are classified into the following groups: 1 - Neutral 1:1 structures: the kaolinite and serpentine group. 2 - Neutral 2:1 structures: the pyrophyllite and talc group. 3 - High-charge 2:1 structures, non-expansible in polar liquids: illite and the dioctahedral and trioctahedral micas, also brittle micas. 4 - Low- to medium-charge 2:1 structures, expansible phyllosilicates in polar liquids: smectites and vermiculites. 5 - Neutral 2:1:1 structures: chlorites. 6 - Neutral to weak-charge ribbon structures, so-called pseudophyllosilicates or hormites: palygorskite and sepiolite (fibrous crystalline clay minerals). 7 - Amorphous clay minerals. Order-disorder states, polymorphism, polytypism, and interstratifications of phyllosilicates are influenced by several factors: 1) a chemical micromilieu acting during the crystallization in any environment, including the space of clay pseudomorphs after original rock-forming silicates or volcanic glasses; 2) the accepted thermal energy; 3) the permeability.

The composition and properties of parent rocks and minerals in the weathering crusts, the elevation, and topography of source areas and climatic conditions control the intensity of weathering, erosion, and the resulting assemblage of phyllosilicates to be transported after erosion. The enormously high accumulation of phyllosilicates in the sedimentary lithosphere is primarily conditioned by their high up to extremely high chemical stability in water-rich environments (expressed by index of corrosion, I_{KO}). Clastic material eroded from weathering crusts and transported in rivers contains overwhelming amounts of phyllosilicates inherited from original rocks. In geological literature, the newly formed phyllosilicates crystallizing in weathering crusts including soils as dominating global source of argillaceous lutite accumulations in the sedimentary lithosphere have been overestimated for a long time. The dissolution of silicates in different dense rocks under conditions of weathering and the crystallization of newly formed phyllosilicates has been strongly and for long periods influenced by chemical microenvironments within each clay pseudomorph. Coarser fragments of eroded argillaceous rocks and crystals of phyllosilicates from different bedrocks and soils are very sensitive to impacts and pressure from fragments of co-transported harder and denser rocks and minerals in turbulent fluvial and similar currents. This is the most important mechanical phenomenon supporting the enormous accumulation of lutite rocks rich in phyllosilicates in the sedimentary lithosphere. The summarized new observations and interpretations are stressed in eleven key points. Erosion and water transportation of detrital material are explained in the terms of hydration, softening, swelling, physical disintegration, grinding, milling, abrasion, delamination, dispersion, and sorting. The deposition of phyllosilicates in different fluid dynamics of streams is expressed by Re and Fr numbers and explained as unflocculated and flocculated suspensions. Phyllosilicates and accompanying detrital minerals in recent marine muds covering vast areas of seas and oceans as well as in lacustrine muds correspond with those transported in fluvial suspensions.

KEYWORDS: phyllosilicates, clay minerals, structural variability, sediment-forming processes, weathering, rock-forming silicates, erosion, transportation, deposition, chemical stability, index of corrosion, crystallization, volcanic glass, chemical microenvironment, clay pseudomorphs, capillary system, river suspensions, lutites, deflocculation, coagulation, fluvial, lacustrine and marine muds

1. INTRODUCTION

The questions on sources, distribution, physical and chemical properties, the most effective determinative methods, and role of phyllosilicates together with their behaviour in different environments of the sediment-forming processes assume one of the foremost places in the research of sedimentary lithosphere followed by several generations of earth scientists. Especially, phyllosilicates with properties of clay minerals in the sediment-forming processes and in the argillosphere affected by post-depositional processes are a great theme, which attracts attention of geologists and other experts examining argillaceous and lutite accumulations developed through the geological history of the Earth. Plasticity, green and dry strength, shrinkage during drying besides a very fine size distribution (usually taken with the upper boundary of 2 or 4 μm) are the bulk properties being empirically well known for a long time and typical of the majority of unconsolidated clay aggregates after addition or removal of liquid water.

According to global geochemical data (Ronov, 1964), the sedimentary lithosphere formed and epizonally transformed during last 3800 million years from the total geological history of the Earth (almost 4500 million years) contains about 75 mass % of lutite accumulations (<0.063 mm) rich in phyllosilicates and their low-grade metamorphic equivalents known under the following terms: clay mud, lutite mud, clay, claystone, argillite, mudstone, clay shale, shale, black shale, consolidated lutite, silty shale, slate, and phyllite. According to the stratigraphic measures (Ronov, 1964), the argillaceous lutite accumulations take up almost 50 bulk % of the sedimentary and related lithosphere (including weathering crusts and soils). The remaining about 25 mass % or 50 bulk % go to all other sedimentary accumulations, i.e. arenites (greywackes, arkoses, quartzites, quartz sandstones up to quartz sands), rudites, ferrolites including jaspilites, bauxites, manganolites, silicites including diatomites, radiolarites, spongolites and cherts, carbonate sediments (dolomites » limestones), phosphorites, salt sediments or evaporites, sulphur, kaustobiolites, analcimolite, and related sediments. Clay minerals and coarser phyllosilicates may be omnipresent in these nonargillaceous sediments as variable admixtures.

Excellent books were written on the composition, formation, sources, transformation, and further history of clay and accompanying minerals in the sediment-forming and post-depositional processes (Weller, 1960; Berner, 1971; Garrels and Mackenzie, 1971; Chamley, 1989; Weaver, 1989; Potter et al., 2005; Jeans and Merriman, 2006). The results and data of extensive original research are quoted in the mentioned books. Nevertheless, the research further continues in sedimentology, sedimentary petrology and clay science, and the authors come with new data, observations or new ideas and interpretations. My contribution, serving as the introductory lecture to one of the research and discussion themes of the 18th Clay Conference of the Czech National Clay Group, is focused on the research dealing with genuine sediment-forming processes and on the in literature still preserved erroneous presumptions and interpretations. I shall start with a short survey of the groups of phyllosilicates and their common species based on the arrangement of their atoms acting as cations or anions, on the order-disorder states of polymorphs and polytypes, a great phenomenon of interstratifications, followed by description of genetic processes of phyllosilicates in weathering crusts including soils controlled by various chemical microenvironments; then I shall tackle the erosion of both preexisting as well as newly formed mineral species in different source rocks, their transportation, grinding, milling, abrasion, swelling, delamination and fragmentation, disintegration and sorting in streams, coagulation, up to deposition, while carefully regarding the most important properties of rock-forming minerals and their mutual destructive action. And finally, I shall try to define or complete some discoveries in eleven key points resulting mostly from my research respecting the studies of quoted authors, and sum up the main effects acting in the formation of argillosphere. Each of them, however, still requires a more thorough and deeper investigation.

The post-depositional processes labeled by the term diagenesis in broad sense or "burial diagenesis" (see Dunoyer de Segonzac, 1969; Jeans, 1984) represent another great theme. It seems to be the most deeply and the most widely examined research theme of clay sedimentology (from Weaver, 1956; Kossovskaya and Shutov, 1955, 1958, 1963; Shutov et al., 1969; Burst, 1969; Dunoyer de Segonzac, 1969; to Meunier et al., 1998; Beaufort et al., 1998; Drits et al., 1998; Jeans and Merriman, 2006). The great progress in the investigation of diagenetic transformation of clay minerals in sedimentary basins of different geological ages has occurred thanks to the 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 and successful research activities can be found in seven specialized issues of the *Clay Minerals* journal published by the Mineralogical Society (UK) between 1982-2006 in England (volumes 17, 19, 21, 24, 29, 35, 41, together containing 7 introductory and 113 original papers). Hunt (1979) in his unique book "Petroleum Geochemistry and Geology" also accentuated the role of tiny lutite particles of phyllosilicates, accompanying organic matter, in the genesis of petroleum deposits. The literature quoted in this paragraph provides sufficient information on the topic which deals with the post-depositional processes affecting the phyllosilicates. They deserve another special monograph.

2. GROUPS OF PHYLLOSILICATES, THEIR COMMON SPECIES AND STRUCTURAL STATES IN THE SEDIMENT-FORMING PROCESSES OF THE ARGILLOSPHERE

Structurally and chemically, crystalline clay minerals are defined as phyllosilicates whose crystal structure is built of tetrahedral $(T)^{IV}$ and octahedral $(O)^{VI}$ planar sheets firmly connected in two- ($T^{IV}:O^{VI} = 1^{IV}:1^{VI}$), three- ($T^{IV}:O^{VI}:T^{IV} = 2^{IV}:1^{VI}$) or four-sheet ($T^{IV}:O^{VI}:T^{IV}:O^{VI} = 2^{IV}:1^{VI}:1^{VI}$) layers. The leading cationic atom in the tetrahedral sheets is Si^{4+} which can be partially substituted by Al^{3+} or very rarely and in minute amount by other elements. Cationic atoms in the octahedral sheets are mostly Al^{3+}, Mg^{2+}, Fe^{3+} and Fe^{2+}. The number of shielding oxygens of one tetrahedron remains four and the number of shielding oxygens+hydroxyls of one octahedron is six. The atoms in all basal structural planes are pseudohexagonally arranged. The total negative charge of fundamental structural layers caused by the cationic substitutions in tetrahedrons and octahedrons of some phyllosilicates is balanced by cations trapped in the interlayer space (mostly K^+, Na^+, Ca^{2+}, Mg^{2+} and OH_3^+, but also NH_4^+ as in some black shales and similar sediments, in idealized crystallochemical formulae as M^+ or M^{2+} written here for a half unit cell). The d_{001} spacing of all phyllosilicates is of primary importance for their identification because the basal planes (001) are occupied by the densest alignment of atoms (Fig. 1). The other planes with fewer atoms give not as strong X-ray reflections. The expansion of d_{001} spacings of expansible phyllosilicates after saturation of a suitable polar liquid (ethylene glycol or glycerol, which have larger size of molecules than water) and shrinkage after heating at 400 °C (loss of molecular water) and at 550 °C (transformation of kaolinite to metakaolin and disappearing of the 7.2 Å X-ray reflection) are necessary procedures having been applied for more than 50 years in the determination of the phyllosilicate groups. A distinction between dioctahedral and trioctahedral phyllosilicates can be made on the basis of the 060 reflection. A detailed description of determinative methods of phyllosilicates and accompanying minerals can be found in several handbooks (Brindley, 1951; Vikulova and Zvyagin, 1958; Brown, 1961; Drits and Sakharov, 1976; Thorez, 1976; Carroll, 1979; Brindley and Brown, 1980; Reynolds, 1985; Wilson, 1987; Moore and Reynolds, 1989; Reynolds and Walker, 1993; Meunier, 2005; Bergaya et al., 2006).

2.1. A BASIC STRUCTURAL AND CHEMICAL CLASSIFICATION OF PHYLLOSILICATES

The crystalline phyllosilicates occurring in argillaceous and detrital lutite accumulations of any geological age, including their epizonally metamorphosed equivalents but still recognizable as original sediments, can be divided into six groups (Fig. 1).

2.1.1. NEUTRAL 1:1 STRUCTURES: THE KAOLINITE AND SERPENTINE GROUP

Kaolinite, $(Al_2)^{VI}(Si_2)^{IV}O_5(OH)_4$,
whose d_{001} spacing 7.16 Å is for well ordered triclinic structure and about 7.18 Å for disordered pseudomonoclinic kaolinites. The value 7.16 Å for the kaolinite monoclinic polytypes **dickite** ($2M_1$) and **nacrite** ($2M_2$) counts for d_{002}. Fully hydrated **halloysite** has d_{001} spacing of 10.1 Å and **metahalloysite** has d_{001} spacing between 7.2 - 7.7 Å. Metahalloysite is highly disordered kaolinite. The disordered kaolinite minerals have lower number of d_{hkl} X-ray reflections and some of the reflections are more diffuse. All kaolinite minerals, varieties, and polytypes lose their basal and other reflections if heated to 550 °C for 1 hour and alter to metakaolin.

Serpentine, $(Mg_3)^{VI}(Si_2)^{IV}O_5(OH)_4$,
having d_{001} spacing between 7.2 - 7.35 Å and Mg^{2+} possibly substituted with some Fe^{2+}.

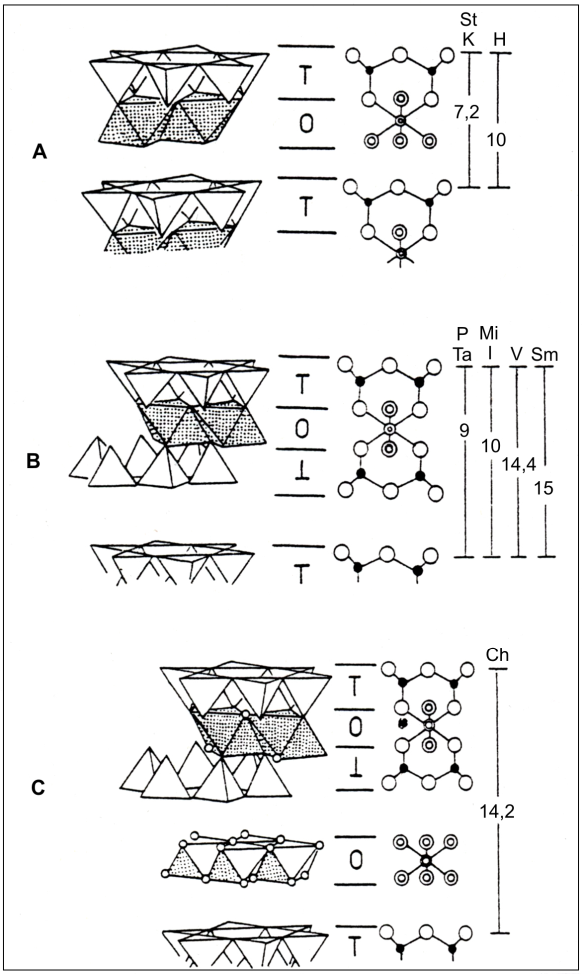


Fig. 1 Similarities and differences in crystal structures of typical crystalline phyllosilicates divided into groups, illustrated by perpendicular sections to the base plane. **A** - Neutral 1:1 structures: the kaolinite (K) and serpentine (St) group, in which two-sheet layers alternate: T = tetrahedral sheet, O = octahedral sheet. K is kaolinite, metahalloysite (dehydrated halloysite), dickite, nacrite, H is halloysite containing molecular water in the open interlayer space. The c_o basal parameter for the fundamental unit cell of St minerals is 7.2 to 7.35 and for K minerals about 7.2 Å but for halloysite it is 10 Å. **B** - The 2:1 structures - the neutral 2:1 structures: the pyrophyllite (P) and talc (Ta) group; the high-charge 2:1 structures: micas (Mi) including illite (I); the low- to medium-charge 2:1 structures, expansible phyllosilicates in polar liquids: vermiculites (V) and smectites (Sm). One octahedral sheet (O) is always closed between two tetrahedral sheets oriented with the apices against each other. The c_o parameter increases from 9 Å in pyrophyllite (9.16 Å) and talc (9.3 Å) up to 15 Å in smectites with Ca^{2+} interlayer cations. **C** - Neutral 2:1:1 structures: minerals of the chlorite group (Ch) in whose crystal structure regularly alternate the three-sheet layers of the T:O:T type, of the T:O ratio 2:1, with one octahedral sheet (O) so that the total T:O ratio = 2:2. The c_o parameter is about 14.2 Å (after Mattias, 1981; modified by Konta, 1995).

2.1.2. NEUTRAL 2:1 STRUCTURES: THE PYROPHYLLITE AND TALC GROUP

Pyrophyllite, $(Al_2)^{VI}(Si_4)^{IV}O_{10}(OH)_2$, and **talc**, $(Mg_3)^{VI}(Si_4)^{IV}O_{10}(OH)_2$
have no or barely traceable substitution for Si in tetrahedra and for Al or Mg in octahedra. Their interlayer space is free of cations or water. Consequently, d_{001} spacings are reduced to a stable value of 9.15 Å for pyrophyllite and 9.30 Å for talc. Their affinity to adsorb water molecules and their wettability is very limited in contrast to the charged oxygen planes of micas and expansible 2:1 phyllosilicates with interlayer cations. Pyrophyllite and talc have lyophob surface.

2.1.3. HIGH-CHARGE 2:1 STRUCTURES, NON-EXPANSIBLE IN POLAR LIQUIDS: ILLITE AND THE DIOCTAHEDRAL AND TRIOCTAHEDRAL MICAS, ALSO BRITTLE MICAS

Example of an ideal formula of the most common, in water non-expansible clay mica, **illite,** can be written $(Al_2)^{VI}(Si_{3.1-3.2}Al_{0.9-0.8})^{IV}O_{10}(OH)_2K_{0.8-0.9}$. A very small substitution of octahedral Al^{3+} by Fe^{3+}, Fe^{2+} and Mg^{2+} is common. Real illites known from many localities differ from muscovite crystallizing at higher temperatures by a lower substitution of Si^{4+} with Al^{3+} and thus by a lower number of interlayer potassium (also Na^+ or NH_4^+) ions, always being near 0.8 - 0.9 atoms per a half unit cell.

Glauconite, $(R^{2+}_{\leq 0.8}R^{3+}_{1.2})^{VI}(Si_4)^{IV}O_{10}(OH)_2K$,
where R^{2+} is mainly Mg^{2+}+Fe^{2+} and R^{3+} is Al^{3+}+Fe^{3+} with a high substitution of ($Fe^{3+}Fe^{2+}$) > Mg^{2+} for Al^{3+}.

Celadonite, $(R^{2+}_{1.0}R^{3+}_{1.0})^{VI}(Si_4)^{IV}O_{10}(OH)_2K$,
contains more AlMg than Fe^{3+}>Fe^{2+} in the octahedral sheet.

Muscovite has the following ideal crystallochemical formula: $(Al_2)^{VI}(Si_3Al)^{IV}O_{10}(OH)_2K$.

The smaller size of Na^+ interlayer cation in sodic micas as in **brammallite** (sodium illite) or in that crystallizing at higher temperatures, as **paragonite**, is the cause of their smaller d_{001} spacings, around 9.6 Å, in contrast to the 10 Å spacing for illite and muscovite containing the potassium interlayer cation.

Biotite, $(Mg,Fe^{2+})_3{}^{VI}(Si_3Al)^{IV}O_{10}(OH)_2K$,
is the main representative of trioctahedral micas, but in sediments it occurs rarely or sporadically as a clastic mineral.

Phlogopite, of an ideal crystallochemical formula $(Mg_3)^{VI}(Si_3Al)^{IV}O_{10}(F,OH)_2K$, is a relatively rare mineral occurring in some epizonally metamorphosed limestones, dolomites or marlstones.

Brittle micas are phyllosilicates formed at a higher temperature and pressure during low grade regional metamorphism of the argillaceous and related sediments. The most common brittle micas are dioctahedral **margarite,** $(Al_2)^{VI}(Si_2Al_2)^{IV}O_{10}(OH)_2Ca$, dominantly trioctahedral **clintonite** and **xanthophyllite,** $(Mg>Fe,Al)_{2-3}{}^{VI}(Si_{1.3}Al_{2.7})^{IV}O_{10}(OH)_2Ca$, and **chloritoid,** $(Al,Fe^{2+})_{2-3}{}^{VI}(Si_2Al_2)^{IV}O_{10}(OH)_2(Mg,Fe^{2+})$.

In contrast to the common true micas, Ca^{2+} or Mg^{2+} and Fe^{2+} are the main interlayer cations in brittle micas. The bivalent cations, namely, better compensate the increased substitution of Si^{4+} with Al^{3+} in tetrahedra than monovalent cations because with increasing temperature a larger amount of aluminium enters into the tetrahedral coordination.

2.1.4. LOW- TO MEDIUM-CHARGE 2:1 STRUCTURES, EXPANSIBLE PHYLLOSILICATES IN POLAR LIQUIDS: SMECTITES AND VERMICULITES

Idealized crystallochemical formulae of most common **dioctahedral smectites**:
montmorillonite,
$(Al_{1.67}Mg_{0.33})^{VI}(Si_4)^{IV}O_{10}(OH)_2M^+_{0..33}.nH_2O$,
beidellite, $(Al_2)^{VI}(Si_{3.67}Al_{0.33})^{IV}O_{10}(OH)_2M^+_{0.33}.nH_2O$,
nontronite,
$(Fe^{3+})_2{}^{VI}(Si_{3.67}Al_{0.33})^{IV}O_{10}(OH)_2M^+_{0.33}.nH_2O$
Example of a **trioctahedral smectite**:
saponite, $(Mg_3)^{VI}(Si_{3.67}Al_{0.33})^{IV}O_{10}(OH)_2M^+_{0.33}.nH_2O$.
Example of a **trioctahedral vermiculite**:

$[(Mg_{2.87}Fe^{3+}_{0.10}Cr^{3+}_{0.03})^{VI}(Si_{3.01}Al_{0.81}Fe^{3+}_{0.18})^{IV}O_{10}(OH)_2]^{0.86}$
$M^{2+}_{0.43}.nH_2O$.
3.00 (charge +0.13) 4.00 (charge -0.99)
(M charge +0.86:2 = 0.43)

Smectites change their d_{001} spacing of 12.5-15 Å obtained at room temperature and strongly controlled by interlayer cations with molecular water to about 10 Å if heated to 400 °C (loss of molecular water), and expand to about 16-17 Å after saturation with ethylene glycol or to about 17.7-18 Å with glycerol.

2.1.5. NEUTRAL 2:1:1 STRUCTURES: CHLORITES

Chlorites represent a large group of 2:1:1 phyllosilicates of at least 16 mineral species strongly differing in chemical composition. Their theoretical crystallochemical formula per a half unit cell can be written as

$$(Mg_{6-x-y}Fe^{2+}_yAl_x)^{VI}(Si_{4-x}Al_x)^{IV}O_{10}(OH)_8 .$$

The 2:1 three-sheet layer alternates in the direction of the *c* axis with a gibbsite ($Al[OH]_3$) or brucite ($Mg[OH]_2$) octahedral sheet. The commonest species in sediments are the Mg- and Fe^{2+}-rich trioctahedral chlorites, namely **clinochlore** and **chamosite**, and the Al-rich dioctahedral species, **donbassite.** An example of crystallochemical formula of **trioctahedral chlorite, clinochlore,** is

$$([Mg,Fe]_{4.75}Al_{1.25})^{VI}(Si_{2.75}Al_{1.25})^{IV}O_{10}(OH)_8$$

and that for **dioctahedral chlorite, donbassite,** respecting the proper gibbsite sheets, can be written as $(Al_2)^{VI}(Si_4)^{IV}O_{10}(OH)_2(Al_2)^{VI}(OH)_6$.
Chlorites do not change their d_{001} spacing values of about 14 Å if heated to 400 or 550 °C/1 hour and do not swell in polar liquids.

2.1.6. NEUTRAL TO WEAK-CHARGE RIBBON STRUCTURES, SO-CALLED PSEUDOPHYLLOSILICATES OR HORMITES: PALYGORSKITE AND SEPIOLITE (FIBROUS CLAY MINERALS)

Ideal crystallochemical formula of **palygorskite** written for a half-unit cell is
$(Mg»Fe^{2+}Al)_5{}^{VI}(Si»Al)_8{}^{IV}O_{20}(OH)_2M^{+}{}_{0.5}(OH_2)_4.4H_2O$
and that of **sepiolite**
$(Mg»Fe^{2+}Fe^{3+})_8{}^{VI}(Si»Al)_{12}{}^{IV}O_{30}(OH)_4(OH_2)_4M^{+}{}_{0.5}.8H_2O$.

Their crystal structures are made up of talc-like layers arranged in long ribbons stuck together to form the fibres. Their shortened sheets of octahedral-tetrahedral linkages are alternately inverted. The octahedral sheet is similar to that in the phyllosilicates, but it is continuous in only one direction. The ribbons are separated by channels parallel to the fibre axis. The channels are occupied by water and exchangeable ions. They are referred to as structural micropores having a section area of 13.4 x 6.7 Å. Besides the structural pores, larger pores of diameters between 20-200 Å also occur among fibres. Above 450 °C under vacuum, the anhydrous sepiolite loses its hydroxyls, its structure is folded and then transforms into enstatite.

2.1.7. AMORPHOUS CLAY MINERALS

Amorphous clay minerals occur in the geologically youngest accumulations, mostly in some soils, in larger amounts especially in andosols and vertisols, or as fissure fillings of crucks in some rocks, or in weathering crusts (regoliths) and muds. They are "amorphous" to X-rays due to a short-range ordering of structural units analogous to those in the crystalline clay minerals. **Allophane,** $Al_2O_3.(1\ to\ 2\ SiO_2).nH_2O$, usually occurs as an aggregate of spheric particles of a diameter mostly around 40 Å. **Imogolite,** chemically close to allophane, has fibrous tube-like forms. **Hissingerite,** $Fe_2O_3.(1\ to\ 2\ SiO_2).nH_2O$, is a ferruginous amorphous analogue of allophane.

Final remark:

The X-ray diffraction technique using specifically oriented and randomly oriented specimens of <2 or <4 µm size fractions enables according to d_{001} and d_{060} to determine the respective group or subgroup of clay minerals present in any sample. The determination of the phyllosilicate species usually demands also the chemical analysis and sometimes calculation of its crystallochemical formula. The oriented preparations are studied in natural dry and humide state at room temperature (about 20 °C), then after glycolation (or glycerolation) which causes swelling of expansible clay minerals, then after heating at 400 °C for 1 hour, evolving loss of molecular water and shrinkage of expansible phyllosilicates, and finally after heating at 550 °C/1 hour leading to the structural destruction of kaolinite and serpentine minerals. In some cases, it is necessary to substitute the interlayer cations by a single known cation.

A detailed description of the crystal structures of the sediment-forming phyllosilicates and their diagrammatic sketches can be found in standard textbooks on clay minerals, (e.g. Grim, 1953 and 1968, 1962; Caillère and Hénin, 1963; Stoch, 1974; Brindley and Brown, 1980; Nemecz, 1981; Barrer and Tinker, 1984; Velde, 1992; Meunier, 2005; Bergaya et al., 2006). Also, these books give information on the methods of identification of clay minerals and in some cases on the quantitative determination of clay minerals in mixtures.

2.2. ORDER-DISORDER STATES, POLYMORPHISM, AND POLYTYPISM

The initial research of crystal structures of phyllosilicates by X-ray diffraction between 1928-1955 was based on an ideal imagination of the symmetric hexagonal arrangement of atoms in all planes and sheets. The more detailed investigation, the continuing refinement of crystal structures in all groups of phyllosilicates, their polymorphs, and polytypes in later decades has shown many irregularities. Today, we know that the phenomenon of different order-disorder states is common not only in phyllosilicates but also in any crystalline material (Lidiard, 2003).

The continuing investigation of the crystal structures of phyllosilicates, including clay minerals, revealed different **order-disorder states** such as the layer stacking (polytypism and turbostratic structures, first discoveries: Hendricks, 1938, 1939; Heinrich and Levinson, 1955; Newnham and Brindley, 1956), mixed-layer structures (Hendricks and Teller, 1942; Bradley, 1945; Caillère et al., 1950), domains and disordered distributions of cations in fundamental sheets (Gatineau, 1964), heterogeneity and variability of layer charge in 2:1 phyllosilicates together with the distribution of interlayer cations (Besson et al., 1974; Stul and Mortier, 1974; Lagaly and Weiss, 1976) and point inconformities determined as a direct localization of atoms and hydroxyls in the structure (Bailey, 1975; Drits, 1975; Olivier et al., 1975). The different order-disorder states in phyllosilicates are primarily due to the cationic substitutions in tetrahedral and octahedral sheets and interlayer spaces. The compositional irregularities are accompanied by irregularities in cell dimensions, composition limits, interatomic forces, symmetry and distortion of octahedra and tetrahedra, twists and tilts of the tetrahedral TO_4 groups, and corrugated surfaces of basal oxygen planes (Radoslovich, 1959, 1960, 1962, 1963a,b,; Radoslovich and Norrish, 1962; Veitch and Radoslovich, 1963). These order-disorder phenomena were then found and further studied in all groups of clay minerals by many authors during the second half of the 20th century (see literature by Konta, 2000) until the present. It has been gradually shown that the perfect, idealized, geometrically and chemically regular atom structure of crystal lattices, as we know it from many published diagrammatic sketches or projections of small volumes, does not factually exist in the entire body of clay mineral crystals. Instead of the idealized schemes, there is a marvelous and multiform inconformity and imperfection within the admirably developed structures.

The classical division of order-disorder states in phyllosilicates was published in the Brindley and Brown (1980) monograph: 1) disorder in distribution of cations; 2) disorder in layer stacking; 3) long-range and short-range order; 4) order-disorder in mixed-layer systems; 5) finite crystal size as a lattice disorder. The published reviews of the order-disorder states in phyllosilicates vary, however, as everything in science, with authors and time.

According to Rodriguez Gallego (1985), structural imperfections in phyllosilicates can be classified into the following groups: 1) point defects; 2) line defects or dislocations; 3) plane defects (polytypism etc.); 4) volume defects (intergrowth, exsolutions, etc.). The mineralogical view excludes quantum defects related to lattice vibrations (phonons, excitons, etc.). Plane defects including polytypism are easily treated by an X-ray diffraction analysis, or more recently, by HRTEM, which is a highly effective technique for the detection of line defects. Point defects such as cation space ordering, vacant sites, interstitial cations, and electron holes, are less treatable by conventional X-ray diffraction studies. For the detection of point defects, suitable spectral methods, nuclear or electron resonance methods supported by HRTEM method are successfully applied.

According to Tchoubar (1985), the actual crystal structure of any clay mineral always displays important departures from the ideal well-ordered structure. Structural defects in clay minerals can be classified in three categories: 1) those affecting the layers themselves (*cis*- or *trans*-vacancies, order-disorder in the isomorphous substitutions, etc.); 2) those specific to the interlayer space (positions of the cations and of the intercalated molecules); 3) stacking faults (including a change in the nature of stacked layers).

Plançon (2001) distinguished the following types of order-disorder in clay mineral structures: 1) order-disorder in mixed-layer systems; 2) order-disorder in the distribution of cations; 3) polymorphous transformations (semiquantitative determination of *trans*-vacant and *cis*-vacant layers in illite-smectites and illite-smectite-vermiculites, cation migration during dehydroxylation-rehydroxylation process); 4) order-disorder in layer stacking; 5) finite size of particles as a lattice disorder; 6) heterogeneity as a disorder.

The new and different order-disorder states in the structure of phyllosilicates are usually discovered by physicists or chemists and by mineralogists-crystallographers. Their experimental and mathematical approach, however, is not familiar to general geologists, sedimentologists, soil scientists, civil engineers, and other experts in spite of their almost daily contact with argillaceous accumulations. The applied X-ray, electron- or neutron-diffraction methods and methods of absorption spectroscopy using different radiations and resonances (e.g. infrared, Raman, Mössbauer spectroscopy, nuclear magnetic resonance and others) are described in specialized manuals (e.g. Farmer, 1974; Fripiat, 1981; Reynolds and Walker, 1993; Zvyagin, 1997).

Polytypism of phyllosilicates is a phenomenon where fundamental 1:1 (kaolinite minerals, serpentines), 2:1 (micas, vermiculites, smectites, pyrophyllite, talc) or 2:1:1 (chlorites) structural layers of identical structure, symmetry, and composition reveal different stacking along the *c* axis, namely by an axial or rotational shifting. The resulting structures with translation and rotation inconformities do not show periodicity in the a_o and b_o directions in the lattice. Phyllosilicates with such inconformities have (001) X-ray reflections not affected, but the (hk0) and (hkl) reflections resolve in asymmetrical bands or vanish.

The discovery of disorder and polytypism in the chemically simple kaolinite subgroup is a good example of specialized crystallographic research starting in 1938 and continuing for decades. Dickite and nacrite are chemically identical to kaolinite but have their layers stacked in alternative regular sequences. Nacrite has a 6-layered monoclinic cell (Hendricks, 1938) and dickite has a 2-layered monoclinic cell (Newnham and Brindley, 1956). Halloysite has a disordered stacking and one layer of molecular water in the interlayer space. Its d_{001}, therefore, is 10.1 Å. Metahalloysite, after expelling most of the interlayer water, shrinks to about 7.4 Å, but disordered stacking remains. If ethylene glycol replaces interlayer water in halloysite, it swells to 11 Å. Kaolinite itself occurs as well ordered triclinic and poorly ordered or disordered partially monoclinic polymorphs. Partial monoclinicity of the symmetry increases with the disorder of the kaolinite. Dickite and nacrite are examples of the monoclinic polytypes forming at increased temperatures in deeper zones of the burried sedimentary lithosphere or under hydrothermal conditions.

The investigation of stacking sequences and the displacement in the (001) planes of phyllosilicates of other groups, and especially of micas and chlorites with wider diversity of central tetrahedral and octahedral cations, has shown that many more complex cells are possible among their polymorphs and polytypes. Four **polymorphs** (M, O, T, and H) and three monoclinic (M) polytypes of micas, first described by Smith and Yoder (1956), were denominated as 1M, $2M_1$, $2M_2$, 2O, 3T, 6H, where the first numbers mean number of structural layers in a unit cell, M means monoclinic, O = orthorhombic, T = trigonal and H = hexagonal; the indices $_1$ and $_2$ are for diverse shifting along *a* and *b* axes recognizable after d_{hkl} reflections. The mica polymorphs and polytypes most commonly occurring in nature are the 1M, $2M_1$, 3T, and $2M_2$ (see more in Nespolo, 2001). The so-called clay micas can have stacking sequence of structural layers producing three different monoclinic shifts: a) in the same direction when a one-layer polytype forms (1M = 1-layer monoclinic polytype); b) disordered one-layer polytype (1Md) giving least number of X-ray d_{hkl} reflections and usually more diffuse; c) if the shift along *a* or *b* axes (*a/3* or *b/3*) repeats itself every two structural layers (2M = 2-layer monoclinic polytype). These polytypes are detectable using randomly oriented preparations (Smith and Yoder, 1956; Velde, 1992). Common illite, forming at low temperature and occurring in Il-Sm irregular interstratifications with small amount of smectite, occurs as 1Md or 1M polytype. Pure glauconite and celadonite occur as 1M polytype. The 2M polytype is typical of clay micas and muscovite forming at higher temperatures (see more in Nespolo, 2001). Chlorites, theoretically, can build up to 24 different stacking arrangements for the constituent talc layers and brucite sheets. Only four of them, however, are statistically important. The IIb polytype occurred in about 80 % of studied samples (Bailey and Brown, 1962: from 303 different chlorites studied). The Ib polytype occurred in 12 %, and IIa and Ia polytypes occurred in about 4 % each. Numbers I and II refer to the positions of cation sites in the brucite sheet towards a fixed set of hexagonal axes above the lower hexagonal OH rings. The letters a and b distinguish different superpositions of the interlayer octahedral sheet on the upper talc sheet. The Ia and Ib polytypes crystallize at lower temperatures during the weathering or diagenesis, while the IIb polytype occurs in metamorphic rocks. Direct observation of the stacking sequence up to different types of the ordering of individual ions in phyllosilicates by high-resolution transmission electron microscopy (HRTEM) is now a very effective method combined with NMR spectroscopy, X-ray diffraction and electron diffraction study.

Modern geologists and sedimentary petrologists wishing to study some parts of argillosphere in more detail should have in their research team a specialized crystallographer for the investigation of order-disorder states and polytypism of phyllosilicates. The new modular crystallography enables to simultaneously detect components, polymorphism, polytypism, and order-disorder diversity in any group of phyllosilicates (Zvyagin, 1997, 2001).

Key point 1: The different and numerous irregularities in the structure of crystallizing phyllosilicates might have several causes. One of them lies in variable bond lengths between cations and shielding anions (O^{2-} in tetrahedra, and O^{2-}+OH^- in octahedra). This variability is caused by the different sizes of central cations. The cation-anion bond length increases with the size of cations. The leading central cation in tetrahedra is Si, but it may occur partially substituted, for example, by larger Al or Fe^{3+} cations. The central cations in octahedra are mostly Al, Fe^{3+}, Mg, Fe^{2+}, rarely Li^+ or other cations; in addition, vacances exist among the octahedra if they are occupied with trivalent cations only. The larger the irregularity in the chemical substitution in tetrahedra and octahedra in a mineral species or group, the more variable the resulting cell dimensions, symmetry, interatomic forces and their local balance, deformation, and distortion of octahedra and tetrahedra in the final structure can be. The result is that actual sheet and layer structures depart from the ideal hexagonal arrangement (a simple example in Fig. 2). The general phenomenon of the deformation of tetrahedra and tetrahedral sheets and octahedra and

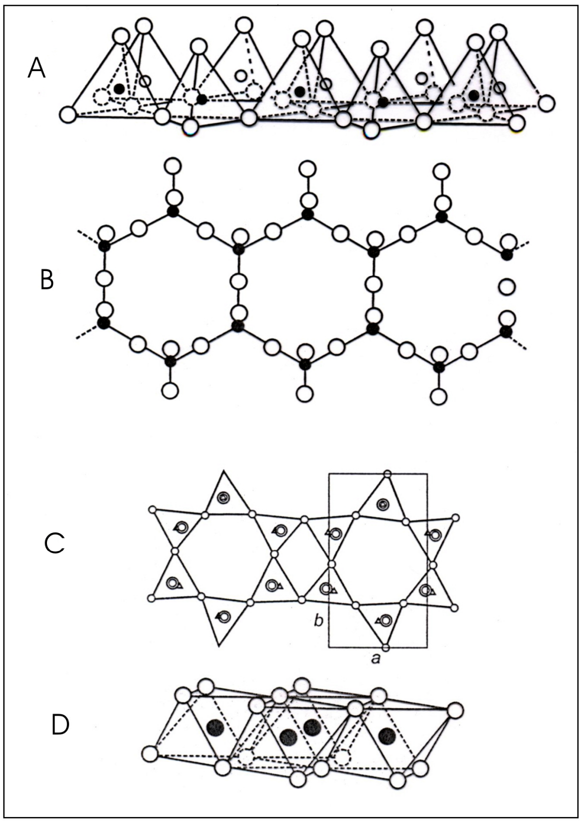


Fig. 2 Fundamental structural sheets of crystalline phyllosilicates. **A -** Idealized plane sheet of silicon-oxygen tetrahedra in the projection nearly parallel with (001). **B -** The same view perpendicular to (001). **C -** One actual pseudohexagonal sheet of tetrahedra influenced by a partial torsion, view perpendicular to (001). **D -** Idealized plane sheet of aluminium-oxygen-hydroxyl octahedra.
A,B,D from Grim (1962), C from Suitch and Young (1983): The rotation in tetrahedral sheet has the angle torsion 7°, triangle = Si, double circles = apical oxygens, small simple circles = remaining oxygens in the distances of 2.70 Å and 3.23 Å from basal plane.

octahedral sheets leading to the crystallization of polytypes has been compiled and summarized in detail by Weiss (2004). Already in 1959-1963, Radoslovich with his coworkers drew the crystallographers' attention (quoted in detail above, and by Konta, 2005) to the fact that the energetic state expressed in "local balance of forces" in layer structures may provide a means of structural control over polytypism. The first cause of order or disorder in the structure of phyllosilicates and the resulting polymorphs and polytypes as well as of the interstratification phenomenon lies in the chemical micromilieu acting during the crystallization. The second cause contributing to the diverse polymorph, polytype, and interstratification formations (including indexes of crystallinity) is the accepted low or higher thermal energy. Higher temperature and permeability acting for a longer time span support better ordering in mixed-layer systems but not in the substituting cations in tetrahedral or octahedral sheets.

2.3. INTERSTRATIFICATIONS (MIXED-LAYER STRUCTURES)

Mixed layering of crystal structures is a common phenomenon among phyllosilicates in which a crystal contains two or more structurally and mostly also chemically different types of layers or interlayers. In one-word terminology this mixed-layering is called interstratification. Interstratifications of phyllosilicates are known from weathering crusts, soils, sediments of various diagenetic stages, hydrothermal accumulations and finally also from low-metamorphic rocks. The most important literature on the original research of this part of clay science can be found in the historical review by Konta (2000).

The interstratification of structurally and/or chemically different phyllosilicate types is either irregular (random) or regular (Fig. 3). Irregularly stratified crystals of phyllosilicates are much more common in nature than the regular interstratifications. In sediments of different geological formations, phyllosilicate interstratifications were discovered and investigated as many combinations, especially with expansible clay minerals in the oil-bearing strata accompanying all continents (Brown and Green-Kelly, 1954; Weaver, 1956; Shutov et al., 1969; Burst, 1969; Dunoyer de Segonzac, 1969, and many others; see also a volume containing the most modern research of clay mineral cements within the main types of hydrocarbon reservoirs in the North Sea and other offshore areas of the British Isles edited by Jeans and Merriman (2006) with ten papers published mainly by leading British authors).

The mixed layering of phyllosilicates can be illustrated by a common example as the alternation of structural layers A (e.g. illite) and structural layer B (e.g. smectite) in the direction of the *c* axis. An irregular interstratification can be written, for example, as ABBABAAB (Fig. 3 left). Many other possible combinations exist in nature. Regular interstratifications of the one-to-one type, ABABABAB, (R = 1, Fig. 3 right) have been named as mineral species. R means a range, or in German "Reichweite", in the case when A layer is surrounded by B layer on each side and reversely in the direction of *c* axis. Dioctahedral regular interstratifications of this type are: **rectorite** (Il-Sm, with K^+ or Na^+ mica) and **tosudite** (Ch-Sm); trioctahedral are: **aliettite** (Ta-Sa), **corrensite** (Ch-Sm which is low charge, and Ch-Ve which is medium charge), **dozyite** (Sp-Ch), **hydrobiotite** (Bi-Ve), **kulkeite** (Ta-Ch), and **Bi-Ch** which is not yet named. (Il = illite, Sm = smectite, Ch = chlorite, Ta = talc, Sa = saponite, Ve = vermiculite, Sp = serpentine and Bi = biotite). Regular interstratifications of the ABBABBABB type or with still more adjoining B layers are also known among phyllosilicates.

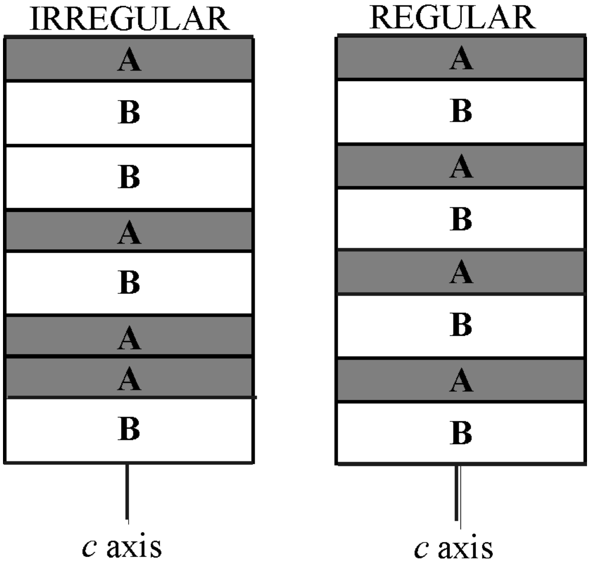


Fig. 3 Examples of two different types of interstratifications of phyllosilicates: irregular (random) and regular (R = 1 ordered). **A** can be e.g. a 10 Å and **B** a 15 Å clay mineral.

Interstratifications built of two or more different structural layers (e.g. illite-smectite, chlorite-vermiculite, mica-chlorite or illite-smectite-vermiculite, etc.) are heterotypic interstratifications. Mixed layered crystals built of the same structural layers but differing in polytypism are called homotypic interstratifications. And finally, mixed-layering of a phyllosilicate structure with different and alternating interlayer cations only are interlayer heteroionic interstratifications. Fig. 4 is an example of an X-ray diffraction pattern showing the 2 theta regions where the different types of reflection maxima occur for heterotypic phyllosilicate interstratifications.

The determination of many possible interstratifications occurring in different mineral assemblages is not easy. It requires perfect knowledge of X-ray diffraction and preparatory methods including on-going support by necessary literature

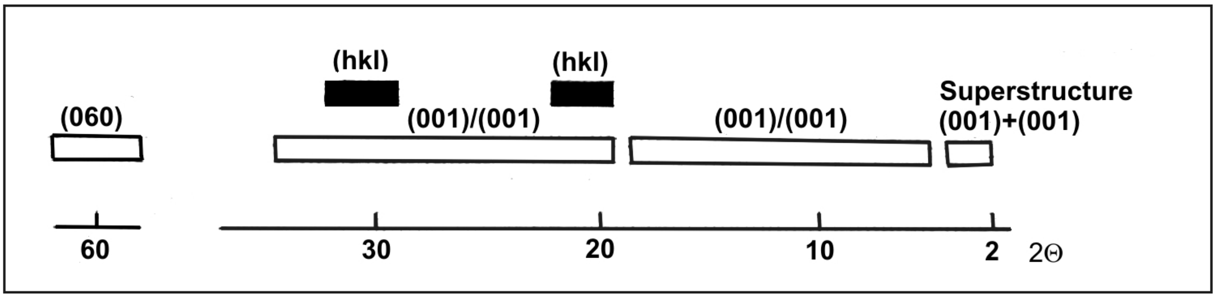


Fig. 4 The 2 theta regions in an X-ray diffraction pattern where the different types of reflection maxima occur for heterotypic phyllosilicate interstratifications. The region for superstructure is for the sum of (001) reflections of two different structures.

(Reynolds, 1985; Lanson et al., 1998; Sakharov et al., 1999). Direct observation of the stacking sequence in phyllosilicates by high-resolution transmission electron microscopy (HRTEM) is now an invaluable technique for investigating interstratifications or polytypes and disordered stacking sequences (McKee et al., 1978; Olives and Amouric, 1984; Guthrie and Veblen, 1989; Środoń et al., 1990; Kameda et al., 2007).

3. PHYLLOSILICATES IN THE SEDIMENT-FORMING PROCESSES: EFFECTS OF PARENT ROCKS AND ACTING FACTORS

Phyllosilicates of the sedimentary lithosphere have different sources and pass through several variable environments of the sediment-forming processes under the action of numerous factors. Clay minerals are important and omnipresent constituents of the system "solar energy - lithosphere - water - air - life" reshaping the surface of the Earth for almost 3.5 to 4 billion years. The hitherto attained knowledge on individual processes is described under different accents of authors in standard textbooks of general geology, sedimentary petrology or in specialized sedimentological monographs (cf. Twenhofel, 1939; Hatch et al., 1957; Kettner, 1957; Pettijohn, 1957; Huang, 1962; Füchtbauer and Müller, 1970; Kukal, 1970; Galloway and Hobday, 1983; Colman and Dethier, 1986; Dixon and Weed, 1989; Einsele, 2000; Middleton, 2003; Hsü, 2004; Meunier and Velde, 2004; Potter et al., 2005).

3.1. WEATHERING

Physical weathering is characterized by mechanical fragmentation of rocks, their minerals, and volcanic glass exposed at the earth's surface. In its initial phase, physical weathering sensitively reacts to the tensile strengths developed during cooling of magmatic rocks, or superimposed cleavage structure of some metamorphic rocks, or developed by repeating heating and cooling of the surface of any rock exposed to insolation, freezing and thawing of water penetrated to different depths of the lithosphere. Water easily enters the bedding planes of sedimentary rocks through fractures and joints, and the metamorphic rocks along the foliation. The penetration of meteoric and soil water into rocks takes place by gravitation through joints or cracks of different origin (see a detail description by Mandl, 2005), e.g. along tension joints, shear joints, hydraulic fractures, tectonic faults, or through pores of relatively larger dimensions in some sedimentary rocks. From these broader paths, water infiltrates by capillary forces acting in narrower pores and in the cleavage network of rock-forming minerals or irregular and less frequent thin cracks in volcanic glass. The physical weathering predominates over the chemical weathering in cooler as well as hot arid regions and in mountaineous areas. Glacial plucking belongs also to the mechanical fragmentation, but it immediately passes into the glacial transportation.

Chemical weathering occurs wherever the rocks, their minerals and volcanic glass are in contact with aqueous solutions under atmospheric conditions. Chemical weathering increases with increasing concentration of protons in water and with its total volume coming into contact with the rock-forming constituents. Chemical weathering is especially strong in humid tropical and subtropical regions with high rainfall and of relatively flat topography, low elevation and low relief.

Both of these types of weathering participate in biological weathering in any climatic belt, where the root system of living plants and the activity of bacterial world together with other microorganisms, actinomycetes, fungi, and also organic remains and excrements substantially contribute to the chemical as well as physical weathering.

3.1.1. THE IMPORTANCE OF THE PHYSICAL/CHEMICAL WEATHERING RATIO AND CHEMICAL MATURITY

Both, physical and chemical processes are usually not sharply divided. Their mutual ratio, however, has a decisive impact on the weathering products of rocks including soils of different climatic regions. There is no doubt that a large series of weathering crusts developed in geological history under changed positions of the equator, drifting continents and the resulting climatic belts. Their phyllosilicates, and especially those of relatively low index of corrosion I_{KO} (Konta, 1984), i.e. dioctahedral micas and kaolinite, were able to preserve even several weathering events, repeated erosion, transportation and deposition. The long-term chemical persistence of kaolinite under tropical weathering processes has been documented from middle part of the Amazon basin, Brazil (Balan et al., 2007). The well-ordered kaolinite of sedimentary rocks changes here into poorly-ordered kaolinite, the content of which increases from a depth of 9 m into the upper levels of the lateritic profile. A considerable portion of the original well-ordered kaolinite, however, still remains in the profile for a long time. After erosion, both kaolinites can become a part of further sediment-forming processes. The phyllosilicates of higher I_{KO}, and thus of lower chemical resistivity, e.g. biotite, chlorites rich in Fe and Mg and expansible sodium 2:1 phyllosilicates (smectites and vermiculites) have better chance to resist the long-lasting weathering in climatic belts and environments of a high physical/chemical weathering ratio.

The relatively high chemical resistivity of phyllosilicates in parent rocks exposed to the weathering in a mild cool climatic belt is documented, for example, by original research of Scandinavian soils performed by Gjems (1967). Gjems studied clay fraction (<2 μm) by means of X-ray diffraction analysis in 670 samples from 222 soil profiles (A, B, C horizons) of podsols, brown earth, semipodsol, iron humus podsol and humus podsol from different geological formations sampled in Norway, Sweden, Finland, and Denmark. He showed that: 1) Clay mineral assemblages in the studied soils reflect variations influenced by different parent rocks and their preglacial weathered material. 2) Kaolinite was not formed in these soils; it is restricted to places where the mineral is also found in the neighbouring rocks. 3) Minerals of the illite (dioctahedral micas) and chlorite groups have been inherited from the source areas. 4) Expansible phyllosilicates in amounts over 10 % in the subsoils have relation to known occurrences of the minerals in the bedrock or weathered mantle; it is not clear whether expansible phyllosilicates formed in the subsoils after glacial deposition. Vermiculite is common in clay fractions but it is frequent in bedrock also; vermiculite is a primary phyllosilicate but it may form in subsoil from illite (mica) and chlorite. The same applies to the mixed-layer minerals Il-Ve and Ch-Ve occurring in the studied soils.

Later research performed by numerous authors in other regions of the world has shown that soils contain the parent rock constituents of various stability or their remains including original phyllosilicates besides newly formed minerals. Phyllosilicates and Fe^{3+}-oxyhydroxides dominate among the authigenic minerals. The resulting structure and chemical composition of the newly formed crystalline and amorphous minerals is controlled by the chemistry of the parent rock and its constituents (Fig. 5). The resulting mineral assemblage may change vertically in each weathering profile. Normally, chemical maturity increases with the vertical distance from the parent rock. The average chemical maturity of weathering profiles changes with climate and is highest in the soils of the tropical forests and lowest in tundras and deserts. Chemical maturity (Ch_M) of any horizon of the weathering profiles can be expressed by the ratio between the least soluble element (Al in solutions from 5 to 9 pH) and the sum of the three most mobile elements (Na, Mg, Ca); Ch_M = Al % : (Na+Mg+Ca) %. The same ratio was applied for chemical maturity of suspended matter with predominating phyllosilicates in rivers by Konta (1985). A big diversity exists in the classification of world soils as compiled by Bridges (1978).

Key point 2: Vast areas of tills and tillites in arctic parts and adjacent areas of the Earth, together with debris in mountaneous and arid regions in other climatic belts, contain immense volumes of chemically almost intact phyllosilicates. They originate from different sedimentary, metamorphic, and igneous parent rocks. The composition and properties of parent rocks and minerals in the weathering profiles, the elevation, relief and topography of source areas and the climatic conditions, especially rainfall and temperature, control the resulting assemblage of phyllosilicates to be transported after erosion. A simple division of recent global soil zonality with the most typical phyllosilicates, practical for global sedimentology, was published by Chamley (1989). It can be summarized as follows: *lithosols* formed in very cold or hot-dry climate are a rich source of the original phyllosilicates contained in parent rocks; *podzols* typical of cool-wet climate contain, depending on horizons, any original phyllosilicates (Gjems, 1967) preserved according to their chemical persistence (expressed by index of corrosion, I_{KO}) as well as newly formed 2:1 and 2:1:1 phyllosilicates and their irregular interstratifications, kaolinite and free silica, but podzols can form also in other climatic conditions; *brown and chestnut soils* formed in temperate-humid climate contain phyllosilicates inherited from parent rocks, as well as newly formed illite, vermiculite, smectite, and chlorite minerals including their irregular interstratifications, kaolinite, and also allophane; *tchernozems, vertisols and related soils,* rich in dioctahedral smectites with some admixtures of illite and irregular interstratifications of 2:1 structures, and in some location containing calcite, form in temperate to warm-subarid climate; *calcrete,* also called *caliche,* a lateral equivalent of vertisols developed on calcareous rocks, usually contains newly precipitated calcite, Mg-smectite, palygorskite, and sepiolite; *laterites and latosols* formed in hot-wet

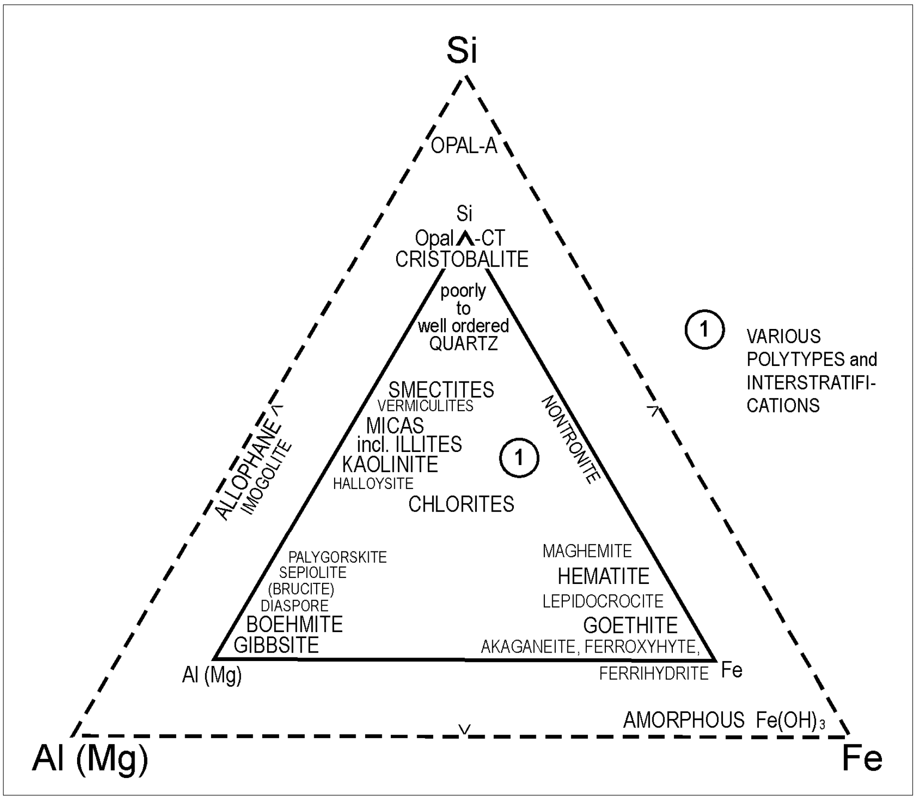


Fig. 5 A simple Si-Al(Mg)-Fe triangle showing central tetrahedral (without Mg) or octahedral (without Si) cations as a basis of the common newly formed minerals in weathering crusts and soils or minerals inherited from preexisting bedrocks and both transported, milled and sorted in rivers, and finally deposited in a favourable environment.

Table 1 Mineral stability series of common rock-forming silicates during weathering (Goldich, 1938), among which are the major parent minerals as a source for the formation of clay minerals. The chemical stability increases from olivine or Ca-plagioclase to muscovite and quartz.

OLIVINE	
	Ca-PLAGIOCLASE
AUGITE	
	Ca-Na-PLAGIOCLASE
HORNBLENDE	**Na-Ca-PLAGIOCLASE**
	Na-PLAGIOCLASE
BIOTITE	
K-FELDSPARS	
MUSCOVITE	
QUARTZ	

climate are rich in kaolinite, gibbsite and iron oxyhydroxides. Chemical decay decreases with the depth of weathering profiles. (Main minerals see Fig. 5.) Clastic material eroded from profiles and fragmented debris in horizons where physical fragmentation of primary constituents prevailed over their deeper chemical changes usually contains overwhelming amounts of phyllosilicates inherited from original rocks.

3.1.2. CHEMICAL STABILITY AND SOLUBILITY OF ROCK-FORMING SILICATES UNDER THE CONDITIONS OF WEATHERING (AND VOLCANIC GLASS)

Chemical stability of rock-forming silicates in aqueous solutions was first explained by Goldich (1938) for major minerals occurring in igneous rocks. His "mineral stability series" (Table 1) illustrates the relative persistence of the primary silicates arranged

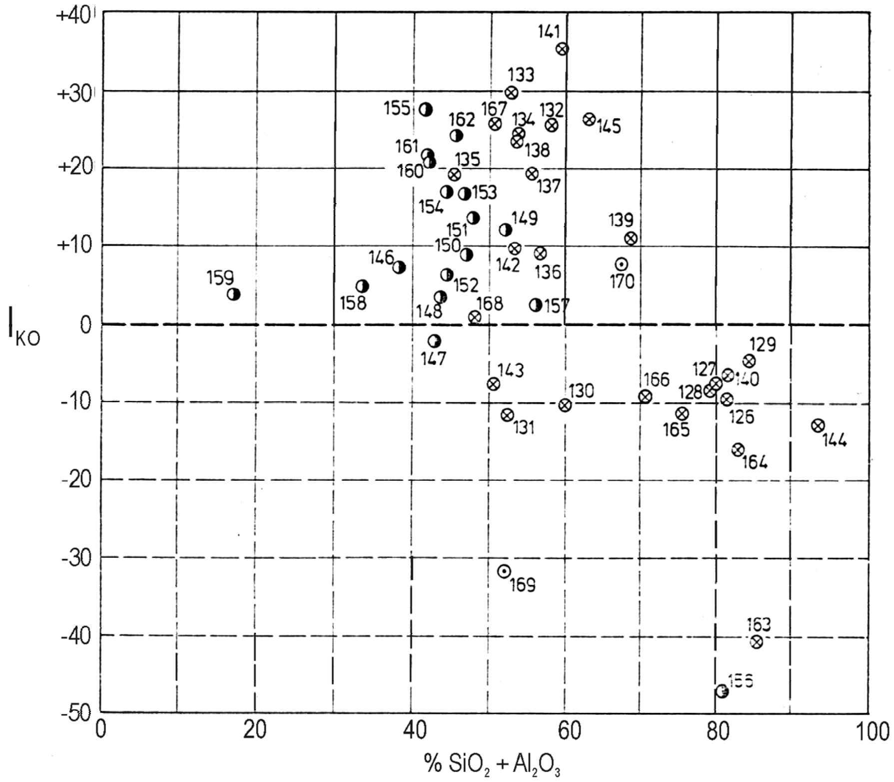


Fig. 6 Correlation between the index of corrosion, I_{KO}, and % (SiO_2+Al_2O_3) in the series of phyllosilicates (Konta, 1984): 126, 127 - muscovites, 128 - illite, 129 - paragonite, 130, 131 - glauconites, 132 - phlogopite, 133, 134, 135, 136, 137, 138 - biotites, 139 - zinnwaldite, 140 - margarite, 141 - xanthophyllite, 142, 143 - stilpnomelanes, 144 - pyrophyllite, 145 - talc, 146 - thuringite, 147 - chamosite, 148 - delessite, 149 - sheridanite, 150 - ripidolite, 151 - clinochlore, 152 - brunsvigite, 153 - pennine, 154 - diabantite, 155 - kämmererite, 156 - cookeite, 157 - amesite, 158 - greenalite, 159 - cronstedtite, 160 - chrysotile, 161 - lizardite, 162 - antigorite, 163 - kaolinite, 164 - hydromuscovite, 165 - illite, 166 - montmorillonite, 167 - saponite, 168 - vermiculite, 169 - apophyllite, 170 - prehnite. Calculated from chemical analyses published in Sheet Silicates (Deer et al., 1962).

into two series: the mafic (rich in Mg and Fe) and the felsic (with components of high concentrations typical of feldspars and quartz, rich especially in Al_2O_3+SiO_2 or pure SiO_2) minerals. The mafic minerals substantially poorer in Al_2O_3+SiO_2 generally weather more rapidly than the felsic minerals. The relative chemical stability of minerals of both series is illustrated by their mutual positions from the top to the bottom in the scheme. Muscovite and quartz are the most stable abundant minerals in the igneous rocks exposed to the chemical weathering. The extremely limited cleavage and relatively high hardness of quartz still contribute to its chemical and physical stability under weathering conditions. These properties act against the effect of the increasing specific surface area and reduce the penetration of aqueous solution into quartz grains.

Another comparative stability scheme includes the rock-forming silicates occurring also in metamorphic and sedimentary rocks (Konta, 1984). It is based on the original Reiche's (1943) "potential index of weathering" but with a considerable modification. The new index of relative stability, "index of corrosion" I_{KO}, includes not only the amount of the constitutional oxides but also the ionic potential Z/r, the parameter controlling the behaviour of ions in aqueous environment, where Z represents the valency of the cation and r is its radius. Index I_{KO} of any crystalline silicate can be calculated according to the following equation:

$$I_{KO} = 200\ [(\Sigma A_i(Z_i/r_i) - C(Z_{H^+}/r_{H^+})/10]:\Sigma A_i(Z_i/r_i)+\Sigma B_i(Z_i/r_i)\ ,$$

where Σ means sum of mole concentration of oxides A_i of those cations which are easily removed, i. e. FeO, MnO, MgO, CaO, SrO, BaO, NiO, Li_2O, Na_2O, K_2O plus some of the smaller cations (C^{4+}, P^{5+}, S^{6+}), i.e. CO_2, P_2O_5, SO_3, while B_i stands for the mole concentrations of oxides of the more insoluble tri-, tetra- and pentavalent cations such as SiO_2, ThO_2, ZrO_2, TiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, B_2O_3, Ti_2O_3, V_2O_5; C is the mol concentration of the chemically bound water (OH plus zeolitic H_2O multiplied by 2.703); Z_i is the cation charge and r_i the ionic radius of the respective ion i, Z/r for $H^+/10$ = 2.703 (for more detail see Konta, 1984).

The larger is the I_{KO} value, the smaller is the chemical persistence of the silicate during weathering (see more in papers by Konta, 1984 and 1992). Fig. 6 shows a correlation between the stability "index of corrosion", I_{KO}, and % (SiO_2+Al_2O_3) for 45 phyllosilicates inclusive micas, brittle micas, pyrophyllite, talc, chlorites, serpentine minerals and kaolinite, smectites and vermiculites. Chemical stability of the rock-forming silicates during weathering increases with their SiO_2+Al_2O_3 content and the decreasing index of corrosion (I_{KO}) (Fig. 7). Fig. 6 shows that among phyllosilicates, the least stable are the trioctahedral micas and other trioctahedral phyllosilicates together with chlorites. The most stable phyllosilicates are dioctahedral species, i.e. muscovite, hydromuscovite, illite, glauconite, pyrophyllite, dioctahedral expansible phyllosilicates, kaolinite, and donbassite with cookeite from chlorites. The stability of chloritoid lies between the stabilities of dioctahedral phyllosilicates and most of chlorites. In order that the alteration of parent silicates would reach up to the kaolinization or finally the lateritization (gibbsite, boehmite, diaspore), large volumes of water with desirable concentration of protons must percolate the rock. It means that a good permeability, conditioned by good connection of joints, capillars and pores, is necessary to facilitate the flow and diffusion of chemical species in solution.

The high ionic potential, Z/r, of Si^{4+} cation in quartz repulses protons in water and together with limited cleavage maximally retards its solution (see Fig. 8). Similarly, other quadrivalent cations contribute to chemical stability of some heavy minerals such as, for instance, zircon with Zr^{4+} and Si^{4+} or rutile and anatase with Ti^{4+}.

Solubility of rock-forming silicates of igneous, metamorphic, and sedimentary rocks during the weathering basically depends on their crystal structure and chemical composition, on their specific reactive area, the pH and Eh of the penetrating aqueous solution, and temperature of water. The specific reactive area of minerals to be dissolved is in direct relation to the density and penetrability of the existing cleavage system, which is again controlled by the crystal structure. Brantley and Mellott (2000) measured the specific surface area by gas adsorption for a series of particle size fractions of some adequately pure laboratory-ground rockforming minerals. The specific surface area in all size fractions increased in order: quartz (no cleavage), olivine (less regular cleavage {001}), albite < oligoclase, bytownite (cleavage of feldspars {001} and {010}) < hornblende, diopside (stark crossing cleavage {110}). In their discussion, the authors did not take into account that the increase of the specific surface area could be influenced by the crystal structure and the density of very thin cleavage fractures developed in solid fragments during the grinding.

Crystalline silicates react with an aqueous solution incongruently (Garrels and Mackenzie, 1971). It means that the analytically determined components as SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O etc. occur in other ratios in the solution than in the solid silicate.

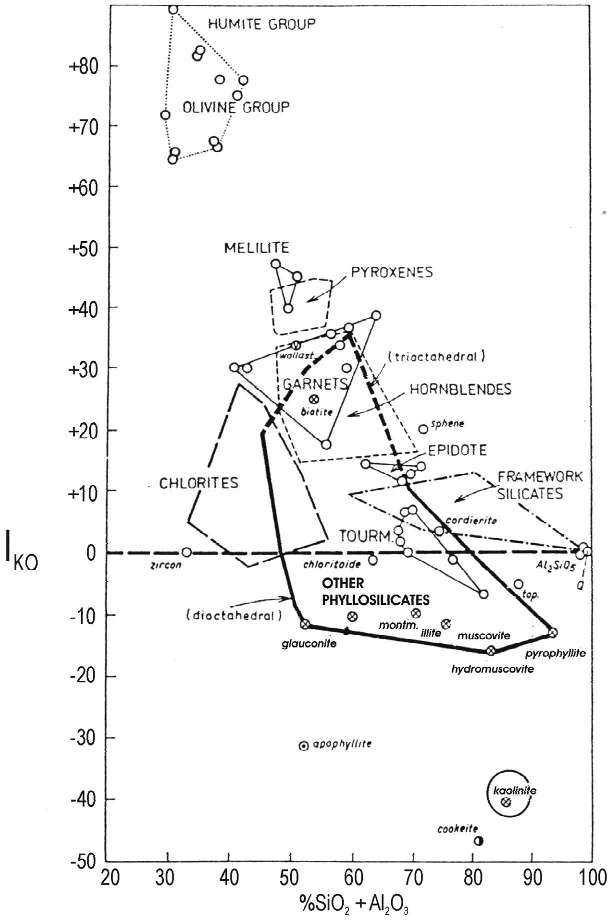


Fig. 7 Simplified diagram showing correlation between the corrosion index (I_{KO}) and % (SiO_2+Al_2O_3) in the commonest rock-forming silicates. Chemical stability of the silicates during weathering increases with the (SiO_2+Al_2O_3) contents and the decreasing I_{KO} values (see more in Konta, 1984).

The destructive action of water itself on rock-forming silicates can be *hydratational,* if water molecules are electrostatically attracted to the surface cations by the oxygen sphere and to the anions by the hydrogen sphere, or *hydrolytic,* if water molecules are dissociated: for instance, K-feldsparK^+ + H^+OH^- ↔ K-feldsparH^+ + K^+OH^-. The hydrolytic decomposition is the stronger and the faster, the agressiver is the water, i.e. the more protons (H^+) and hydronium ions (H_3O^+) and then hydroxyls (OH^-) it contains and the faster the dissolved ions are removed from the mineral. The climatic conditions and among them especially the volume of atmospheric precipitations, their pH, higher temperature, as well as good drainage in the profiles of weathering crust are especially important for the intensity of chemical decomposition. The concentration of protons in soil water increases

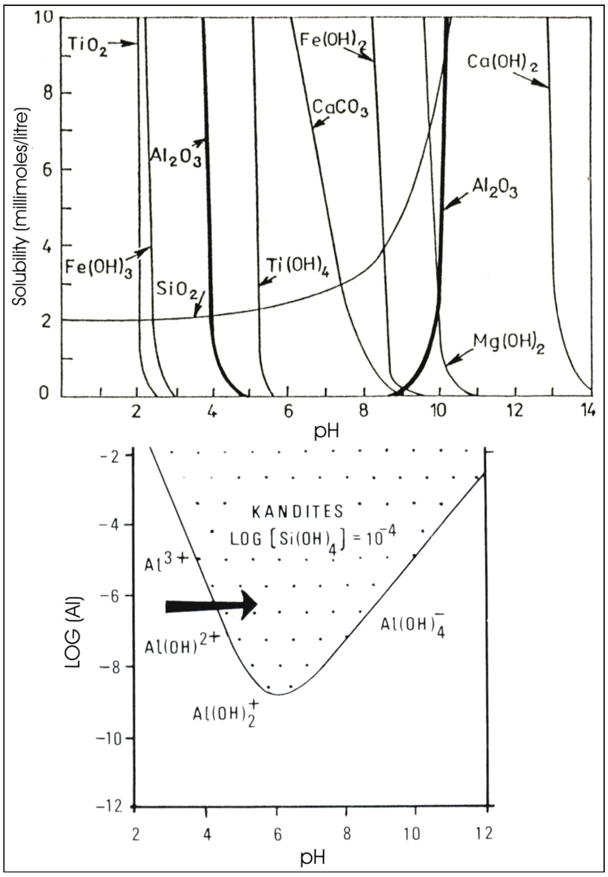


Fig. 8 The solubility of common chemical components during weathering in relation to pH (above: Loughnan, 1969). The zero solubility of Al_2O_3 and the $Al(OH)_3$ polymerization lies between 5 - 8.5 pH; the polymerization of $Mg(OH)_2$ is possible under much higher pH values, above 11 pH in the Mg-rich environment. The optimum pH range for the polymerization and precipitation of $Al(OH)_3$ lies beteen 6-7.5 pH (below: Curtis, 1983, from Kantorowicz, 1984).

with the content of common acids as H_2CO_3, H_2SO_4, H_2S and some organic acids (Degens, 1965).

The roots of plants and especially their hair rootlets of big specific surface area (Keller, 1957), the microorganisms in soils respiring CO_2, and lichens producing oxalic acid in the direct contact with rocks participate in the production of acids and protons. Oxidation of organic remains in soils is the main source of CO_2, the chief acid-forming gas in this environment. The humine compounds and chelates (Lehman, 1963) formed from organic remains contribute also to the dissolution and removal of dissolved ions.

The capillary pores in minerals of weathering profiles are saturated with aqueous solution wherever they come into contact with penetrating water. The movement and transport of dissolved matter is achieved by flow and by diffusion. The transport of chemical species through pores passes under similar conditions to those in clays (see more in Konta, 2001). A considerable part of silica is removed as sodium or potassium silicates easily soluble in water.

Key point 3: The mutual comparison of the I_{KO} values (index of corrosion, Konta, 1984) of rock-forming silicates leads to a conclusion that a considerable volume of phyllosilicates in the sedimentary lithosphere, apparently comparable or still larger than that occupied by clastic quartz, has a source in preexisting phyllosilicates of different bedrocks (sedimentary, metamorphic, and igneous) affected by weathering and erosion. The enormously high accumulation of phyllosilicates in the sedimentary lithosphere is primarily conditioned by their high up to extremely high chemical stability in water-rich environments. This property is remarkable despite the fact that clay minerals in sediments are noted for their large specific and thus reactive surface area during the long-term contact with water. The high production of phyllosilicates in weathering crusts and soils under favourable weathering conditions, especially in tropical and subtropical climatic belts, is yet another but secondary source of clay minerals transferred into the sedimentary lithosphere. In geological literature, the newly formed phyllosilicates - crystallizing in soils as the dominating global source of argillaceous accumulations in the sedimentary lithosphere - have been overestimated for a long time. It is, however, difficult to differentiate the same phyllosilicate species of the size of physical clay originating in bedrocks from those newly formed in weathering crusts, jointly eroded, transported, and later occurring together in argillaceous sediments.

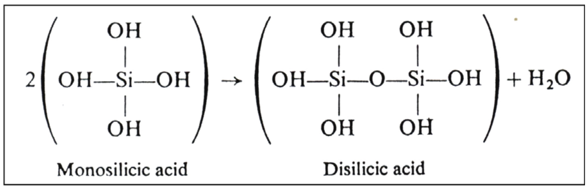
Key point 4: ***Volcanic glass*** in contact with water is less stable and its argillization proceeds more rapidly, compared with the behaviour of crystalline primary silicates of the corresponding chemical composition. The removal of dissolved components from glass, however, is retarded due to a limited system of cracks and no dense cleavage system typical of most crystalline minerals. This is the reason why, despite their faster dissolution, volcanic glasses still better preserve their geochemical milieu than crystalline primary silicates (compare the results by Gilg et al., 2003).

3.1.3. CRYSTALLIZATION OF NEWLY FORMED PHYLLOSILICATES

The reason of the incongruous behaviour of silicates lies in the property of some major cations, especially Al^{3+}, but under favourable conditions also Fe^{3+}, Mg^{2+} and Fe^{2+}, in strongly polarizing water molecules, repulsing half of their protons and attracting the remaining hydroxyls. Still more important is a higher concentration of hydroxyls in the aqueous solution and its increasing pH value achieved in the presence of alkaline and alkaline-earth hydroxides. In weathering crusts, the alkalies and alkaline-earth ions are among the first getting into the solution. The $Al^{3+}/OH^{-} \sim 1:3$ and $Mg^{2+}/OH^{-} \sim 1:2$ ratios in the aqueous solutions of pores are ideal for the precipitation and polymerization of hexagonally arranged $Al(OH)_3$ and $Mg(OH)_2$ into a planar framework. This is well known from the synthesis of some phyllosilicates under laboratory conditions. Precipitation of these positively charged hydroxides reacting with the negatively charged silicic acid from enough dilute solutions is the process leading to the formation of the initial octahedral and tetrahedral sheets firmly connected in the newly formed phyllosilicates in soils and weathering crusts (Hsu and Bates, 1964, figure for Al-hydroxides). The major cations of sufficiently dense positive charge precipitate in the connection with hydroxyls at suitable pH ranges (Fig. 8, above).

In the case of the crystallization of kaolinite minerals, the penetrating aggressive acid water progressively dissolves suitable primary silicates. The released alkalies and alkaline earths locally neutralize the solution to a slightly acid or neutral up to an ideal Al^{3+}/OH^{-} ratio close to 1:3. The strongly hydrated monovalent and bivalent cations are extremely mobile and easily removed by flow and diffusion. The resulting slightly acid or neutral solution supersaturated with respect to kaolinite is favourable for the crystallization of kaolinite minerals (Fig. 8, below; Curtis and Spears, 1971; Kantorowicz, 1984). This process is supported by time and higher temperature. Chemical reactions in weathering crusts and soils have much in common with diagenetic processes in detrital sediments (see Curtis, 1983; Jeans, 1984; Morton, 1984; Huggett, 1984; Kantorowicz, 1984; Blackbourn, 1984; and other authors of papers in *Clay Minerals*, vol. 19, Nr. 3; Curtis, 1985).

The polymerization of dissolved silica from monosilicic acid H_4SiO_4 to disilicic acid forming siloxane bonds –Si–O–Si– (Berner, 1971) is supported just by continuing deprotonization (Fig. 9). The high positive charge on the small surface of Si^{4+} cation, namely, is still denser than the charge on the surface of Al^{3+} cation. The Si^{4+} cation, therefore, is capable of repulsing all protons connected with the surrounding OH groups. If deprotonized, and in higher concentrations in an aqueous solution amorphous silica can precipitate also alone beside some of the newly formed smectite, vermiculite or chlorite, illite, kaolinite, Al- and Fe^{3+}-oxide hydrates, X-ray amorphous Al-hydroxide, aluminosilicate hydrates, and rarely zeolites. Under lower concentrations, all deprotonized silica can be simply attracted to just polymerized gibbsitic or brucitic sheets. Here, it is pseudohexagonally organized into the $[SiO_4]^{4-}$ tetrahedral sheets in the structure of phyllosilicates.



$$2\left(\mathrm{OH{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}{-}OH}\right) \rightarrow \left(\mathrm{OH{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}{-}O{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}{-}OH}\right) + H_2O$$

Fig. 9 The initial step to the polymerization of dissolved H_4SiO_4 by forming siloxane bonds - Si - O - Si - (Berner, 1971).

The ratios among the remaining alkalies and alkaline earths, as well as their concentrations in the HO–Al(Mg, Fe)–O–Si–O newly formed precipitates and their total negative charge, are decisive in the resulting clay mineral assemblage within the individual pseudomorphs. The microenvironment rich in K^{+} prefers the crystallization of illite, while that rich in Na^{+} or Ca^{2+} or Mg^{2+} prefers the crystallization of smectite or vermiculite. The affinity of smectites for exchangeable K^{+} should only increase with increasing negative charge density (Shainberg et al., 1987). The substitution of Al^{3+} for Si^{4+} in the tetrahedral sheets and the common substitution of Mg^{2+} or Fe^{2+} for Al^{3+} or Fe^{3+} in the octahedral sheets give rise to a differently large net negative charge of the structural layers. The negative charge is balanced by exchangeable cations of pore waters, commonly by Na^{+}, K^{+}, Ca^{2+} or Mg^{2+} according to their ionic potential and the activity (concentration) ratios. If the interlayer cations with the corresponding portion of silica are successively removed from the pseudomorph by continuing percolation and degradation, differently ordered kaolinite minerals together with illite or expansible 2:1 phyllosilicate crystallize among the newly formed clay minerals. The crystallization of common chlorites or trioctahedral 1:1 phyllosilicates of the serpentine subgroup prefers the space of primary silicates or environment poorer in SiO_2 and richer in Mg and Fe, as, for example, that of biotite, amphiboles or pyroxenes, and other mafic minerals.

Hydration force together with activities of interlayer cations in the aqueous solution controls their fixation in the interlayer space of 2:1 phyllosilicates. Cations with a lower hydration force are preferentially adsorbed by the negatively charged oxygen surfaces of clay minerals. The magnitude of the hydration force, F_H, generally depends on the electric field strength of the cation surface, i.e. [(cation valence)^2:ionic radius]. The hydration force in two common series of homovalent cations, i.e. alkalies Cs^{+}, Rb^{+}, K^{+}, Na^{+}, Li^{+}, and alkaline earths Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, increases with decreasing ionic radius, that is from the left to the right in both series. It is substantially larger in the series of bivalent cations.

The role of *capillary forces* acting as hydrostatic tension in capillary water during the dissolution and initial crystallization in the clay pseudomorphs is not yet known. Nevertheless, these forces amount to several hundreds of kg/cm^2 (Winterkorn, 1943).

The temperature changes in soils and other weathering crusts highly influence the action of water. The increasing temperature supports the mobility of water, the wettability of solid surfaces, and the dissociation of H_2O to $H^+ + OH^-$.

Key point 5: The dissolution of silicates in different dense rocks under weathering conditions and the sequential crystallization of newly formed phylosilicates is strongly and for prolonged periods influenced by chemical microenvironments existing within the space of each primary mineral. The clay pseudomorphs after potassium feldspars, Na- or Na-Ca-feldspars, biotite or amphibole in deeply weathered igneous rocks testify that the sequentially crystallizing clay mineral species, their chemistry, structural ordering, and morphology are under the influence of long-range outlasting geochemical microenvironments in the space of the original silicates (Proust and Velde, 1978; Konta, 1979, 1981; Konta et al., 1972; and later Banfield and Eggleton, 1990). The clay pseudomorphs after primary rock-forming silicates in weathering crusts preserve the traces of chemical micromilieu of original minerals not only in the deep parts but also in the completely argillized upper parts of the regolith profiles. The movement of aqueous solutions is initially controlled by the fractures of different origin but mainly by the capillary system of the original cleavage and by the crystal structure of individual primary silicates. Sooner or later, the flow is combined with ion diffusion in the very dense capillary system within the newly formed clay matter. The narrow capillary and interlayer pathways, their tortuosity, and large specific surface area of newly formed clay matter retard any big scale equilibrium in dense igneous and metamorphic rocks. The individual chemical and microstructural micromilieu in each clay pseudomorph plays a big role during the entire sequential argillization of igneous and metamorphic rocks. The influence of chemical microenvironments of original rock-forming silicates and their clay pseudomorphs, however, can strongly or totally be reduced in rocks of higher porosity and permeability, such as, for instance, in kaolinized arkoses. In soil horizons, the different chemical microenvironments after primary silicates are still more or less apparent despite the percolation of aqueous solutions is exceedingly open, accelerated, and the mutual mixing of chemical species in newly formed clay minerals much broader and easier (Wilson, 2004).

3.1.4. PHASE DIAGRAMS

In the second half of the 20th century, phase diagrams based on the concept of thermodynamic stability of phyllosilicates and accompanying minerals became increasingly popular and were published by numerous authors. Thermodynamic or kinetic reaction diagrams may be of assistance 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). Lippmann (1981), especially, showed the importance of the diagrams for the explanatory side in earth sciences. If a certain clay mineral or an assemblage within a known geological framework is studied, and if we even know something about the possible parent material, then the stability diagrams can help to explain why the mineral(s) determined, and not others, have formed in that particular environment. Lippmann (1981) calculated the diagrams for the systems: $K_2O–Al_2O_3–SiO_2–H_2O$, $MgO–Al_2O_3–SiO_2–H_2O$, and $K_2O–MgO–Al_2O_3–SiO_2–H_2O$ from thermochemical data at 25 °C available in the literature with the assumption of Al_2O_3, being an essentially immobile component. Let us consider at least one phase diagram showing the transformation of a potassium feldspar, microcline, to newly crystallized phyllosilicates and some accompanying minerals (Al hydroxides, amorphous SiO_2 and allophane). The diagram (Fig. 10) shows the fields for the stable mineral species (printed in CAPITALS) and metastable species reacting in metastable equilibrium (in *Italics*, first letter capital) under the variable activity of H_4SiO_4 and K^+/OH^- as well as the K^+/H^+ ratios.

The monograph by Meunier and Velde (2004) concentrated on a single clay mineral, is a good example of detailed complex knowledge of illite describing e.g. its thermodynamic stability, formation in soils and weathered rocks or the dynamics of the smectite to illite transformation.

Readers who want to get acquainted with some basic thermodynamics and kinetics needed for

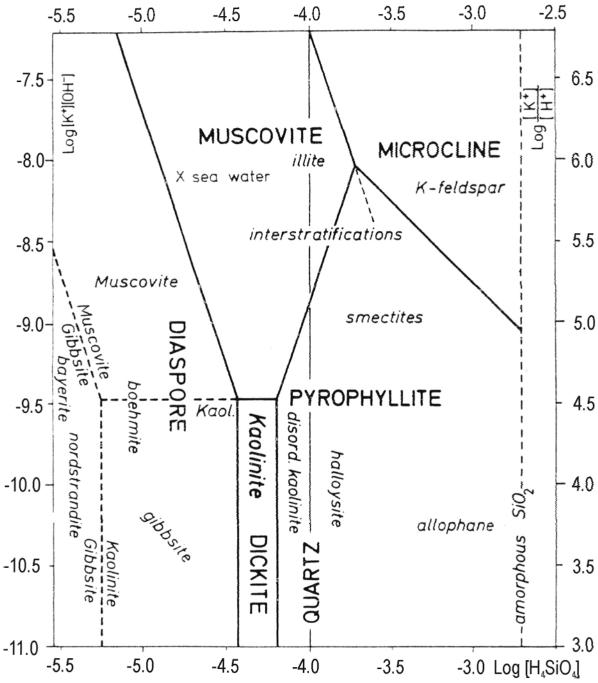


Fig. 10 The system $K_2O-Al_2O_3-SiO_2-H_2O$ in a phase diagram showing the probable fields of formation of metastable, unstable (both in *italics*) and stable mineral phases (in capitals) (Lippmann, 1981).

a detailed investigation of some mineral transformations should read at least the book *Principles of Mineral Behaviour* by Putnis and McConnell (1980).

3.1.5. WEATHERING OF ROCKS: A QUANTITATIVE APPROACH

The weathering of rocks, their minerals, and the genesis of weathering profiles including soils is controlled by various factors. These factors can be described by a series of primary variables. In natural sciences, the acting factors which can be numerically expressed are always more valuable than mere words. Nevertheless, all mineralogical changes must be carefully described and documented.

According to Konta (1990a), *the rock properties* from the physical point of view can be expressed by one of the three following parameters (1, 2, 3) determined for fresh and weathered samples:

1. *The axial compressive strength* of dry rock (which is mainly influenced by the porosity and the sizes of the textural components) expressed in MPa (1 megapascal = 10 $kg.cm^{-2}$); it also reflects the destructive effects of tectonic and other movements acting on the rock.
2. *The porosity*, expressed in % (the axial compressive strength decreases with increasing porosity).
3. *The imbibition capacity* for water, measured in mg per 8 $hours/cm^2$ (perpendicularly to the stratification in sedimentary rocks) *of smoothed rock surface at 20 °C* (see more in Konta, 1990a); nearly all fresh igneous and metamorphic rocks have porosities and imbibition capacities equal to zero.

Chemical changes can be numerically expressed by the index of corrosion for fresh and weathered rock:

4. *The index of corrosion*, I_{KO}, calculated from the chemical composition of the rock by the same way as for a mineral (see the subchapter 3.1.2). If the sample contains precipitated salts, e.g. sulphates and carbonates, they must be subtracted from the chemical composition before the calculation of I_{KO}.

The climatic and chemical parameters for the macroenvironment are given by:

5. *The amount of annual rainfall,* in mm/year.
6. *The pH value* of the reacting water (normally between pH 3 and 10).
7. *The degree of continentality* (K), given by $K = [(1.7 \, . \, T_m)/\sin(\text{phi} + 10^o)] - 4$, where T_m is the annual temperature deviation and phi the geographic latitude (for Verkhoyansk, Siberia, K is equal to 100, while for the equatorial low lying sites K becomes zero, hot arid areas have K equal to 45), see more in Konta (1985).

The intensity of weathering (I_w) increases with decreasing parameters 1 and 4, and increasing parameters 2, 3 and 5, increasing or decreasing parameter 6 (depending on whether the pH value is above or below pH = 7), and decreasing or increasing parameter 7 (from K = 45 for most arid hot regions to K = 0 for equatorial low lying sites, or to K = 100 for areas with the highest degree of continentality).

Key point 6: Figures 6, 7 and 11 together with their explanations (Konta, 1992) show that most phyllosilicates in different rocks have a good chance to survive in the weathering crusts of climatic belts between 15^o and 90^o latitudes north and south of the equator. Even in the tropical humid belt along the equator, about 30^o latitude wide, the phyllosilicates rich in aluminium, i.e. kaolinite and dioctahedral micas, have a chance to withstand the weathering. Smectites, vermiculites, chlorites, and all trioctahedral phyllosilicates are less resistant because they still contain more mobile cations (Na, Ca, Mg, Fe) in susceptible amounts. These phyllosilicates can endure the strong chemical destruction even in the tropical belt if the elevation, the relief, and the topography of an eroded region create a sufficiently higher physical/chemicall weathering ratio of the exposed rocks.

3.2. EROSION AND TRANSPORTATION: HYDRATION, SOFTENING, SWELLING, PHYSICAL DISINTEGRATION, MILLING, ABRASION, DELAMINATION, DISPERSION, AND SORTING

Erosion of weathering crusts including soils and bedrocks is a start of any transportation of their solid fragments in the sediment-forming cycle. The material

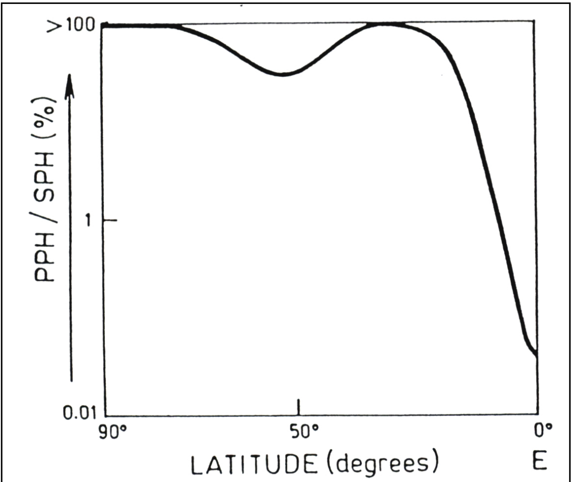


Fig. 11 Graph globally generalizing the ratio between the preexisting (PPH) and newly formed (SPH) phyllosilicates in soils and weathering crusts in clay fraction of fluvial sediments and in fluvial suspensions. E = Equator. (Konta, 1992).

getting into movement can be eroded and transported by three major media: water, air, and ice under continual action of the gravitation. No regularity over space and time exists in the **transportation** between the initial erosion and final deposition of the detrital material. The transported fragments may pass from one medium to another, even several times, before they are deposited more or less permanently. Earth gravitation and moving energy of the acting medium control the speed of transportation or deposition of the fragments together with their size, specific density and shape. Research in earth sciences has shown that it is possible to presume that the surface of Earth in contact with water during the geological history underwent the same physical and chemical laws as it does today. The formation and behaviour of crystalline phyllosilicates in the sediment-forming processes of the known geological history were controlled by the same laws under variable environmental conditions.

The rate of erosion generally increases with the elevation, with the volume of atmospheric precipitations, and with the decrease of the vegetation mantle. Each part of nonarid regions is interwoven by a dense net of the initial tiny transport rills during rains or thaw. They finely end in a mighty river system. The constituents of soils and mechanically disintegrated rocks on the earth surface easily get loose in the erosion process. The finest of them disperse and make the streams muddy. The apparent viscosity of the muddy water increases with the amount of suspended matter and so does its transport capacity.

The repeated shifts and partial delamination along the basal cleavage planes during the milling and grinding in streams may transform some well ordered fragments of phyllosilicates into poorly ordered particles. The sorting of phyllosilicates and other fragments in streams highly depends on the apparent viscosity of suspensions. The ideal separation, sorting, and deposition of successive size fractions of a transported clastic material takes place in the least turbid streams. This is valid also for the size distribution of the transported and deposited clay particles and silt grains in clays with predominating particles of the size below 2 or 4 µm, silts (4-63 µm) or lutites (below 63 µm). The countlessly operating erosion is proper to the bottom transient sediments and banks of each river, especially at elevated discharges.

The authors who globally tried to express the modes of erosion and transportation of the detrital material of the Earth concordantly stress the importance of aquatic environment, the leading role of rivers, and transportation in suspension. Lopatin (1952) already more than 50 years ago estimated that the main solid terrigenous material is transported in rivers as suspended particles and represents 3.5 times more material than the amount of that in solution, and 12.5 times more than that in bed load. Lisitzin (1972) calculated that detrital material transported yearly by the rivers of the world into seas and oceans amounts to about 13.10^9 tons, which represents about 70 % of the globally deposited material in marine sediments. Further material is of volcanic (11.2 %), glacial (5.6 %), eolian (5.6 %), coastal (0.8 %, Gilluly, 1955), and of chemical or biogenic origin (6.8 %). Milliman and Meade (1983) and Meybeck (1984) calculated that the loose solid material transported in rivers represents globally more than 90 % of the eroded earth surface. The rest is shared by landslides, avalanches, glaciers, solifluction movements, and wind erosion. Suspended matter with predominating phyllosilicates and fine-grained quartz outweighs the dissolved load of rivers by roughly 5.8 times globally.

Key point 7: The erosion and transportation of the greatest part of the earth surface takes place in water. Phyllosilicates transported in contemporary streams have different sources. They occur as constituents in eroded fragments of various igneous, metamorphic, and sedimentary rocks, from where they are loosened. They also occur as newly formed clay minerals from weathering crusts and soils. Sedimentary rocks may contain phyllosilicates that already passed one or more weathering events due to their extremely high chemical stability. This counts especially for kaolinite and dioctahedral micaceous clay minerals rich in Al as the representatives of common mineral species in argillaceous sediments (see their I_{KO}, Figs. 6 and 7). The strong hydration capability of most clay aggregates and crystals of phyllosilicates (excepting talc and pyrophyllite) still leads to their softening, swelling, easy physical disintegration, and dispersion in fluvial currents. The eolian dust, volcanic ash, submarine volcanic effusives, and hydrothermal effluences can variably contribute to the composition of any sediment rich in phyllosilicates deposited in water.

3.2.1. *MOVEMENT OF SOLID MATERIAL IN STREAMS AND ITS PARTIAL DEPOSITION*

The classic Hjulström's (1935) graph explains the behaviour of cohesive and loose accumulations composed of different grain sizes in the interaction with flows of different velocities in three sedimentological categories: erosion, transportation, and deposition (Fig. 12). The movement of eroded solid components in rivers runs by traction or rolling (mostly gravel, > 2 mm), saltation (mostly sand, 2-0.063 mm) and in suspension (mostly silt, 0.063-0.004 or 0.002 mm) and clay (< 0.004 or 0.002 mm). The indicated size boundaries represent the nominal diameter converted to isometric volume assuming a density 2.65 g/cm^3. Phyllosilicates occur in any size category of detrital sediments. The largest amount of phyllosilicates is transported in suspension. Log-probability cumulative distribution curves enable to recognize the mode and the amount of size fractions with or without phyllosilicates transported at the bottom by traction (rolling), in periodical suspension

Table 2 Comparison of hardness, density, and cleavage for some common rock-forming minerals transported in rivers.

Mineral	Hardness (Mohs scale)	Density g/cm^3	Cleavage (parallel with)
Most common primary silicates:			
QUARTZ	7	2.65	none (scarce irregular cracks)
FELDSPARS	6 - 6.5	2.55 - 2.58 KF 2.61 - 2.67 NaCaF	perfect (001) and (010)
AMPHIBOLES	5.5 - 6 R 5 - 6 M	2.8 - 3.2 R 3.0 - 3.5 M	perfect (110)
PYROXENES	5 - 6	3.2 - 4.0 R 3.2 - 3.6 M	good (110), (100) and (010)
Phyllosilicates:			
BIOTITE	2.5 - 3	2.88 - 3.18	perfect (001)
MUSCOVITE	2 -3	2.76 - 3.0	perfect (001)
ILLITE and GLAUCONITE	dry aggregates 1.5 - 2	2.4 - 2.8	perfect (001)
KAOLINITE	1	2.5 - 2.6	perfect (001)
CHLORITES	2 - 2.5	2.6 - 2.85 up to 3.40	perfect (001)
VERMICULITES	~ 1	2.4 - 2.7	perfect (001)
SMECTITES	dry aggregates < 2	2.1 - 2.4 2.6 - 2.8 *⁾	
Carbonates:			
CALCITE	3	2.71	perfect (10$\bar{1}$1)
DOLOMITE	3.5 - 4	2.87	perfect (10$\bar{1}$1)

Explanations: R = orthorhombic; M = monoclinic; KF = potassium feldspars; NaCaF = plagioclases; *⁾ values after the removal of molecular H_2O at 110 °C.

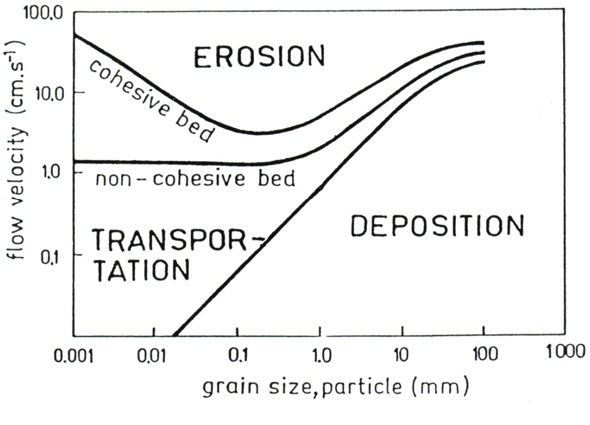


Fig. 12 The classic Hjulström's (1935) graph for erosion, transportation and deposition of different grain sizes of cohesive and loose accumulations under the action of water flows of different velocities.

and suspension of any fluvial sediment (Eschner and Kircher, 1984; Konta, 1992).

Primary phyllosilicates in original shapes may be embedded in gravel or sand fragments of different rocks. The most common muscovite- and biotite-bearing rocks are granitoids, their vein and volcanic equivalents, somewhere with sericitized feldspars or volcanic glass, gneisses, and migmatites. Muscovite is the main mineral of mica-schists. Fine flakes of muscovite (sericite) and chlorite are typical constituents of shales, slates, phyllites, porphyroids, etc. Members of any group of phyllosilicates may be eroded from argillaceous or similar sediments, e.g. clays, claystones, clay shales, marls or marlstones, unconsolidated lutites up to shales and their anchimetamorphic and epizonally metamorphic equivalents. Very fine-grained metamorphic or sedimentary rocks with predominating phyllosilicates, especially, are a huge potential source of detrital phyllosilicates. Many of the phyllosilicates occurring in different rocks easily survive chemical weathering due to their crystal structure and chemical composition. The least stable are biotite and chlorites rich in iron and magnesium (Fig. 7). They are relatively rapidly destroyed in tropical soils.

Key point 8: Coarser crystals of micas, chlorites, vermiculites or kaolinite in different stages of physical weathering disintegrate during continual transportation. The turbulent flow of any river, the impacts and pressure from harder, larger, and heavier fragments make the milling, grinding, and partition of all relatively soft phyllosilicates and their fine-grained aggregates easy. The microscopic or submicroscopic fissures are controlled by the best developed crystal structure planes densely occupied by atoms, but not only along the basis. Phyllosilicates, therefore, are concentrated in clay and fine silt fractions and mostly occur as very thin, irregular flakes. Planar bedding and considerably low aggregate hardness of argillaceous sedimentary rocks and fissility or foliation of metamorphic rocks rich in fine-grained mica and chlorite enable their easy milling or abrasion and disintegration to still thinner and finer flakes of phyllosilicates. Coarser fragments of argillaceous rocks and crystals of phyllosilicates from bedrocks and soils are very sensitive to impacts and pressure from the fragments of co-transported harder and denser rocks and minerals in turbulent streams. This is the most important mechanical phenomenon supporting the enormous accumulation of lutite sediments rich in phyllosilicates in geological history. Table 2 shows a comparison among hardness, density, and cleavage of some common rock-forming minerals reflecting these properties in their rock fragments transported in rivers (see also Fig. 14). The softness of phyllosilicates and their aggregates still increases with hydration.

The aggregates and crystals of expansible phyllosilicates swell and disperse still better in turbulent water streams. The interstratifications of phyllosilicates with expansible layers do not occur in river-suspended matter studied by Konta (1985) in 13 major world rivers, with one slight exception of the Orange flowing through the hot arid zone. The interstratification occurs in the Orange as a petty admixture together with a strongly predominating dioctahedral mica. According to many authors (see original research by Weaver, 1956, and literature quoted in monographs by Weaver, 1989, and Chamley, 1989), however, clay material separated from soils and argillaceous sediments commonly contains interstratifications with expansible phyllosilicates in different amounts. The assemblages of minerals found in the lutite (<0.063 mm) suspensions of 13 rivers, studied from about 40 major world rivers, consist of a limited number of minerals only, yet every river has its individual fingerprint (Konta, 1985). Suspensions of the Mackenzie, the St. Lawrence, the Orinoco, the Caroni, the Parana, the Nile, the Niger, the Orange, the Indus, the Ganges, the Brahmaputra, and the Padma are dominated by phyllosilicates. Amorphous silica with cristobalite, mostly in organic remains, are the major solid constituents of the Waikato. Dioctahedral mica (clastic muscovite + illite) is the principal and omnipresent phyllosilicate with the exception of the Niger, where kaolinite dominates over mica. Chlorite and kaolinite occur in 9 out 13 rivers studied.

Kaolinite is typical in larger portions for the tropical rivers (Niger, Orinoco, Caroni, Parana). Chlorite occurs especially in suspensions poor in kaolinite or without kaolinite (Mackenzie, St. Lawrence, Nile, Indus, Ganges, Brahmaputra, Padma, but also in Orinoco and Parana). Montmorillonite, quantitatively, is the fourth clay mineral in the investigated river suspensions where it was determined in five rivers.

Mowatt and Naidu (1987) studied clay mineral assamblages in deposited bed loads of 10 major rivers of Alaska and adjacent arctic Canada (among them the Yukon and the Mackenzie). The separated <2 μm fractions contained the following phyllosilicates according to their concentrations: illite/mica>>chlorite>kaolinite and expansible phyllosilicates. The kaolinite/chlorite ratio varied between <0.1 and 0.9 with an average value of 0.4. Mowatt and Naidu interpreted the obtained results similarly as Gjems (1967) regarding the assemblages of clay phyllosilicates determined in Scandinavian soils: The most important in determining the mineral assemblages to be found in sediments of the associated fluvial system draining a land area is the nature and composition of the source materials (bedrock and surficial), as well as the topography of the source terrains. The effect is still enhanced in regions where physical weathering is more effective than chemical weathering, and this is the case, in general, at the higher latitudes as well as with some terrains of high relief. Remarkable is also their determination (Mowatt and Naidu, 1987) of mixed-layer structures of indetermined character in the more detailed studied sediments deposited in the Colville River, which "presumably represent weathered/altered micaceous and/or chloritic phases, as well as mixed-layer materials (illite-smectite, etc.) of diagenetic origin derived from sedimentary rocks". The found interstratifications with expansible layers could be explained by their relatively short milling and transportation in turbulent currents and relatively rapid sedimentation.

Emeis and Stoffers (1982) using the X-ray diffraction method did not find any interstratifications of phyllosilicates among crystalline minerals in suspended solids of the Orinoco, the Parana, and the Caroni. Emeis (1985) investigated suspended solids from 9 major world rivers (Yangtse, Waikato, Nile, St. Lawrence, Indus, Parana, Orinoco, Caroni, and Mackenzie) and did not find any interstratification of phyllosilicates. The suspensions studied were generally dominated by micaceous clay minerals, chlorite, and quartz. In the mouth of the Yangtse, phyllosilicates accounted for more than 80 % of its crystalline load. Silt size minerals of the illite/muscovite group dominated.

Key point 9: The absence or very rare and extremely slight admixture of the phyllosilicate interstratifications containing expansible layers in suspended solids of the 13 major world rivers studied can be explained by the following interpretation: These mixed-layer structures rapidly swell in the dynamic environments of rivers and their milling process, disintegrate, and disperse up to very fine almost monophase particles of nonexpansible (mainly micas and chlorites) and expansible (smectites and vermiculites) phyllosilicates. A considerable admixture of quartz is always present in river suspensions under sufficient current energy. Further detectable non-clay minerals in river suspensions studied are (Konta, 1985): potassium feldspar, acid plagioclase, amphibole, calcite, dolomite (and in the Waikato opal with cristobalite in organic remains). Quartz, acid plagioclase, and potassium feldspar are those primary clastic minerals that commonly occur in suspensions of the 13 rivers in various regions of the world. Amphibole is the fourth primary silicate sometimes occurring. The reason for the common occurrence of these four silicates accompanying the predominating phyllosilicates in river suspensions is that they are the most abundant among the minerals in crustal plutonic rocks (Wedepohl, 1969). The purely eolian and glacial sediments could theoretically contain enough preserved phyllosilicate interstratifications with expansible layers derived from eroded bedrocks or soils.

During the study of minerals in suspended matter of 13 major world rivers, I felt that we still need to investigate: a) similarly sampled suspended solids from a denser net of rivers flowing through a region acceptable by its extent and enough rich variety of rocks, geologically and lithologically well documented in all catchment areas; b) not only suspended matter but also <4 μm, 4-63 μm and 63-2000 μm fractions of the bottom sediments of the same rivers; c) mutual relations among individual minerals in these three fractions with the aim to better recognize the effect of milling and subsequent sorting process acting during the transportation of rock and mineral fragments in each river. The region of the drained river basins of the Bohemian Massif (about 60 000 km^2) seemed to be proper for the recognition of the behaviour of eroded rocks including their soils and minerals (Konta, 1990b). The question of the possible absence of the interstratifications with expansible 14 Å-phyllosilicates transported in turbulent currents of rivers in central Europe was also followed (Konta, 1993).

The continuing research has been concentrated on detrital matter in suspensions and clay fraction (<4 μm) of the recent bottom sediments of 31 rivers draining a region of variable parent rocks in Czech Republic (northern latitude between 49-51 °), central Europe (Konta, 1990b). The determined mineral associations are fairly simple. The substantial minerals are as follows: mica/illite and kaolinite, chlorite, ± vermiculite, ± smectite, and quartz. In deposited muds, 11 - 13.5 Å interstratifications of nonexpansible phyllosilicates (14 Å chlorite and 10 Å mica) occur in lesser amounts in about one third of the studied riverine muds. Calcite was found in some rivers draining calcite-bearing sediments, mostly marlstones of Cretaceous age. Minor or accessory amphibole occurs in several rivers only. Opal in diatom tests is an omnipresent constituent of suspended matter of the rivers. The ratio of detrital minerals content to the biogenic matter content in suspension is time depending and rises with the increasing discharge in each river. Gypsum is a newly formed mineral mostly occurring in clay (<4 μm) or silt (4-63 μm), rarely in sand fractions of the bottom sediments, but never in suspensions. The amount of kaolinite, vermiculite, and smectite in the separated size fractions (<4, 4-63, 63-2000 μm) sharply decreases with increasing grain size in all riverine muds studied (Fig. 13). Clastic mica, mostly muscovite, and also chlorite were found in the highest concentrations either in silt or clay fractions, in few samples in sand fraction. The amounts of auxiliary clastic feldspars and amphiboles are mostly the highest in the silt or fine sand fraction and calcite in the silt fraction. Clastic quartz usually occurs in the highest concentrations in the sand or silt fractions. The size distribution of all these detrital minerals is apparently controlled by the structurally conditioned cleavage fragmentation and the relative hardness of minerals (Table 2). A substantial portion of phyllosilicates in the rivers comes from parent rocks of the sedimentary, metamorphic, and igneous origin. A lesser but undeterminable part formed during weathering in soils. The original minerals of parent rocks, their chemical stability, the intensity of weathering and erosion, mechanical fragmentation based on cleavage and hardness of minerals, size and mass differentiation in turbulent streams, the degree of homogenization in suspended matter, and variable discharges of rivers decidedly contribute to the final composition of suspended solids and separated size fractions of the bottom muds deposited in rivers.

The total contents of chlorite + vermiculite + smectite in the <4 μm fractions of the recent bottom sediments of forty rivers in Czechoslovakia vary from 0 to about 30 per cent (Konta, 1993). The remainder (about 70 to 100 %) consists mainly of mica/illite and kaolinite while quartz, Na-rich plagioclase, K-feldspar, amphibole, calcite (dolomite only in the Danube) and gypsum occur as auxiliary or accessory minerals. All attained results are valid for the selected sampling sites and dates for the rivers studied (Konta, 1990b, 1993). The ratios of X-ray basal first-order reflection intensities of the 14 Å phyllosilicates obtained from variously treated oriented samples of the <4 μm fractions separated from recent bottom sediments [Mg^{2+}-saturated sample dried in air and vapour glycolated; K^{+}-saturated sample dried in air (54 % relative humidity), and vapour glycolated, and

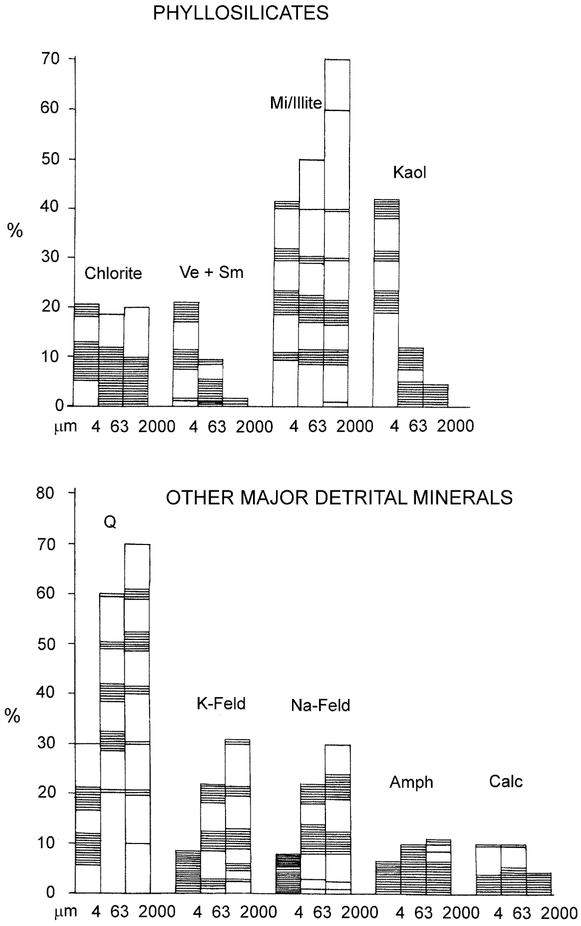


Fig. 13 The concentration relations among rock-forming minerals in three size fractions (<4, 4-63 and 63-2000 µm) of the recent bottom sediments of 31 Bohemian Massif's rivers, based on X-ray diffraction of finely ground samples and microscopic control in silt and sand fractions (Konta, 1990b); some horizontal lines in their dense accumulations may coincide for two or more rivers.

then hydrated above water in a dessicator for 72 hours] are a result not only of different rock-soil sources but also of their transport history. Natural transport and settling conditions of the detrital mineral matter are greatly disturbed by man-made constructions on rivers (weirs, dams, etc.). Varying discharges depend on atmospheric precipitations which influence the depth of erosion and transport energy of each river. Variable ratios among the 14Å-phyllosilicates in nine sites of the Doubrava River and four sites of the Chrudimka River are examples of the influence of different energy on the settling conditions in the stream segments. Each river is a complex hydrodynamic system whose changing energy at any site of the stream may influence the resulting mineral assemblage of the bottom sediment including the 14Å-phyllosilicates (see more in Konta, 1993).

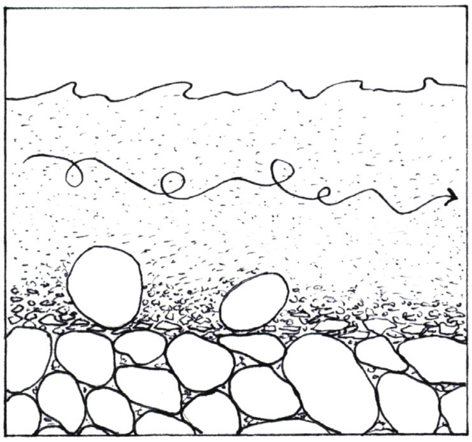


Fig. 14 The most important mechanical process conditioning the huge accumulation of clay- and silt-grain fragments of phyllosilicates in the fluvial "mills" and turbulent currents through the whole history of the Earth. This milling and grinding process of relatively soft phyllosilicates and their aggregates occurs under impacts and pressure from fragments of co-transported harder and denser rocks and minerals.

3.3. DEPOSITION OF PHYLLOSILICATES IN DIFFERENT FLUID DYNAMICS OF STREAMS EXPRESSED BY REYNOLDS (Re) AND FROUDE (Fr) NUMBERS

The deposition of phyllosilicates of any size fraction including clay particles occurs in any river segment considering the longitudinal or transversal profiles. The physical behaviour of transported clastic material in a water flow can be expressed by a dimensionless coefficient, the Reynolds grain number (Re):

$$\mathrm{Re} = \mathrm{U}\ \mathrm{d}\ \rho/\eta\ ,$$

where U is the velocity of the particle ($\mathrm{cm.s^{-1}}$), d is the diameter of the particle (cm), ρ is the density of the particle ($\mathrm{g.cm^{-3}}$), and η is the viscosity of the fluid (poise).

Re varies between 1 and 1000. Laminar, extremely slow flows are characteristic by very low Re. In a flow - during decreasing velocity, turbulence, and apparent viscosity of the aqueous suspension - the fragments fall to the bottom starting with the heaviest and successively continuing to the lightest (cf. some densities of minerals in Table 2). Re usually decreases with the length of a river.

A second important coefficient of fluid dynamics is the dimensionless Froude number (Fr) which is expressed by the following equation:

$$\mathrm{Fr} = \mathrm{u}/\sqrt{g \cdot \mathrm{D}},$$

where u is the average velocity of the flow (m = metre), g is the gravitational acceleration ($\mathrm{m.s^{-2}}$ = 9.82 for Central Europe), D is the depth of the flow (m).

The largest amounts of clays settle from flows of very low Re and Fr. They approach more the laminar than the turbulent flows. This is best fulfilled in the terminal sedimentary basins.

Clay particles, however, may settle in streams in many energetic "shades", especially behind some barriers or on the alluvial planes together with silt and sand grains. The Re and Fr numbers of a river strongly vary not only with sites but also with its seasonal discharge changes (Netopil, 1972; Richey, 1982; Konta, 1992). Smectites occurring as extremely fine flakes cannot settle under strong hydrodynamic conditions, i.e. in the sites of high Re and Fr numbers.

I regret very much that I did not succeed in finding the exact citations of papers published by two British investigators, the authors of Re and Fr numbers in the 19th century (see also Hsü, 2004).

3.3.1. DEPOSITION FROM UNFLOCCULATED AND FLOCCULATED SUSPENSIONS

Granulometric changes in sediment grain size distributions during their evolution from unsorted diamict weathering products (= sedimentary accumulations composed of a wide range of grain sizes) to fluvial bed sediment and material transported in suspension up to its deposition in seas or lakes were described by Kranck (1987) using mathematical equations. He tried to explain that the transportation and deposition of suspended silt or mud depends on the size distribution of the source weathering product, current energy, and flocculation state. Weathering and erosion are considered by Kranck from a pure physical point of view, which is a rare case in earth sciences. Some of his conclusions are important for sedimentology of the eroded and in rivers transported clastic material rich in phyllosilicates. According to Kranck (1987), the principal sites of fluvial deposition are bank areas along the sides of rivers and delta regions with their seaward end or adjacent to lakes along their course. All fluvial bed or bank sediments include both floc and single particle settled accumulations. Floc settled material usually forms less than 20 % of the total. Entirely floc settled sediment has not hitherto been found in fluvial material. Settling from the poorly sorted mud suspensions will deposit well sorted silt (0.063 - 0.004 mm) if the suspension is unflocculated; mud (<0.063 mm) with the same size distribution as that of the parent suspension will deposit if the suspension is completely flocculated. Most fluvial sediments consist of a mixture of both suspension types. We can only add that the fragments of phyllosilicates and angular grains of quartz (<0.063 mm) are the highly predominating constituents of suspended solids in most rivers and deposited lutite sediments. In addition, we must stress still one process and some physical properties of the transported minerals with materially corresponding rock fragments playing principal role in the sediment-forming cycle of phyllosilicates (see key point 10).

The anthropogenic contamination of fresh water in rivers with acids, alkalies, organic polymers etc. leads to drastic changes in the surface electrostatic forces of suspended clay particles. They can cause reduction of repulsive strengths and subsequent attraction and flocculation of electrically neutralized particles. Davis (1983) described depositional systems and the genesis of sediments in different environments from purely geological view.

Key point 10: After the erosion of weathering crusts, the original clastic material transported in fluvial currents is not only sorted but it undergoes strong abrasion, delamination, and dispersion similarly occurring in ball or pebble mills. The abrasion is very strong in the presence of big and hard enough rudite fragments (essentially above 2 mm). Crystals of phyllosilicates and fragments of rocks rich in phyllosilicates reflect their physical properties in relation to co-transported fragments of harder minerals and rocks. The most important physical properties of phyllosilicates and their fine-grained aggregates reflected during the transportation and settling are as follows: a) good cleavage of crystals, b) easy separability of small particles from clay pseudomorphs and fragments of aggregates of bedded, fissile or foliated argillaceous rocks rich in phyllosilicates, but mainly c) their relatively low hardness in relation to other common rock-forming minerals and rock fragments co-transported in streams. In geological history, the easy fragmentation of the phyllosilicate matter transported in streams, together with the natural limitation of their crystal growth under the surface pT conditions, substantially contributes to a huge accumulation of lutite sediments rich in phyllosilicates (see Fig. 15). Coarser flakes,

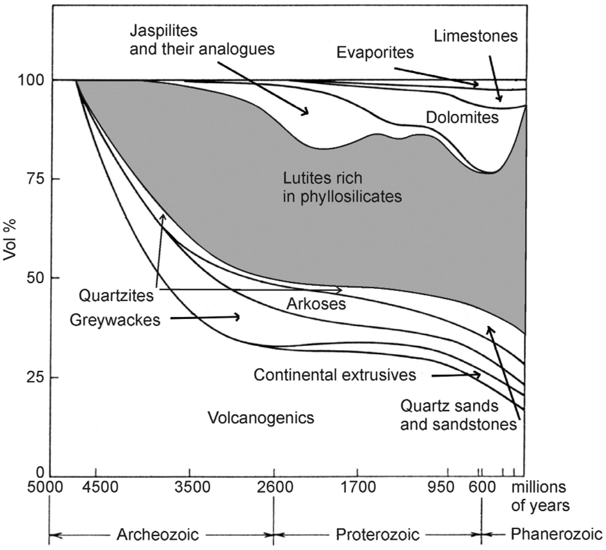


Fig. 15 Volume representation of sedimentary rocks in geological history (Ronov, 1964): lutite sediments (below 63 μm) rich in phyllosilicates and their metamorphic equivalents represent the largest accumulations.

mostly fragments of micas, especially of muscovite, once transported by saltation or traction in streams occur in sands, sandstones, gravels, conglomerates or breccias of fluvial sediments, and in other near-shore sediments of lakes and seas.

The deposition of silt grains (63-4 µm) and coarser clay particles (4-0.5 µm) from water suspensions is under the influence of the gravitational force. The colloidal clay particles (below 0.5 µm) being in the Brownian movement in quiet waters can settle from sols if their coagulation (flocculation) sets in. This is possible under two decisive factors: 1) a higher concentration of colloidal particles and their more frequent collisions (slow coagulation); 2) the decrease of zeta potential (ζ) on the surface of clay particles, which is in relation to the lowering of the thickness of the electric double layer (Stern layer) and the particle surface charge density. The zeta potential (in millivolts) for flat surfaces can be calculated from the equation $\zeta = 4\pi.d.\delta/D$, where d is the effective thickness of the electrolytic double layer, δ the surface charge density, and D the dielectric constant (Marshall, 1949). The electrolytic double layer consists of negative charge of the surface of clay mineral particle and water molecules with condensed positive charges of cations attracted (Fig. 16). Clay particles of any sizes coming into contact with seawater immediately react with its electrolytes. The high concentration of bivalent (Ca^{2+}, Mg^{2+}) and monovalent (Na^+, K^+) cations and also anions leads to their rapid attraction by the electrostatically active surface of clay minerals and by the shrinkage of the original thickness of the Stern layer.

The highly reactive surface of clay minerals is the reason why suspended matter and recent marine mud deposits are concentrated nearshore. According to the extensive studies published by Eisma (1987 and quoted authors), dispersal through a river plume and other seaward flow is concentrated by the estuarine circulation in the estuaries and by a quasi-estuarine circulation in the coastal waters. Further concentration and deposition occur through asymmetric tides and by the absence of waves, by the presence of large tidally or topographically induced eddies, and by organisms fixing suspended particles into larger units (biodeposition). Only small amounts of suspended matter cross the shelf and reach the deep ocean. This occurs primarily where a river mouth is located near or at the shelf edge, where the shelf is very small, or where a canyon funnels suspended material to the deep sea floor. On many shelves a bottom nepheloid layer has been observed that moves slowly in an outward direction. Deposition from this layer involves relatively small amounts of suspended material and occurs chiefly on the continental slope and rise. Mud deposits are found inshore in sheltered areas, and nearshore in the deeper parts where only wave activity during very severe storms can destroy the bottom muds. The hitherto attained observations evaluated by Eisma show that a number of factors tend to keep suspended matter nearshore.

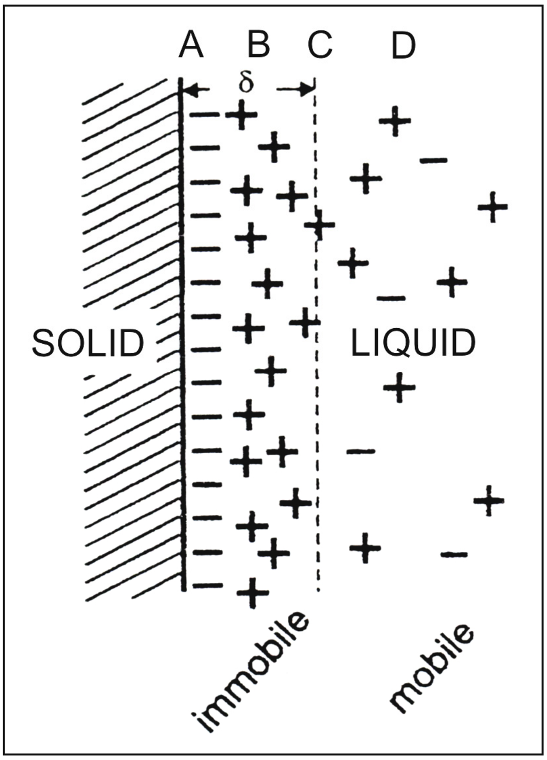


Fig. 16 Electrostatic double layer on the phase boundary solid-liquid. **A** - Negative charges firmly attached to the clay mineral particle (solid phase). **B** - Positive charges of cations in the almost immobile liquid water where water molecules are rearranged by the clay surface. **A-C** (= δ) is the thickness of the attached "immobile" or restrictively mobile layer, which depends on the average distance of cations and water molecules being under the influence of the surface of the solid phase (Stern layer). **D** - Ions under the influence of diffusion in the volume of mobile liquid.

3.3.2. DEFLOCCULATION AND COAGULATION OF CLAY PARTICLES

Deflocculation and coagulation of clay particles in rivers or seas are known from nature and their physics is recognized by experiments (Gibbs, 1983). The equilibrium diameter (D_E) of transported clay flocs or individual particles depends on two processes acting against each other: a) aggregation, caused by the collision of particles, b) dispergation, enabled by erosion and splitting. D_E is a multidimensional function, depending on at least seven variables:

$$D_E = f(C, S, \nu, \rho, D, N, D_o),$$

where C is the concentration of particles ($mg.litre^{-1}$), S is the salinity of water (‰), ν is the kinematic viscosity of fluid ($cm^2.s^{-1}$), ρ is the density of particle ($g.cm^{-3}$), D is the diameter of agitator at the experiment (cm), N is the agitator speed (revolution $number.min^{-1}$; in nature, it is the energy of flow or surf including its turbulence), D_o is the initial diameter of flocs (μm). The equilibrium state is attained when the diameter of flocs does not change with time under existing agitation energy.

The humus compounds and especially the sodium humate, keep fine clay particles in suspension for a long time. This may occur not only in rivers and especially in man-made dams or some small lakes but also in marine environments. The resuspensation of deposited mud and deflocculation of clay aggregates occurs e.g. during a strong storm or flood. The increased cloudiness of the water column reduces the penetration of light into the depth. The long-lasting turbidity and reduction of light in a water basin may have a far-reaching impact on its ecology. Industrial or agricultural waste let out into rivers may change the flocculation and deflocculation conditions of clay particles and thus also the physical and chemical behaviour of one of the most effective natural sorbents.

A mighty coagulation of clay particles takes place in estuaries due to the electrolytic action of salts from marine water causing a drop of the thickness of the Stern electric double-layer of clay minerals. This phenomenon leads to a depositional acceleration of clay particles and oxyhydroxides. It is also the reason why the estuary muds are richer in heavy metals.

3.3.3. SEDIMENTS RICH IN CLAY AND SILT PHYLLOSILICATES COVERING VAST AREAS OF SEAS AND OCEANS

The largest amounts of eroded, detrital phyllosilicates settle as lutite material (<63 μm) in seas and oceans. The following brief summaries of several selected original studies on the minerals of muds collected in different regions of the world ocean, from the present to Cretaceous strata, show that still much deeper research is necessary.

Biscaye (1965) using X-ray diffraction method determined clay minerals in recent deep-sea sediments in about 500 samples collected in the Atlantic Ocean, adjacent seas, and the Arctic Ocean. He also reviewed the most important studies on similar research attained up to that time. The obtained qualitative and semiquantitative data on detrital phyllosilicates, i.e. dioctahedral mica, chlorite, montmorillonite, kaolinite, and some interstratifications, are interpreted from the genetic viewpoint in relation to the world distribution of great soil groups. The genetic presumption regarding the importance of newly formed clay minerals crystallizing in soil horizons as the dominating source of phyllosilicates for marine lutite sediments remained in geological literature almost until the end of the 20th century.

Gibbs (1977) using the same method analyzed 150 bottom muds from the area of the Atlantic Ocean influenced by the Amazon River. The suspended material is carried northwestward by currents on the shelf and was followed after settling in the area for about 1400 km along the eastern shelf of South America. Montmorillonite showed a trend increasing from 27 % to 40 %, the kaolinite decreased from 36 % to 32 %, and the 10Å-mica decreased from 28 % to 18 %. Differential flocculation is shown to be a mechanism of small importance probably because of natural organic and metallic coatings which give all the clay minerals similar flocculating properties. Physical sorting of sediment by size is the dominant mechanism responsible for the laterally changing mineral composition.

Konta (1968) studied phyllosilicates in 122 samples of hemipelagic and pelagic muds from the northwestern region of the Indian Ocean surrounding the Arabian Peninsula. The samples mostly originated from the piston cores provided by Vessel Atlantis II (February to April, 1965), but were also collected as free fall, and some were sampled by the ship Meteor (in the year 1965). The core sediments were mostly deep-sea calcareous clay muds to clayey calcareous muds with variable lutite material deposited in depths between 2100-5000 meters. The amount of biogenic calcite or aragonite (almost all samples with aragonite are from the Persian Gulf) varied between 13-67 weight %; the insoluble residue using the 0.01 N monochloracetic acid contained clastic quartz, feldspars (Na-Ca-plagioclase predominates over K-feldspars), dioctahedral 10Å-mica, chlorite, montmorillonite, some irregular Mi-Mo interstratifications, and pyrite. Biotite was identified under polarizing microscope as a rare accessory in many samples. Kaolinite was not identified by X-ray diffraction method nor by the infrared absorption analysis. If kaolinite is present, then it occurs only in very small quantities. A series of factors influences the accumulation of combustible organic substance together with clay particles in deep-sea sediments. Both the finest materials of the detrital and marine biological origin settle in the relatively deepest depressions of the sea basins as a consequence of the "sedimentary differentiation", namely differentiation during transport.

Kurnosov (1982) analyzed a large number of clay and lutite oceanic samples from deep bore holes along the western, northern, and eastern margins of the Pacific Ocean. The bore holes were performed in the oceanic crust in the water depths mostly between 2000 and 6200 m. The bore cores reached to the depths between 10 and more than 1000 m and penetrated sediments of the Quaternary, Cainozoic, and Mesozoic ages. The terrigenous detrital minerals predominate over the authigenic minerals in all samples studied. The quantitative ratios of dominating phyllosilicates are illustrated in ternary diagrams: smectite - hydromica - (chlorite+kaolinite). Smectites (Sm) mostly, but not always, predominate over dioctahedral hydromica (Mi), and (Sm+Mi) strongly predominate over chlorite+kaolinite. The size fractions less than 1 or 2 μm are always richer in smectite, while the 1-10 μm and 2-20 μm fractions of the same muds are substantially richer in hydromica, chlorite, quartz, feldspars, and amorphous phase.

The determined accessory and trace minerals in most samples are: Ch-Sm interstratifications, carbonates, clinoptilolite, quartz, opal CT, feldspars, and amphiboles. The deep-sea volcanogenic accumulations interlayered with basalt effusives contain the following secondary silicates in semiquantitative relations: saponite > analcime, wairakite > chlorite, actinolite, tremolite > heulandite, clinoptilolite (?), and talc (?).

Naidu et al. (1971) studied less than 2 µm fractions of bottom sediments from the Beaufort Sea and the Arctic Ocean and found that illite is predominating in all of these high latitude sediments. Chlorite and kaolinite occur in significant amounts and smectite is least abundant. Since the generally accepted view related to marine sediments was that kaolinite is a "low latitude" clay mineral, the authors suggested that the use of clay minerals in the inference of paleoclimates should be made with great caution.

Palygorskite and sepiolite, abundant in some deep-sea muds, are authigenic pseudophyllosilicates typical of post-depositional diagenetic processes (Bowles et al., 1971; Church and Velde, 1979; Singer and Galán, 1984; Schallreuter and Konta, 1986). They are also known from sediments of saline lakes in hot arid regions (Parry and Reeves, 1968; Singer and Galán, 1984). Investigation of these Mg-rich clay minerals belongs to a great research region of post-depositional processes marked by diagenetically formed phyllosilicates such as: numerous and different random interstratifications, regular interstratifications (especially corrensite and rectorite), newly ordered chlorites and illites, well ordered kaolinite and dickite.

Key point 11: Phyllosilicates and accompanying detrital minerals in recent marine muds, covering vast areas of seas and oceans, as well as in lacustrine muds correspond with those transported in fluvial suspensions. The resulting quantitative ratios among deposited terrigenous minerals are controlled by the composition of eroded weathering crusts including their bedrocks, by the continuing disintegration and sorting of detrital material during transportation, and by the settling conditions in final depositional environments. Under new environmental conditions during burial, the phyllosilicates tend to new equilibria through chemical and structural changes.

4. CONCLUSION

The most important results cited from literature and from my research regarding the theme "Phyllosilicates in the sediment-forming processes: weathering, erosion, transportation, and deposition" are summed up in eleven key points that can be telegraphically recorded as follows:

1. The first cause of order/disorder states in the structure of phyllosilicates and resulting polymorphism, polytypism or interstratifications lies in the chemical micromilieu acting during the crystallization. The second cause contributing to the diverse polytype and interstratification formations is the accepted low or higher thermal energy. Higher temperature and permeability acting for a longer span of time support better ordering.
2. Clastic material eroded from weathering profiles where physical fragmentation of primary constituents prevailed over their deeper chemical changes usually contains overwhelming amounts of phyllosilicates preserved from original sedimentary, metamorphic or igneous rocks.
3. The mutual comparison of the I_{KO} (index of corrosion) values of rock-forming silicates leads to a conclusion that a considerable volume of phyllosilicates in the sedimentary lithosphere has a source in preexisting phyllosilicates of different bedrocks (sedimentary, metamorphic, and igneous) affected by weathering and erosion. In geological literature, the newly formed phyllosilicates - crystallizing in soils as the dominating global source of argillaceous accumulations in the sedimentary lithosphere - have been overestimated for a long time.
4. Volcanic glasses, despite the fact that they dissolve faster than crystalline primary silicates of the corresponding chemical composition, better preserve their geochemical milieu due to a limited system of cracks and no dense cleavage system typical of most crystalline minerals.
5. The dissolution of silicates in different igneous and metamorphic rocks under weathering conditions and the crystallization of newly formed phyllosilicates in each primary mineral is strongly and for prolonged periods influenced by chemical microenvironments existing in the pseudomorphs. This influence, however, can strongly or totally be reduced in rocks of higher porosity and permeability such as, for instance, in kaolinized arkoses.
6. Most phyllosilicates in different rocks have a good chance to survive in the weathering crusts of climatic belts between 15^o and 90^o latitudes north and south from the equator. A higher physical/chemical weathering ratio of the exposed rocks is favourable for the preservation of phyllosilicates even in the tropical humid belt.
7. Sedimentary rocks may contain phyllosilicates that already passed one or more weathering events due to their extremely high chemical stability, which is valid especially for kaolinite and Al-rich micas.
8. Coarser crystals of micas, chlorites, vermiculites or kaolinite and fragments of fine-grained argillaceous aggregates of any phyllosilicates disintegrate during continual transportation. The turbulent flow of any river, the impacts and pressure from harder, larger and heavier

fragments make the milling, grinding, and partition of all relatively soft phyllosilicates and their aggregates easy. The softness of phyllosilicates and their aggregates still increases with hydration. This is the most important mechanical phenomenon supporting the enormous accumulation of lutites rich in phyllosilicates in the sedimentary lithosphere.

9. The phyllosilicate interstratifications containing expansible layers do not occur in suspended solids of the major world rivers studied due to their swelling and total disintegration to almost monophase particles.
10. The phyllosilicate material, including the species from bedrocks after the erosion of weathering crusts transported in fluvial currents, is not only sorted but it undergoes strong abrasion, delamination, and dispersion similarly occurring in ball or pebble mills.
11. Phyllosilicates and accompanying detrital minerals in recent marine muds, covering vast areas of seas and oceans, as well as in lacustrine muds correspond with those transported in fluvial suspensions. The resulting quantitative ratios among deposited terrigenous minerals are controlled by the composition of eroded weathering crusts including their bedrocks, by the continuing disintegration and sorting of detrital material during transportation, and by the settling conditions in final depositional environments. Under new environmental conditions during burial, the phyllosilicates tend to new equilibria through chemical and structural changes.

Each of the key points, however, requires still a more thorough and deeper investigation. The compiled facts and new interpretations should inspire to a new experimental activity and a more thorough study of samples and processes in nature.

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