

Structural Transformations of Some Clay Minerals Under Pressure in Hydrothermal Conditions

by V. A. Frank-Kamenetzky, N. V. Kotov, E. A. Goilo and G. N. Klotchkova

Department of Crystallography and Lab. of High Pressure, The Leningrad State University, Leningrad B-164, USSR

Abstract

Systematical investigations of the alteration of clay minerals under hydrothermal conditions and the discovery of phases and structural relations of minerals of kaolinite group, montmorillonoids, mixed-layered silicates etc., are of great interest.

In the presence of K, Na chlorides (P=900 kg/cm², T to 500°C, 22-75 hr) kaolinite, dickite and metahalloysite are decomposed to form dioctahedral hydromicas, which are formed through the intermediate disordered mica-montmorillonite mixed-layered formations.

Polymorphic modifications of newly formed micas depend upon the structure of the initial material: from kaolinite, mica 1M prevails; from dickite-mica 2M₁; as from metahalloysite disordered mica.

Under the same conditions, in the presence of Ca chlorides, kaolinite group transforms through the intermediate phases to rectorite and mono-layered hexagonal analog of anortite; and with Mg to tosudite.

The transformations of the dioctahedral montmorillonites depend upon the concentration of the charges in octahedral and tetrahedral positions. From beidellite in the presence of K, Na, Ca Mg chlorides the same phases as from kaolinite are formed, but under considerably lower temperatures. In the presence of KCl, dioctahedral montmorillonite transforms through a whole spectra of disordered mica-montmorillonite phases to hydromica and sandine, and with Na and Ca chlorides to trioctahedral montmorillonite and plagioclase. In the presence of MgCl₂ (trioctahedral) montmorillonite are formed after dioctahedral, and if the duration of treatment is longer, it transforms into talc-montmorillonite mixed-layered phase.

Sepiolite is decomposed (P=800-2000 kg/cm², T=325°, 22-140 hr) and substituted by Mg-montmorillonite; palygorskite under the same conditions is substituted by montmorillonite, then (~500°) by mixed-layered montmorillonite-chlorite, and then by chlorite (<600°) and cordierite+talc (>600°).

In the presence of Ca, Mg chlorides (P=1000 kg/cm², 22 hr.) the lowest temperatures of decom-

position of sepiolite and palygorskite are marked (~250-300°). From sepiolite in the presence of Ca chlorides Mg-montmorillonite+talc+Ca-amphibole are formed; with MgCl₂-Mg-montmorillonite+talc+pyroxene. From palygorskite with CaCl₂ di- and trioctahedral montmorillonite are formed and then talc+anortite (T>450°C).

In the presence of mixture of Na, Ca Mg chlorides (P=1000 kg/cm², 22 hr) sepiolite transforms to Mg-montmorillonite and palygorskite (~250°) and to di- and trioctahedral montmorillonite (~300°). Further, under T=400-450° talc is formed after sepiolite and plagioclase, enrite+talc after palygorskite.

The character of the newly formed phases in the majority of experiments depends on the contents of the original material and upon the type of the mineralizer added, but their structure is defined to the great extent by the structural peculiarities of the initial materials, which are inherited in the process of solid state transformational reactions with the participation of the vapour phase.

Introduction

In the present article are compared the essential features of structural succession that are typical for structural-typeomorphic alteration under hydrothermal conditions of kaolinite group (kaolinite, montmorillonoids, smectites) and layer-ribbon silicates—sepiolites and palygorskites.

As initial materials, the followings were used: kaolinite from Prosjanovsk deposit, USSR, metahalloysite from Micalovec deposit, CzSSR, dickite from Turomensk deposit, USSR, sepiolite from Karamasar, USSR and palygorskite from Pamir, USSR. The samples were held under constant P_{H₂O}=1-2 kb, T=200-650°C conditions in a reactor with a cold lick (Tuttle apparatus type¹) in the presence of pure water or in mixture with chlorides of K, Na, Ca, Mg in ratio 2:1 in sealed ampoules; then they were tempered. Some experiments were carried out under stress by means of an anvil, designed by Bridgman,² and under quasihydrothermal pressure in a cylinder-piston type apparatus. The structural characteristics of newly formed materials were determined mainly by means of X-ray diffractometry.

* Regime of X-ray investigation; CuK α ; Ni-filter; 35 kv, 24 mA; λ : 1200; RC = 1-2 sec.

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The Inheritance of the Structural Motive

The transformations of kaolinite under hydrothermal conditions in the presence of K, Na, Ca, Mg chlorides (Fig. 1) show that the intermediate and final new phases are in general layered silicates and aluminosilicates with similar basis of structure. Even if the samples are treated for 72 hrs at temperatures 200-500°C non-layered phases (zeolites, feldspars, etc.) that are formed under similar conditions from glasses and gels,³ were not formed. Only under higher temperature stability region than that of kaolinite (T>475°C, 3-22 hrs), an admixture of andalusite-like phase was formed.

The specification of synthesized phases is as follows, in different combinations of tetrahedral and octahedral nets with a formation of 2,3,4, and many-layered structures. On the diffractograms of all layered phase which take a part in reactions, this can be seen in the conservation of the position of reflections hK0 (h, k=0), f, 2, 3, ..., h, k, h+k-even) and in essential alteration of the position of reflections 001 and hK (for example—the experiments with KCl and CaCl₂—(Figs. 2, 3). Small variations of parameter b ($\Delta b \approx 0.06 \text{ \AA}$), that is fixed by changing of maximum 001, show that the movement of structure in the basal plane is insignificantly small. It is interesting to compare the sequences of formation of new phases, between the system in which kaolinite minerals were treated under hydrothermal conditions with addition of CaCl₂ and the system in which glasses and gels of analogous composition were used as initial materials. In the first system two main phases are formed: a swelling one—14 Å and non-swelling—7 Å (Fig. 3). The swelling phase, that was examined by X-ray with different treatments, appeared to be montmorillonite (possibly with tetrahedral Al). As the duration of treatment increases and as temperature of synthesis increases up to 400-500°C, this phase is transformed (Fig. 3) into ordered mixed-layered phase, like mica-montmorillonite. The 7 Å phase was examined by electronmicrography and identified to be mono-layered hexagonal analog of anortite; it appears at T=300-500°C in 22 hrs. (Fig. 3) and after the treatment for

70 hours at T 500°C is transformed into two-layered anortite phase. The formation of two-layered phase of anortite composition was reported under similar conditions¹¹ from glasses and gels at T 350°C; at higher temperature crystalline anortite is formed and swelling phases did not appear. Therefore, in the transformations of kaolinite, the metastable layered phases of anortite composition occur at 400-500°C; under the same conditions the stable anortite is formed from gels and glasses of similar composition.¹²

In spite of the similarity of chemical composition

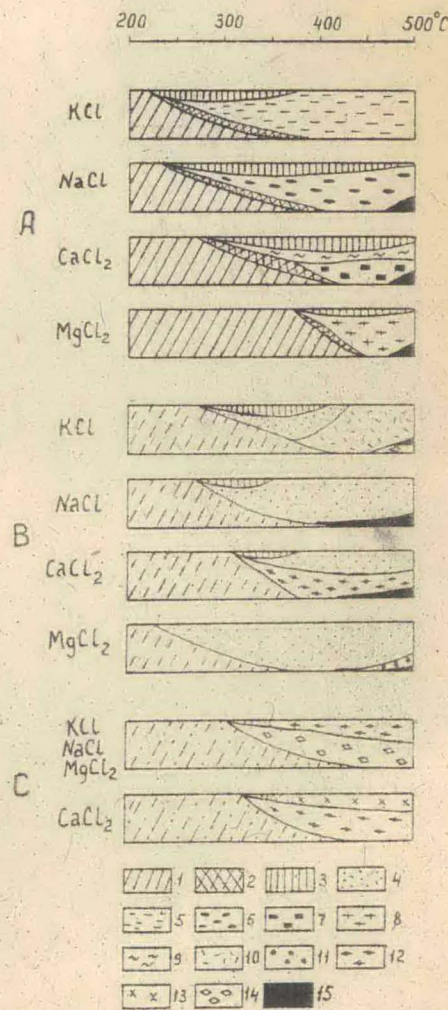


Fig. 1. Phases formed from kaolinite (A), palygorskite (B) and sepiolite (C) under hydrothermal conditions with additions of chlorides ($D_{H_2O} = 1 \text{ kbar}$, 200-500°C, 22-44 hours). Symbols: 1) ordered kaolinite (K); 2) disordered kaolinite; 3) dioctahedral montmorillonite (M); 4) trioctahedral montmorillonite; 5) K-hydromica (HM); 6) Na-hydromica (HM); 7) rectorite (R); 8) tosudite (T); 9) hexagonal analogue of anortite (A); 10) random interstratification of mica and montmorillonite; 11) random interstratification of chlorite and montmorillonite; 12) talc; 13) tremolite; 14) SiO₂; 15) admixtures (X-andalusite in experiments with kaolinite, quartz+biotite+K-feldspar) with K; nepheline+albite with Na; quartz+anortite+cordierite with Ca; talc+quartz with Mg—in experiments with palygorskite. Borders and fields of phase distributions on X-ray data.

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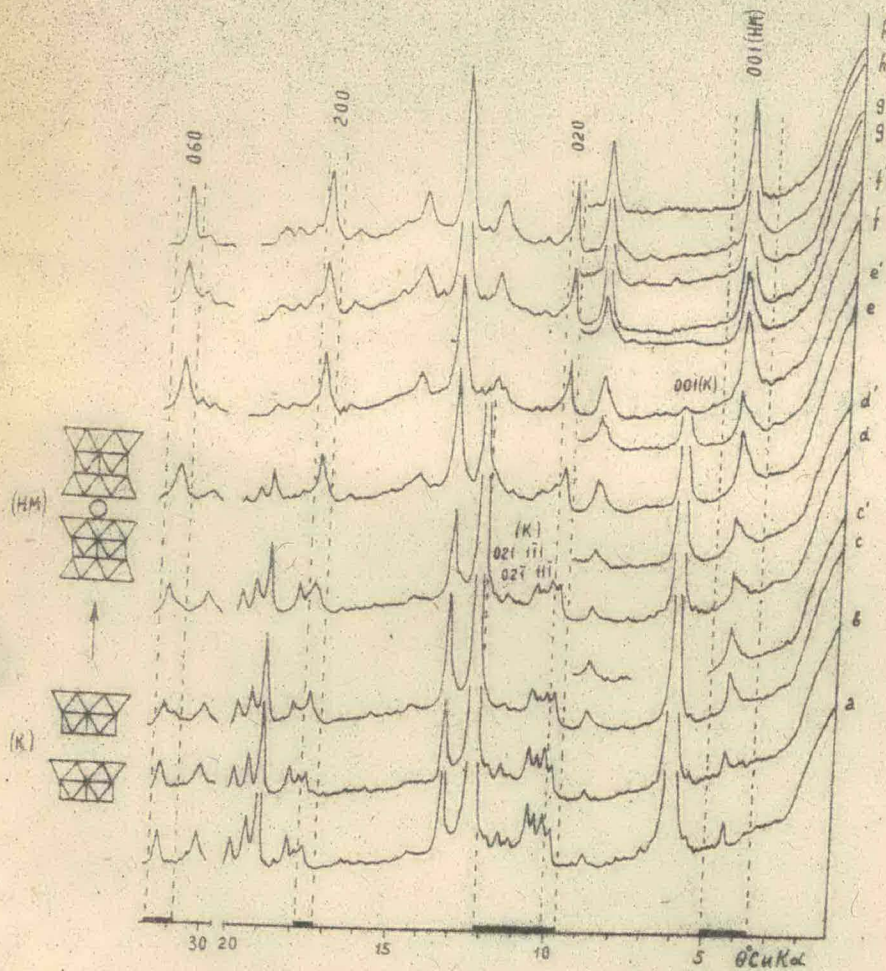


Fig. 2: Succession of structural motive in the basal plane in the transformation of kaolinite to hydromica ($\text{P}_{\text{H}_2\text{O}}=1$ kbar; 200-500°C; 22, 44 hours; with KCl). (1) diffraction curves: a 200°, 22 hrs.; b 250°, 22 hrs.; c 300°, 22 hrs.; d 300°, 44 hrs.; e 350°, 22 hrs.; f 400°, 22 hrs.; g 450°, 22 hrs.; h 500°, 22 hrs.; c-h' for samples c-h saturated with glycol. (2) the scheme of structure (for symbols see Fig. 1, 7).

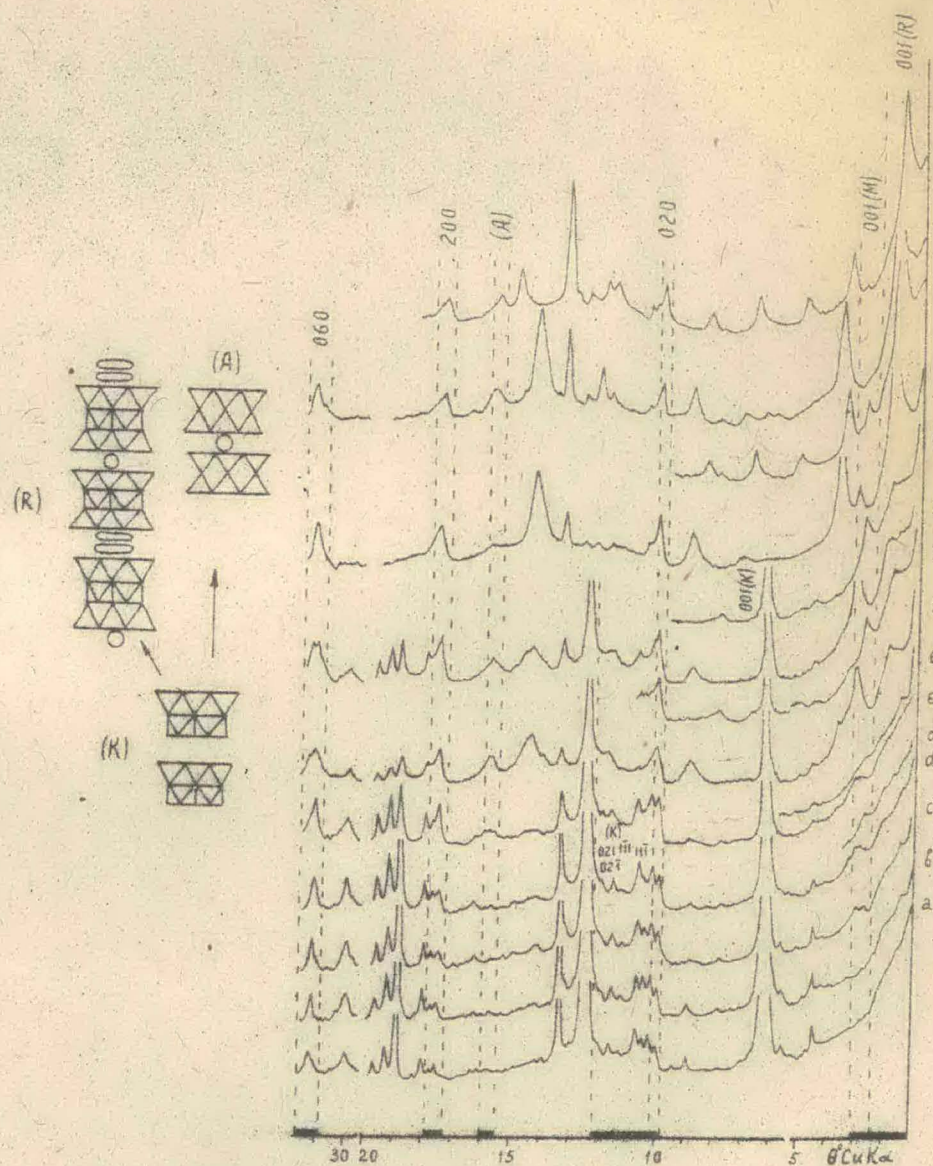
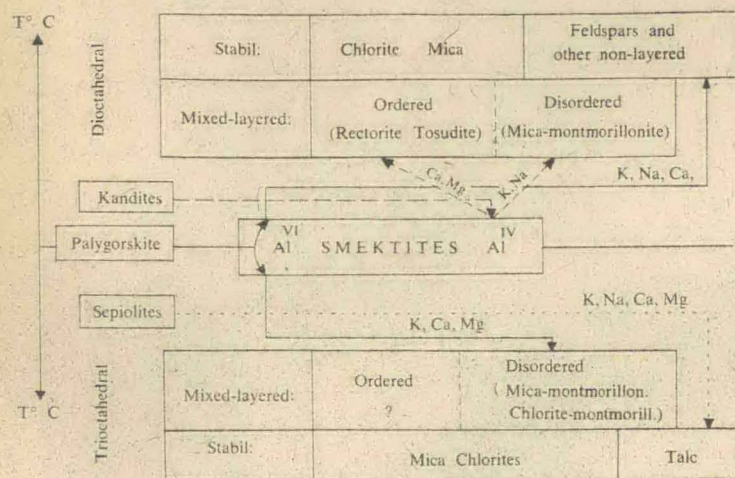


Fig. 3: Succession of structural motive in the basal plane in the transformation of kaolinite to rectorite and to hexagonal analogue of inorite ($\text{P}_{\text{H}_2\text{O}}=1$ kbar; 200-500°C; 22, 44 hrs.; with CaCl_2). (1) diffraction curves: a 200°, 22 hrs.; b 250°, 22 hrs.; c 300°, 22 hrs.; d 300°, 44 hrs.; e 350°, 22 hrs.; f 400°, 44 hrs.; g 400°, 22 hrs.; h 450°, 22 hrs.; i 500°, 22 hrs.; d-i' for samples d-i saturated with the glycol. (2) the scheme of structure (for symbols see Fig. 1, 7).

Schematic Relations in the Transformation of Clay Minerals



from kaolinite (1T) mica with clearly prevalence of modification of 1M over 2M₁ is formed; mica with the prevalence of modification of 2M₁ over 1M is formed from dickite (2M₁). In the examined transformations, the structure, as a whole, undergoes essential alteration from two-layered silicate to three-layered aluminosilicate, but the centres of ditrigons of tetrahedral nets of adjacent layers tend to keep the main layered nature; this shows that the three-dimensional nature of initial structure in newly formed materials is successive.

Octahedral Layer

The above examples show a succession of structural features when transformation of crystalline products takes place without alteration of the character of population of octahedral positions. When K, Na, Ca are added the conservation of dioctahedral nature during the transformation of kaolinite minerals is noticed commonly, but when Mg is added dioctahedral nature increases, which requires special consideration. Small size of Mg-ion and a wide expansion of triocahedral micas, chlorites, montmorillonites, etc., rich in Mg, may give a clue in considering this problem.

Practically, in this case we have a pseudomorphous transformation of kaolinite to dioctahedral montmorillonite. As the duration is extended from 3 hrs. up to 70 hrs. and T from 400 up to 500°C, the montmorillonite transforms into ordered mixed-layered phase, 1:1 chlorite—montmorillonite.^{2,6,7} The character of layered distribution was approximately established by means of one-dimensional Furje-synthesis after the 6 orders 001 for a specimen saturated with glycerol vapours and heated at 550°C (Fig. 6). The relation

of peaks of electron density shows dioctahedral nature of this mixed-layered structure, where Mg essentially enters into brucite layer and into interpacket intervals, but in a three-layered packets we have essentially dioctahedral structure. This conclusion confirms a small shrinkage—1 Å in c* phase during its treatment with LiCl, heated and saturated with glycerol after Greenkelly.¹⁹ In this way an ordered dioctahedral chlorite-montmorillonite is synthesised and this is close to the naturally occurring mixed-layered formation in Japan,^{20,21} whose analog from Crimean alushite was investigated chrysollochemically^{22,23} and called tosudite. It is conjectured that in some time under favourable conditions a dioctahedral layer in such structure can be transformed into a triocahedral one due to the migration of Mg from swelling montmorillonite intervals.

Alteration of Kaolinite Structure during Transformation

In studying the phase transformation of kaolinite, it was noticed that the structure of kaolinite undergoes some regular alterations prior to the beginning of the formation of new phase (up to ~250°C with KCl or up to ~400°C with MgCl₂) in 24 hours, and kaolinite is recrystallized partially and its structure improves. On diffractograms and electronmicrographs this can be seen as better development of 020-111, 021, 021, 130-131 reflections and as increase of numbers of crystallites having regular hexagonal morphology.

When temperature is reached to form any new phase in the presence of any cation addition, it is observed that ordered triclinic kaolinite changes to pseudo-monoclinic with disordered structure in the

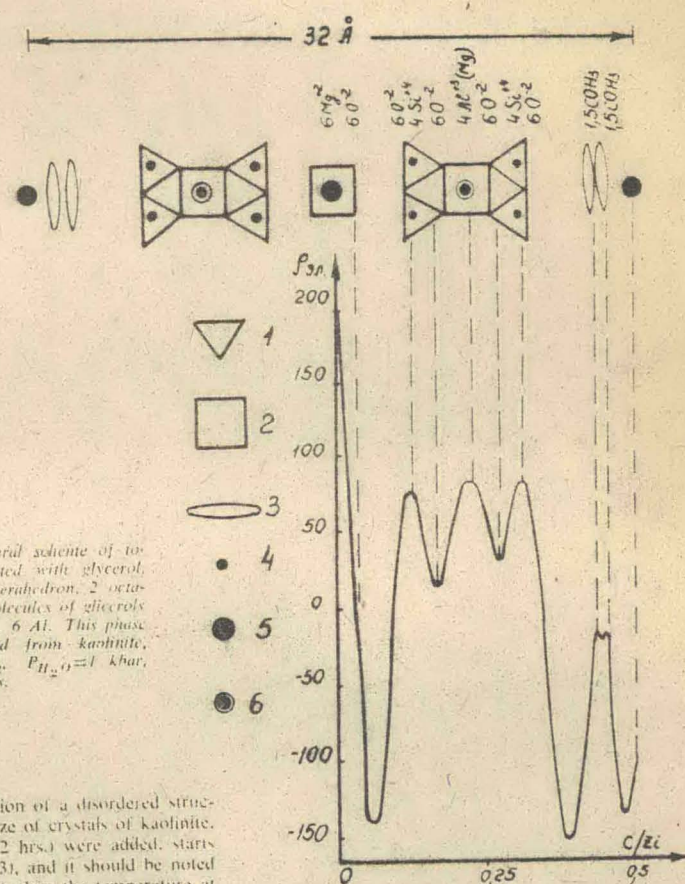


Fig. 6. Structural scheme of tosudite saturated with glycerol. Symbols: 1 tetrahedron, 2 octahedron, 3 molecules of glycerols, 4 Ca, 5 Mg, 6 Al. This phase is synthesised from kaolinite, with MgCl₂, P_{H₂O} = 1 kbar, 450°C, 22 hrs.

basal plane (Fig. 1). Formation of a disordered structure and diminution of the size of crystals of kaolinite, when KCl and CaCl₂ (for 22 hrs.) were added, starts at about 250-300°C (Fig. 2, 3), and it should be noted that this is considerably lower than the temperature at which similar phenomena are observed under "pure" conditions *i.e.*, under the pressure of H₂O-vapour only (~400°C) or with addition of MgCl₂ (~400°C). The worse crystallinity and disordering of the kaolinite structure under hydrothermal conditions with addition of K, Na, Ca, Mg chlorides is followed by the formation of new phases (montmorillonite, disordered mixed-layered phases). Similar structural changes of kaolinite (disordered in the basal plane) take place under the influence of stress pressure, whereas similar amount of hydrostatic pressure gives no effect up to 400°C at P_{H₂O} = 900 gk cm², 22 hrs. Thus, stress and addition of cations lead to disordering of kaolinite structure. The initiation of disordering and the initial temperature of the formation of new phases are determined by the character of cations (Fig. 1). The process of disordering of layers observed here has a dislocation nature. Addition of cations stimulates deformation of the structure (shrinkage or expansion, normal to the base).

A different character of transformation of kaolinite structure, passing through the intermediate montmorillonite-like structure, when K, Na (right) and Ca, Mg (left) are added, is shown schematically in Fig. 7.

Conditions for the Formation of Intermediate Mixed-Layer and Final Layer Structure

The presence of mixed-layered phases which are usually formed as intermediate forms in the course of structural alteration of clay minerals is inferred to the transformation character of the process as well as to the similar layered type of structures. As mentioned above, this process is essentially connected with the chemical nature of the surroundings. When kaolinite is treated in the presence of K, Na chlorides, the intermediate disordered mixed-layered structures of mica-

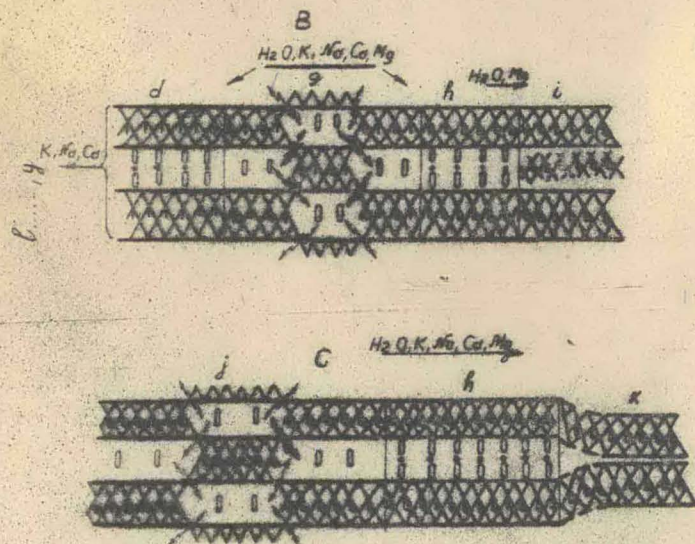
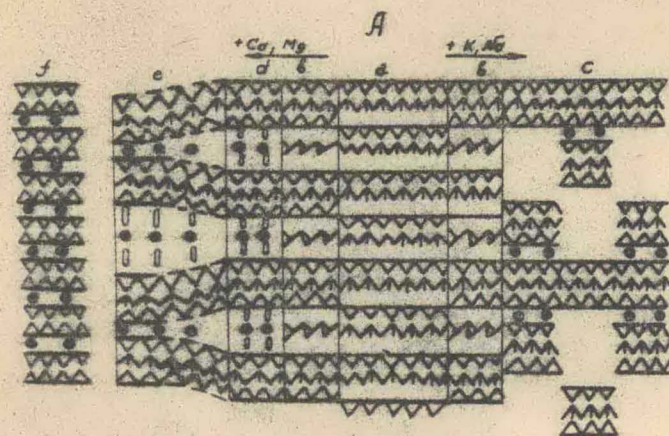


Fig. 7: The scheme of transformation of kaolinite (A), palygorskite (B), sepiolite (C) under hydrothermal conditions with additions of chlorides K, Na, Ca, Mg ($P_{H_2O} = 1$ kbar, 200–500°C, 22–140 hrs.). The schemes of structures: a) kaolinite; b) intermediate beidellite like phase; c) hydromicas (K, Na); d) dioctahedral montmorillonite; e) rectorite (with Ca) and tosudite (with Mg); f) hexagonal analogue of anortite; g) palygorskite; h) trioctahedral montmorillonite; i) trioctahedral chlorite; j) sepiolite; k) talc; l–y) non-layered phases. Symbols: 1) tetrahedra; 2) octahedra and 3) partial distorted octahedra (dioctahedral structures); 4) octahedra in trioctahedral structures; 5) inter-layer cations; 6) water; 7) inter-packet positions in chlorites; 8) the possible destruction positions in palygorskite and sepiolite structures.

montmorillonite type are at first formed, and finally micas of muscovite or paragonite composition are formed. In the presence of Ca and Mg-chlorides, kaolinite changes to an intermediate montmorillonite phase, followed by ordered mixed-layered phases, 1:1 of mica-montmorillonite (Ca) type and chlorite-montmorillonite (Mg).

By structural transformations of palygorskite under pressure of H_2O -vapour and also with $MgCl_2$ dis-

ordered mixed-layered phases of chlorite-montmorillonite type are formed. The process of transformation, described above and the process of which was discussed before^{8,7,5} can be schematically summarized as shown in Table 1.

The principal features of this process are:

1. The varieties of newly formed layered silicates keep their di- and tri-octahedral structural types.

2. Transformations, as a rule, have the intermediate smectite stage (montmorillonite-beidellite type) and their crystallochemical character determines the final phase.
3. Under the hydrothermal conditions and relatively low temperatures, depending on chemical compositions, ordered and disordered mixed-layered phases are formed as intermediate phases.
4. The positions of the fields of smectites, the mixed-layered and stable final phases (Table 1) probably show most common features of structural polymorphous conditions.

Conclusion

It can be said that the above mentioned results can be used for the estimation of some peculiarities of the processes of epigenesis and the first stage of metamorphism. Typical is the transformation mechanism of the process and a wide development of mixed-layered formations. Their nature is principally connected not with thermodynamical parameters (kinetics process), but with the chemistry of the surroundings. Disordered mica-montmorillonite structures are formed by the presence of K and Na in solutions, while Ca and Mg lead to the formation of ordered chlorite-montmorillonite (tosudite) and mica-montmorillonite (rectorite) formation. This process is characterized by the transformation mechanism and the formation of the intermediate smectite phase.

A number of data about the natural metamorphism of clay minerals^{21,24,25} all allows to establish many common features with experimental data discussed above. New investigations of metamorphism of natural clay minerals in details and laboratory experimental investigations in this field will allow to define more accurately and concretely the conception of diagenesis and initial metamorphism of sedimentary rocks.

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