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CRYSTAL CHEMISTRY AND THERMODYNAMICS OF STRUCTURAL TRANSFORMATIONS OF SOME LAYER SILICATES UNDER HYDROTHERMAL CONDITIONS

Abstract. The paper deals with the results of experimental transformations of kaolinite, montmorillonite, sepiolite and palygorskite in the presence of Na, K, Ca and Mg chlorides, sulphates and carbonates under hydrothermal conditions. The obtained intermediate and final products were examined using X-ray, microdiffractometric, electron microscopic and infrared spectroscopic methods. It was shown that stability range of mixed-layer clay minerals is typical for intermediate stages of hydrothermal alteration process. The phenomenon of inheritance of structural patterns of initial minerals by new-formed phases was observed. P-T-X-pH parameters of some experimentally checked reactions were calculated by means of thermodynamic methods. Dehydration and dehydration-ionic models of transformation have been proposed. It was found that the latter is more adequate for interpreting the processes studied that the first one. Thermodynamic approach is very suitable in theoretical study of post-diagenetic, hydrothermal-metasomatic and contact metamorphic alteration of layer silicates.

INTRODUCTION

Crystal chemistry of structural transformations of minerals under high temperature dry conditions is fairly well developed. On the other hand, there are still numerous problems as regards structural mechanism of phase transformation in hydrothermal systems. Therefore, the present authors decided to investigate structural transformations of layer silicates at $P_{H_2O} = 1—2$ kbar and $T = 150—650°C$ in the systems containing K, Na, Ca and Mg chlorides, sulphates and carbonates.

From geological viewpoints, these model experiments are important because of giving valuable data for interpretation of natural kata- and metagenetic, as well as hydrothermal and contact metamorphic processes. The results of these experiments were reported in several papers (Frank--Kamenetsky et al. 1966—1973). Therefore, this paper deals merely with general data and conclusions concerning the most important regularities

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of structural and phase transformations of minerals under investigations: kaolinite, montmorillonoids, layer-ribbon silicates *etc.*

All the experiments were carried out by means of reactors with cold closure using standard method (Kotov, Kopeykin 1972). All the reagents used, preliminarily analyzed (Tab. 1) were placed in platinum tube and kept in salt solutions under constant P, T conditions. During these experiments, the concentrations of salt solutions used were 0.3 to 0.5 molar. When poorly soluble salts were introduced (e.g. dolomite + quartz), their mixture with minerals under study were prepared in proportions from 4 : 1 to 1 : 4 (by weigth) in order to examine sufficiently large mineral : salt ratios. Cationic and anionic composition of solutions were also corresponding to those most widespread in natural conditions. After each experiment, samples were ignited (approx. 5 min.) and examined by means of X-ray, electron microdiffraction and microscopic, as well as infrared spectroscopic and chemical methods.

STRUCTURAL TRANSFORMATIONS

Phase stability fields. X-ray study and semi-quantitative estimation of synthetized phases * allowed to determine stability fields of new formed substances (Fig. 1). Longer edges of each rectangle presented in this diagram correspond to temperature interval of the experiments (200—500°C) whilst the shorter ones to total quantity of phases in the system (100%). Cationc and anionic composition of the systems studied is marked by corresponding symbols. Figure 1 contains basic experimental data concerning phase composition of products and variation of their proportions with changing P-T-X-pH parameters. During comparatively short-time experiments (1—3 days) both stable and intermediate metastable phases are formed. These experiments with short exposition were carried out especially to trace phase character of structural transformations of initial samples, through intermediate phases to final ones (micas, chlorites, talc, non-layer silicates *etc.*). Let us present now the results of the best studied structural transformations of layer and non-layer phases.

CHARACTERISTIC FEATURES OF STRUCTURAL PHASE TRANSFORMATIONS DURING SYNTHESIS OF MICAS

Dioctahedral micas (d_{060} = 1.50—1.52 Å) were obtained by treating kaolin minerals, montmorillonite and palygorskite with potassium chlorides, sulphates and carbonates. As follows from Figure 1 mica-forming processes are low temperature in character and during experiments with short expositions these minerals appeared already at $T \sim$ 200°C. Very low temperature synthesis of mica from montmorillonite (T = 150—170°C) is explained by admixture of beidellite phase (identified by means of Green-Kelly's method) in the initial mineral. Three-sheet (2 : 1) structure

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* V. A. Shitov, Iguen Tat Chama, G. N. Klotschkova, L. P. Pokorina and A. A. Ryushina participated in these experiments and in evaluation of the obtained data.
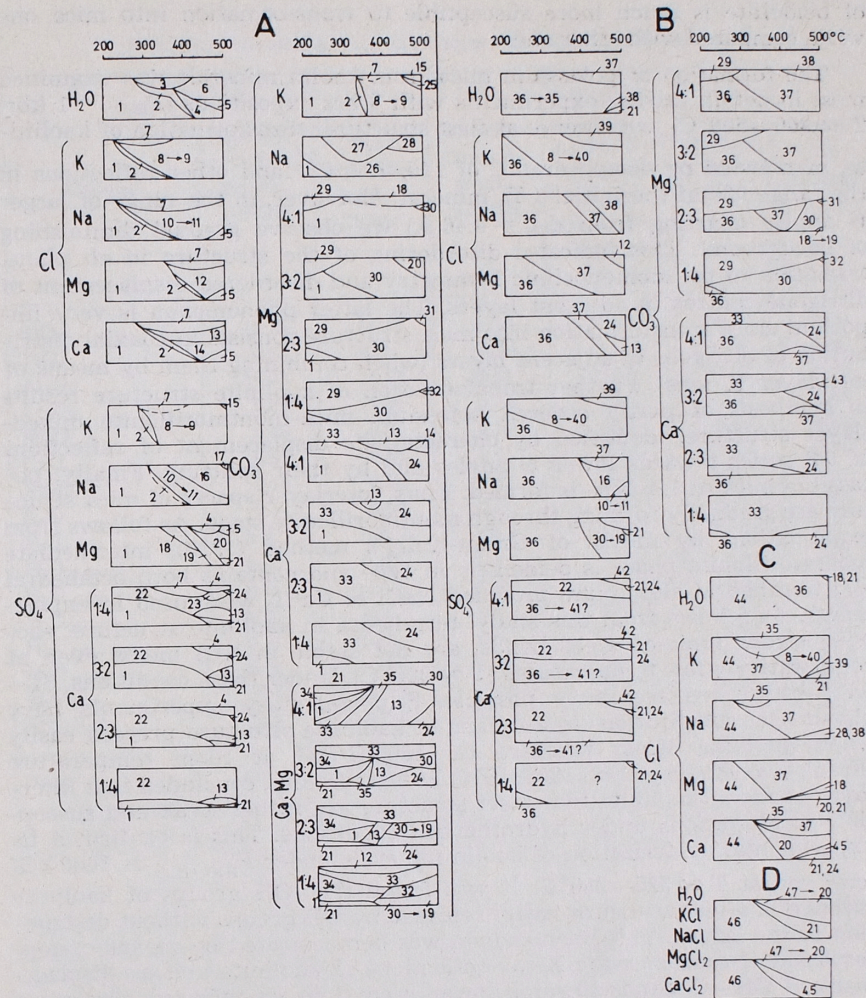
Fig. 1. Phase transformations of kaolinite, dioctahedral Al, Mg, Fe-montmorillonite, palygorskite and sepiolite in K, Na, Ca, Mg-chloride, sulphate and carbonate hydrothermal solutions at P_{H_2O} = 1000 kG/cm², T = 200—500°C, t = 1—3 days

Transformations of: A — kaolinite, B — montmorillonite, C — palygorskite, D — sepiolite. Phases: 1 — kaolinite, 2 — disordered kaolinite, 3 — ordered mixed-layer pyrofillite-montmorillonite, 4 — hydralsite, 5 — andalusite, 6 — pyrofillite, 7 — beidellite phase, 8 — partly ordered mixed-layer K-mica-montmorillonite phase, 9 — muscovite, 10 — partly ordered mixed-layer Na-mica-montmorillonite phase, 11 — paragonite, 12 — tosudite, 13 — rectorite, 14 — hexagonal modification of anorthite, 15 — kalsilite, 16 — albite, 17 — nosean, 18 — partly ordered hexagonal natrodavyne, 19 — chlorite (14 Å), 20 — talc, 21 — quartz, 22 — anhydrite, 23 — margarite, 24 — triclinic anorthite, 25 — leucite, 26 — hexagonal natrodavyne, 27 — analcite, 28 — nepheline, 29 — magnesite, 30 — Al, Mg-serpentine, 31 — forsterite, 32 — brucite, 33 — calcite, 34 — dolomite, 35 — dioctahedral Al-montmorillonite, 36 — dioctahedral Al, Mg, Fe-montmorillonite, 37 — trioctahedral montmorillonite, 38 — oligoclase, 39 — potassium feldspar, 40 — phengite, 41 — vermiculite, 42 — cristobalite, 43 — wollastonite, 44 — palygorskite, 45 — tremolite, 46 — sepiolite, 47 — Mg-montmorillonite

of beidellite is much more susceptible to transformation into mica one when compared with other ones.

The formation of potassium mica from kaolin minerals was examined most in detail. During experiments with 3 hrs expositions ($P_{H_2O} = 1$ kbr, $T = 300—500°C$), we observe at first structural transformation of kaolinite, manifested by disappearance of $\overset{\pm}{110}$, $\overset{\pm\pm}{111}$, $\overset{\pm}{021}$ and other reflections in the range 020 of the initial $1\,T_c$ mineral. Moreover, in the range of larger Θ angles (starting from $d_{020} = 4.46$ Å) we observe gradual diminishing of background. This indicates disordering of the structure in ab plane, transition to pseudomonoclinic symmetry and disordered displacement of ditrigone centres in adjacent layers. The latter phenomenon is very important since transformation into mica structure consists in coaxial distribution of ditrigons of adjacent layers (when combining them by means of interlayer K ions). Further transformation of kaolinite structure results in synthesis of partly ordered potassium mica-montmorillonite mixed-layer structure, identified by characteristic displacement of reflections of $00l$ series towards lower Θ angles and by their splitting. Finally, potassium mica of $1M$ type is formed. Thus, interlayer spaces of mica structure are gradually forming through montmorillonite stage. As follows from examinations by means of Green-Kelly's method (1953), intermediate montmorillonite phase is beidellitic in type and contains both octahedral and tetrahedral aluminium provided NaCl or CaCl$_2$ were used in experiments. As follows from this study, tetrahedra in kaolinite structure, showing strong ionic-covalent bonds, are not stable in KCl media even at comparatively low temperatures ($T \sim 200°C$). Under these conditions, Si—Al substitutions are fairly possible. Supplementary experiments have shown that substitutions in ab plane of kaolinite structure proceed easily when applying stress pressure ca. 150 kG/cm^2 at room temperature (Frank-Kamenetsky $et\ al.$ 1966, 1970). It is, therefore, concluded that interlayer bonds in kaolinite two-sheet structure are rather weak and susceptible to alterations under hydrothermal conditions. This is confirmed by experimental deuterization of kaolin minerals under $P_{H_2O \div D_2O} = 1000$ kG/cm^2 and at $T \sim 325—350°C$. It was found that OH groups of kaolinite layers are, after two hours, easily replaced by OD groups without destruction of the lattice. This phenomenon was demonstrated by means of preservation of characteristic X-ray reflections of kaolinite and by displacement of OH—O bands towards lower ν cm^{-1} in its infrared absorption spectrum. Such an easy OH—OD substitution is due, most probably, to high mobility of H$^+$ ions, being responsible for deprotonization of kaolinite during mica formation.

All the above data indicate that the transformation in question represents a reaction in solid state, during which structural fragments of initial substance are preserved. This conclusion is confirmed by electron microscopic study, indicating preservation of kaolinitic hexagonal forms in the stage when their marginal parts display diffuse spots and rings of intermediate beidellite-like phase (Frank-Kamenetsky $et\ al.$ 1968, 1972b, 1973c). The problem consists in determining the sizes of these structural fragments. Special investigations of kaolin minerals displaying similar composition but different structures (Tab. 1) have shown that in KCl medium ($P_{H_2O} = 1000$ kG/cm^2, $T = 400—500°C$) $1\,T_c$ kaolinite and $2M_1$ metahaloi-

Table 1

Chemical composition of clay minerals used in experiments

Oxides	Kaolinite (Prosyanovsk, USSR)	Metahaloisite (Michalovice, CSRS)	Dickite (Turominsk) RFSSR	Dioctahedral Al, Mg, Fe-montmorillonite (Askansk, Georgia)	Palygorskite (Pamir)	Sepiolite (Karamazar)
	1	2	3	4	5	6
SiO$_2$	46.15	44.76	44.15	50.92	56.12	60.81
TiO$_2$	0.58	n.d.	traces	n.d.	n.d.	n.d.
Al$_2$O$_3$	36.53	36.13	39.87	17.19	11.62	5.45
Fe$_2$O$_3$	0.67	1.20	0.31	2.80	3.48	2.62
MgO	0.28	0.07	0.10	4.10	9.06	16.54
CaO	0.97	0.66	0.57	2.60	0.14	0.77
Na$_2$O	0.13	0.13	0.02	0.72	n.d.	n.d.
K$_2$O	0.34	0.06	0.09	0.86	n.d.	n.d.
P$_2$O$_5$	n.d.	n.d.	0.08	n.d.	n.d.	n.d.
H$_2$O $_{>620°}$	n.d.	n.d.	n.d.	n.d.	—	1.85
H$_2$O $_{<400°}$	n.d.	n.d.	n.d.	n.d.	12.00	3.36
H$_2$O $_{250—620°}$	n.d.	n.d.	n.d.	n.d.	—	—
H$_2$O $_{250—400°}$	n.d.	n.d.	n.d.	n.d.	2.00	—
H$_2$O $_{<250°}$	n.d.	n.d.	n.d.	n.d.	6.00	7.90
H$_2$O $_{105°}$	0.91	2.31	0.08	13.00	n.d.	n.d.
Ign. loss.	13.81	14.75	14.70	7.62	n.d.	n.d.
Sum	100.37	100.07	99.97	99.81	100.42	99.30

A n a l y s t s : $1, 2$ — Pototskaya, 3 — Titomirova, 4 — Gurova (Chem. Lab. Inst. Earth Crust, Leningrad University), $5, 6$ — Garshenina (Chem. Lab. Geol. Inst. Tadzhikistan).

site are generally transformed into $1M$ modification of mica. On the other hand, $2M_1$ dickite changes into $2M_1$ mica and $2M_2$ nacrite — into $2M_2$ modification of mica. Identification of synthetic $2M_2$ mica was carried out by Soboleva and Zvyagin using electronographic method.

These conclusions concerning spacial structural similarity of initial minerals and new-formed phases clearly indicate that most probably, the sizes of structural fragments, participating in solid phase reactions under consideration are such as to facilitate inheritance of polytypic features of kaolin minerals in resulting micas. The formation of mica structure through intermediate beidellite-like phase is presented schematically in Figure 2. Transformation of two-sheet composite layers into three-sheet ones with possibly minimal destruction of the formers consists in liberation of some part of Al from decomposed Al—OH bonds and in substitution of Si by Al, accompanied by removal of some silica in water vapour phase. It is supposed that the formation of phases, being non-transitional in nature, is due just to these elements. In fact, $1M$ modification of potassium mica, forming as admixture during synthesis from nacrite and dickite,
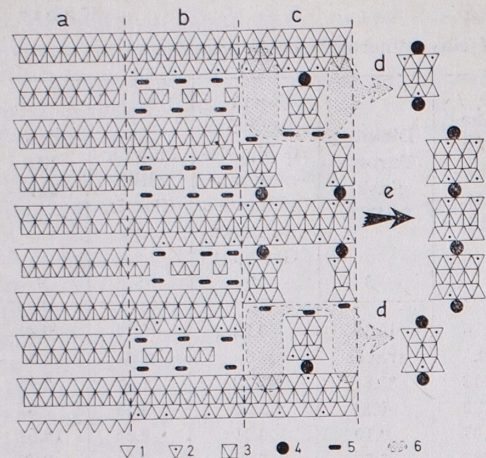
Fig. 2. A scheme of subsequent structural transformations of kaolinite into mica in Na, K-chloride hydrothermal environment

a — kaolinite, b — intermediate beidellite-like phase, c — partly ordered mixed-layer mica-montmorillonite phase, d — mica, resulted from removal of Al, Si-bearing matter in vapour phase, e — mica of transformational origin resulted from solid phase transformation of partly ordered mixed-layer phase, 1 — Si—O-tetrahedra, 2 — (Si, Al)—O-tetrahedra, 3 — octahedra, 4 — interlayer cations, 5 — exchange cations and water molecules, 6 — (Al, Si) portion dissolved and removed by vapour phase

should rather be assigned to non-transitional substances. Similar is the case with andalusite-like phase and boemite observed in our experiments as intermediate products during synthesis of paragonite in the system: kaolin minerals + NaCl + H₂O. However, the majority of paragonite formed in this system is rather of transformational origin. It is formed through intermediate stage of mixed-layer partly ordered mica-montmorillonite phase whereby final products, similarly to potassium micas, are inheriting polytypic modifications of initial minerals.

MIXED-LAYER PHASES AS INTERMEDIATE PRODUCTS IN STRUCTURAL TRANSFORMATIONS OF LAYER SILICATES

As follows from author's experiments, structural reconstitution of kaolin minerals in hydrothermal environment proceeds without their complete decomposition into ions or atoms. Thus, we may suppose that alternative variants of such solid phase transformations are limited.

The first variant admits disordered replacement of Si by Al according to beidellite-like structure during formation of three-sheet composite layers, whilst the second variant — ordering of the layer structure.

Examination of the process of formation of mixed-layer phases is of essential importance for correct interpretation of structural mechanism of transformation of initial layer and pseudolayer minerals. As follows from experimental data (Fig. 1), there are two most probable topological schemes of structural reconstitution of kaolin minerals which can be applied for their transformation into other layer phases. Their type depends on the nature of chemical agents introduced into hydrothermal system. If potassium or sodium chloride solutions are used, there appear the above mentioned partly ordered mica-montmorillonite mixed-layer phases whereas in the presence of Ca and Mg chlorides — the ordered ones. In the latter case, there are forming mineral phases displaying ordered (1 : 1) alternation of unswelling and swelling (montmorillonite-type) layers (Ca-

-rectorite) or of chlorite and montmorillonite type (Mg-tosudite). It was observed that the trend of local transformation of kaolin minerals in hydrothermal conditions is ordering in character. During these processes, Ca and Mg cations surrounded by hydrate shells (displaying high hydration energies) are the best fixing agents of such ordered transformed structures. On the other hand, the presence of entirely mobile K and Na ions (showing low hydration energies) results in the formation of only partly ordered mixed-layer mica-montmorillonite phases. This conclusion was
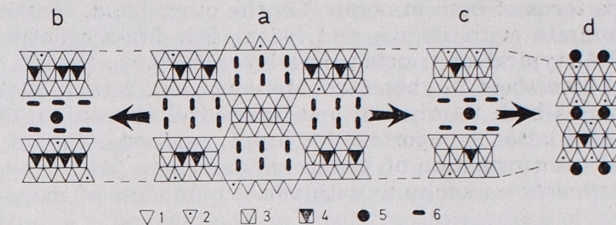

Fig. 3. Schematic presentation of the sequence of structural transformations of palygorskite in hydrothermal KCl-bearing solutions

a — initial palygorskite, b — new-formed trioctahedral montmorillonite, c — dioctahedral montmorillonite, d — K-mica, 1 — Si—O-tetrahedra, 2 — (Si, Al)—O-tetrahedra, 3 — dioctahedra, 4 — trioctahedra, 5 — potassium, 6 — exchange cations and water molecules

confirmed by simple experiments (Frank-Kamenetsky, Kotov, Goilo, Shitov 1970a). Thus, e.g., from artificially disordered kaolinite and dickite, powdered in agate mortar and treated at $P_{H_2O} = 1$ kbar and $T = 400°C$ for 22 hours with CaCl₂, Ca-montmorillonite instead of rectorite was obtained. As follows from Figure 1, no rectorite and tosudite are formed from palygorskite. Layer-ribbon structure of this mineral, when treated with CaCl₂ solutions, decomposed into tri- and dioctahedral montmorillonites and rectorite could form from the latter one (Fig. 3). However, during such decomposition of palygorskite structure into two of montmorillonite type, there is rather no possibility for any ordered distribution of Si and Al in layers of new-formed three-sheet structure. Therefore, no formation of rectorite was observed. Very interesting results were obtained during attempts to transform natural beidellite into rectorite. It was observed (Koldayev et al. 1974) that the former mineral, examined by means of Green-Kelly's method, and containing both octahedral and tetrahedral aluminium, forms selectively from plagioclase in weathering crust of gabbroid rocks. Consequently, it is difficult to expect in this mineral any ordered distribution of Si and Al. In the presence of calcium chloride, hydrothermal synthesis of rectorite from this beidellite proceeds much more difficult than from kaoline minerals *. As follows from these data, we have to distinguish ordered beidellites (formed after kaolinite) and disordered ones (originated from plagioclase), differing in distribution of Al in (Si, Al)—O sheets of adjacent layers.

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* Obviously, it was not possible to obtain pure beidellite samples (formed after plagioclase) by means of elutriation method only.

STRUCTURAL RELATIONS OF KAOLIN MINERALS AND SYNTHETIC (Al, Mg)-SERPENTINES

(Al, Mg)-serpentines were synthetized in the system kaolinite + + $MgCO_3$ + H_2O at $T \sim 150—200°C$ i.e. similarly as micas (Fig. 1). X-ray diffraction patterns of disordered (as regards the ab plane) kaolinite and synthetic (Al, Mg)-serpentine were found to be very similar. So e.g. we observe close position of basal reflections (7.14, 8.56 Å etc.) and characteristic asymmetry of diffraction peak 020. This is connected with similar structural patterns of both minerals. On the other hand, contrary to dioctahedral kaolinite with its $d_{060} = 1,486$ Å, (Al, Mg-serpentine displays $d_{060} = 1.533$ Å, typical of trioctahedral layer silicates, though these both minerals are two-sheet in character. Moreover, the lattice of Al, Mg-serpentine contains both tetrahedral and octahedral aluminium (Nelson and Roy, 1958). The latter is important for proper understanding of the nature of structural transformation of kaolin minerals into (Al, Mg)-serpentines. In our experiments on kaolinite with various amounts of magnesium car-
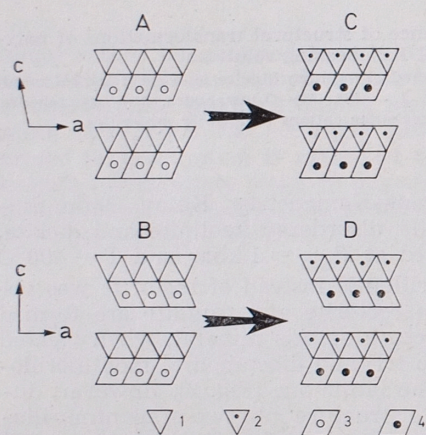

Fig. 4. Schematic presentation of structural transformations of kaolin minerals under hydrothermal conditions into Al, Mg-serpentines in the presence of $MgCO_3$ admixture (projection of structures on ac plane)

A — dickite, B — nacrite, C and D — new formed Al, Mg-serpentines, showing the same orientation of octahedra in adjacent layers as in initial minerals, 1 — Si—O-tetrahedra, 2 — (Si, Al)—O-tetrahedra, 3 — Al—OH octahedra, 4 — (Al, Mg)-octahedra

bonate added we never observed any free silica which would liberate during substitution of Si by Al in tetrahedral position. Besides, no aluminium phases were found that could result from Si-Al octahedral substitutions. Since trioctahedral nature of (Al, Mg)-serpentines is unquestionable, we have to accept some kind of „opening" of kaolinite octahedra during the synthesis in question with liberation of alumina. However, it is not clear either there is any simultaneous opening of Si-O tetrahedra in kaolinite to enable Al-Si substitution or the process consists in addition of new Al tetrahedra to the initial Si ones. In order to trace the course of eventual decomposition of kaolinite structure, additional experiments with kaolinite, dickite, metahaloisite and nacrite were carried out at $P_{H_2O} = 1$ kbar, $T = 450°C$ and $t = 24$ hrs with magnesium carbonate. The following polytypes of (Al, Mg)-serpentines were obtained: 1) from $1T_c$ — kaolinite — $1M$ ($3T$) modification, 2) from $2M_1$ metahaloisite — $1M$ ($3T$) or $2M_1$ one, and 3) from $2M_1$ dickite and $2M_2$ nacrite — a mixture of $2H$ and $6T$ modifications. Consequently, during transformations of

dioctahedral structures into trioctahedral ones, there were preserved both mutual orientation of layers (particularly of octahedral ones) and relative displacement of the projections of ac plane. Dioctahedral structures of kaolinite $\sigma_2\tau_{-}\sigma_2...$ metahaloisite $\sigma_3\tau_{+}\sigma_3\tau_{-}\delta_3$ and dickite $\sigma_1\tau_{+}\sigma_5\tau_{-}\sigma_1...$ (Zvyagin, 1962), displaying the same orientation of octahedral layers of adjacent sheets with τ component (along a axis) = 0, are transformed into their trioctahedral analogue of structural type B (Zvyagin et al., 1965). The latter is characterized by the same orientation of octahedral layers and displacement (translation) τ component along a axis equal to 0. Consequently, nacrite $\sigma_1\tau_6\sigma_2\tau_3\delta_1...$, showing opposite orientation of octahedral sheets in adjacent layers and total τ component along a axis for two layers equal to zero, is transformed into (Al, Mg)-serpentine modification displaying minimal orthogonal two-layer periods of D structural type (Fig. 4). These data indicate that, similarly is an the case of mica formation, during synthesis of (Al, Mg)-serpentines the structure of initial kaolin minerals does not decompose completely into individual ions or atoms but is inherited in spatial distribution of elements. It is, thus, concluded that structural inheritance is possible during phase transformations of layer silicates under hydrothermal conditions not only within dioctahedral group (as observed by Velde, 1965) but also between di- and trioctahedral modifications.

STRUCTURAL TRANSFORMATIONS OF LAYER SILICATES IN THE PRESENCE OF CaMg(CO$_3$)$_2$ AND WATER

Investigations on the influence of dolomite admixture in hydrothermal transformation of kaolinite is very important because of the possibility of tracing the character of phase transformations in the presence of both calcium and magnesium ions. As follows from the results of X-ray examination of products of these experiments (Fig. 1), dolomite at $P_{H_2O} = 1$ kbar is unstable in the system studied already at $T \sim 150°C$. It decomposes into Mg^{2+}, Ca^{2+} and $CaCO_3$ (containing some isomorphic admixture of $MgCO_3$). The obtained products consists of the following phases: Al-montmorillonite, Al, Mg-serpentine, rectorite, tosudite-like phase etc. Structural transformations in comparatively simple systems containing calcium and magnesium chlorides (A) as well as more complex dolomite-bearing one (B) are presented in Figure 5. As follows from experimental data, the reaction of rectorite formation (with calcium) proceeds more rapidly than that of Al, Mg-serpentine one (with magnesium). Consequently, the first process consists in stabilization of polar three-sheet structure by Ca which is subsequently transformed into ordered mixed-layer rectorite structure. Under these conditions, the synthesis of Al, Mg-serpentine does not proceed below 150°C. When dolomite concentration in the system increases, the amount of Mg in gaseous phase is so high that tosudite-like phase is formed as the lowest temperature stabilization product of beidellite-like phase (Fig. 1) instead of rectorite one. The formation of Al, Mg-serpentine is again of secondary importance. Another specific feature of these transformations in simple (with calcium chloride) and more complex systems (with dolomite) consists in the formation of one-layer hexagonal analogue of anorthite in the former case and of its common triclinic modification in the latter. In the system kao-

linite-$CaCl_2$-H_2O, the synthesis of hexagonal variety of anorthite belongs to transformation process with structural inheritance. Comparison of structural scheme of kaolinite and layer anorthite (Fig. 5A) clearly indicates that transformation of the former into latter is not a complicated process (Frank-Kamenetsky, Kotov, Goilo, Shitov 1970a). On the other hand, transformation of Al, Mg-serpentine into layer anorthite would be much more complicated since in this case it would be necessary to remove Mg ions from octahedral positions of the former mineral. It is supposed that this is just the reason of formation of triclinic anorthite instead of its layer modification in the system kaolinite-dolomite-water.
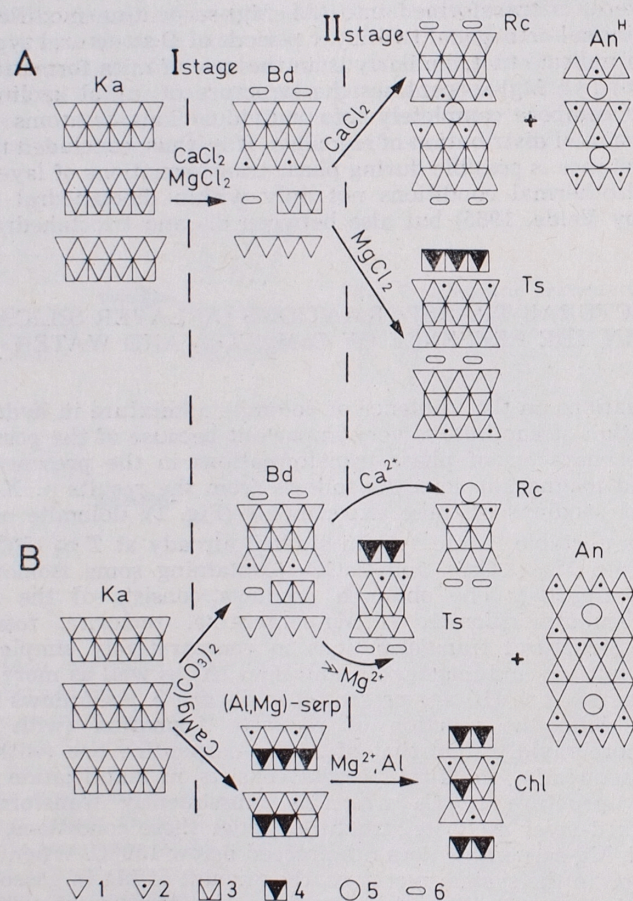

Fig. 5. A comparison of schemes of structural transformations of kaolinite under hydrothermal conditions in the presence of $CaCl_2$, $MgCl_2$ and $CaMg(CO_3)_2$
A — transformation scheme of kaolinite in the presence of Ca and Mg chlorides, B — the same with dolomite admixture. Symbols of phases: Ka — kaolinite, Bd — beidellite-like phase Rc — rectorite, Ts — tosudite, An^H — hexagonal modification of anorthite, An — triclinic anorthite, (Al, Mg)-serp — (Al, Mg)-serpentine (7 Å), Chl — chlorite (14 Å). Explanation of symbols 1—6 see Figure 2

SPECIFIC FEATURES OF STRUCTURAL TRANSFORMATIONS OF LAYER-RIBBON SILICATES AND OF DIOCTAHEDRAL Al, Mg, Fe-MONTMORILLONITES

The nature of structural transformations of these widespread phases was discussed in detail by the present authors in earlier papers (Frank-Kamenetsky et al. 1969b, 1970d, 1971, 1972a, 1972c, 1973c; Kotov, Shitov 1971). Consequently, only some essential data concerning this problem will be presented here.

As regards sepiolite and palygorskite, their common structural pattern consists in ribbon arrangement of layers of talc and montmorillonite type. However, these minerals differ considerably in chemical composition (Tab. 1). The former contains nearly no alumina whilst the latter is chemically close to Al, Mg, Fe-montmorillonite. Experiments under stress pressure and room temperature have shown that weak parts of structure of these both minerals are O-Si-O bridge bonds, combining layers into ribbons. These bonds were found to be the least stable under hydrothermal conditions. In this case, fragments of structure of talc type in sepiolite are combining into layers of Mg-montmorillonite which in turn, after loosing water and interlayer cations, is transformed into talc. Similar transformations are observed in palygorskite (Fig. 3) but the presence of Al, Mg and Fe in octahedral sites of this mineral results in the formation of di- and trioctahedral montmorillonites. The course of further processes depends on cationic composition of the environment (Fig. 1). Limited possibility of $3Mg \leftrightarrows 2Al$ substitutions in dioctahedral Al, Mg, Fe-montmorillonite of the "Ascangel" type resulted in its decomposition into two montmorillonites — dioctahedral aluminic and trioctahedral Mg-Fe one, behaving similarly under hydrothermal conditions.
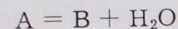
THERMODYNAMIC MODELS

As follows from the above data, experiments with short expositions were quite sufficient and in some cases even necessary for determining the regularities in structural transformations of layer silicates. However, the results of these experiments, including the obtained data on metastable intermediate phases (as presented e.g. in Figure 1) are not sufficient to be described in terms of simple thermodynamic models which are convenient for interpretation of natural processes. In fact, the duration of natural post-diagenetic processes corresponds e.g. to millions of years and for their correct presentation it would be necessary to eliminate kinetic factors, time etc. It is obvious that we cannot carry out these experiments for several years to get reversible equilibrium conditions. Therefore, we tried to calculate equilibrium thermodynamic data for some comparatively simple reactions, in order to find minimal values of P-T-X parameters necessary for them to proceed. It is quite comprehensible that the knowledge of minimal values of these parameters is necessary to indicate natural conditions under which such processes (of the same type as the modelled ones) could proceed, providing there is enough time for them to develop. The importance of experimental data (Fig. 1) for such calculations consists in the fact that so we can find which are the real reactions, contrary to those numerous ones which could proceed but in theory.
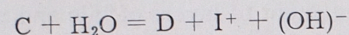
As follows from experimental data (Fig. 1), all the reactions studied can be assigned to two essential types:

1. purely dehydration reactions:

$$A = B + H_2O$$

and

2. dehydration-ionic ones:

$$C + H_2O = D + I^+ + (OH)^-$$

where: A, B, C, D — solid phases,

I^+ — ions in gaseous phase.

Gibbs-Korzinsky phase rule for reactions of the first type can be expressed as follows:

$$n = K_{in.} + (T + P_{H_2O}) - \varphi$$

i.e. $n = K_{in.} + 2 - \varphi$,

and for the second type (if one ion participates in the process):

$$n = K_{in.} + (T + P_{H_2O} - a_{I^+}) - \varphi$$

i.e. $n = K_{in.} + 3 - \varphi$,

where: n — number of independently variable degrees of freedom,

$K_{in.}$ — number of independent inert components,

φ — number of phases.

Application of phase rule in calculations allows for better understanding of the topology of systems in question, to find metastable phases *etc.*

Thermodynamic calculations of reactions of the first type were carried out according to the equation:

$$\Delta Z_{reac.}^{T_1} = - \left\{ (\Sigma V_{fin.}^s - \Sigma V_{in.}^s) P_1 \right\}/41.293 - \int_1^{P_1} V_{H_2O} \, dP,$$

where: $V_{fin.}^s$ — molar volumes of final solid phases,

$V_{in.}^s$ — molar volumes of initial solid phases.

Numerical values of the last integral term of this equation were taken from tables. By means of these equation it was possible to deduce monovariant curves if there were corresponding convenient $P_1 - T_1$ parameters at least for one point. This is important if no exact data for Z_{298}° of the phases in question are available. The value of P_2 in any subsequent point of monovariant curve for T_2 was computed by means of the following equation:

$$\Delta Z_{reac.}^{T_2} + \left\{ (\Sigma V_{fin.}^s - \Sigma V_{in.}^s) P_2 \right\}/41.293 + 4.575 \, T^\circ K \lg P_2 = 0$$

Calculations were carried out by means of methods used by other authors (Nikolayev, Dolivo-Dobrovolsky 1961, Ivanov 1970, Fonarev 1967, Karpov *et al.* 1971).

When computing thermodynamical data for reactions of dehydration-ionic type, in which P_{H_2O} pressure was exceeding 1000 kG/cm², following values were calculated for each phase:

$$\Sigma Z_{fin.}^{T_1} - \Sigma Z_{in.}^{T_1}; \left(\Sigma V_{fin.}^{S, \, ions} - \Sigma V_{in.}^{S, \, ions} \right) P_{1/41.293};$$

$$\int_1^{P_1} V_{H_2O} \, dP$$

The sum of these values determines $Z_{reac.}^{T_1, P_1}$, allowing to use the following equation:

$$Z_{reac.}^{T_1, P_1} + RT (\ln a_{I^+} + \ln a_{OH^-} - \ln a_{H_2O}) = 0$$

Since: $\ln a_{OH^-} = \ln K_w^* - \ln a_{H^+} + \ln a_{H_2O}$

where: $K_w = a_{H^+} \cdot a_{OH^-}/a_{H_2O}$,

Table 2

Some dehydration reactions of layer and pseudolayer silicates

Reactions	Non-variant point in Figure 6	Initial conditions for calculation of equilibria *		Remarks
		$T^\circ C$	P_{H_2O} kG/cm²	
0.86 Pl + H₂O = 1.12 di-M + 0.4 tri-M + 0.84 Q		200	1400	after Mumpton and Roy (1958)
2.9 Sep + 3 H₂O = 3 Mg-M + 2.8 Q		200	1400	
3 Mg-M = 2.9 T + 0.4 Q + 0.4 H₂O	A	245	1000	after Ames and Sand (1958)
3 Sep + 2 H₂O = 8 T + 4 Q		—	—	—
0.4 Sep + 2.8 T + 0.8 H₂O = = 4 Mg-M		—	—	—
10 Di-M = Chl + 6.5 Py + 11 Q + + 2 H₂O		350	1400	after Mumpton and Roy (1958)
		355	2000	Authors data
5.8 di-M = tri-M + 4.3 Py + + 2.1 Q + 1.8 H₂O	B	350	1000	
11 tri-M + 33.65 Py + 15.6 H₂O = = 42.8 di-M + 2.1 Chl		—	—	—
10 tri-M + 5.3 Py + 6.4 H₂O = = 5.8 Chl + 42.8 Q		—	—	—
5.3 di-M + 6.5 tri-M + 3.1 H₂O = = 4.3 Chl + 33.65 Q		—	—	—

* These data are used for calculations of equilibria (Fig. 6) by means of experimentally determined points on monovariant curve (Ivanov, Gusynin, 1970). Symbols of phases: Pl — palygorskite, di-M — dioctahedral montmorillonite, tri-M — trioctahedral montmorillonite, Mg-M — magnesian montmorillonite, Q — quartz, T — talc, Sep — sepiolite, Chl — chlorite, Py — pyrophyllite.

Table 3

Termochemical constants | of minerals and ions

Compound	$-\Delta Z^\circ_{298}$ and $-\Delta Z^T$ cal/mol				V cm³/mol	S°_{298}	$C_p = a + bT - cT^{-2}$			References
	T°K									
	298	373	473	573			a	$b \cdot 10^3$	$c \cdot 10^{-5}$	
Q — SiO_2	204 644	203 652	202 220	200 493	22.0	10.0	11.22	8.2	2.7	Karpov et al. (1968) Nikolayev, Dolivo-Dobrovolsky (1961)
Ka — $Al_2(Si_2O_5)(OH)$	901 400	897 226	890 153	881 581	99.0	48.53	57.47	35.30	7.87	Ivanov (1970)
Na-Bd — $Na_{0.33}Al_2(Al_{0.33}Si_{3.67}O_{10})(OH)_2$	1 282 900	1 277 406	1 268 389	1 257 769	133.7	64.9	67.00	18.71	1.28	Authors data
Par — $NaAl_2(AlSi_3O_{10})(OH)_2$	1 327 400	1 321 682	1 312 066	1 300 458	134.0	67.0	90.57	26.82	20.36	Chatterjee (1970), Karpov et al. (1971), Ivanov, Gusynin (1970)
Ab — $NaAlSi_3O_8$	884 580	880 365	873 445	865 219	101.0	50.2	61.70	13.90	15.01	Ivanov (1970)
Py — $Al_2(Si_4O_{10})(OH)_2$	1 260 000	1 254 595	1 245 563	1 235 896	130.3	63.3	75.63	24.87	8.56	Fonarev (1967)
C — Al_2O_3	376 770	—	—	—	25.6	12.18	22.08	8.97	5.23	Karpov et al. (1968)
Dp — $HAlO_2$	—	—	—	—	17.8	8.43	10.43	7.6	—	} Ivanov (1970)
And — Al_2SiO_5	—	—	—	—	51.6	22.28	41.22	6.24	12.12	
Sep — $Mg_8(Si_{12}O_{30})(OH)_4$	—	—	—	—	437	168	193.2	45.17	7.65	Authors data, Christ et al. (1973)
Pl — $Mg_2Al_2(Si_8O_{20})(OH)_2$	—	—	—	—	266	114.5	116.18	59.97	7.92	}
di-M — $H_{0.5}Al_{1.5}Mg_{0.5}(Si_4O_{10})(OH)_2$	—	—	—	—	132	64.16	51.6	27.91	9.54	Authors data
tri-Chl — $Mg_5Al(AlSi_3O_{10})(OH)_8$	—	—	—	—	171.4	96.0	119.7	25.26	9.55	
H_2O gas	54 635	—	—	—	18.1	45.11	7.17	2.56	0.08	Nikolayev, Dolivo-Dobrovolsky (1961), Naumov et al. (1971)
H_2O liq	56 687	53 834	50 198	46 690	18.1	—	—	—	—	
OH^-	37 594	32 920	25 580	16 820	−4.1	—	—	—	—	} Naumov et al. (1971)
Na^+	62 670	64 040	65 880	67 110	−1.2	—	—	—	—	

the final expression for computing dehydration-ionic equilibria is as follows:

$$-Z^{T_1, P_1}_{\text{reac.}} = 2{,}3 \cdot 1.98\, T°K\, [\lg (a_{I^+}/a_{H^+}) + \lg K_w]$$

The values of K_w are actually well known (Holzapfel, Frank 1966). When computing [I⁺] values, the activity coefficients of ions (γ) were considered to be equal to 1. ΔV^{ions} at elevated P—T parameters were also taken into account. All these simplification did not introduce any essential errors in final results of calculations for moderate temperature conditions. The same refers to computations of some thermochemical constants carried out by means of approximation methods (Ivanov, Gusynin 1970, Fonarev 1967, Karpov et al. 1971, Landiya 1962). The constants used in our calculations are presented in Table 3.

DEHYDRATION MODEL

Initial data used for computing this model are presented in Tables 2 and 3 and the results in Figure 6. Apart from monovariant curves, this Figure contains the contours of P—T parameters of fields of early and late katagenesis, as well as that of metagenesis after Logvinenko (1968).

Detailed discussion of the data presented in Figure 6 is contained in other papers (Kotov 1973, 1974). Therefore, we have to emphasize here merely that upper temperature stability limits of the most important clay minerals — kaolinite, montmorillonoides and layer-ribbon silicates — correspond, according to these model, to very high temperatures. As follows from Figure 6, kaolinite + SiO_2 as well as common di- and trioctahedral montmorillonoids should occur within all the range of P_{H_2O} — T conditions of kata- and metagenesis. Their disappearance is expected but during greenschist metamorphism. However, according to field observations, these minerals are usually not preserved even during catagenesis and their occurrence in rocks of greenschists facies is extremely rare. Since there are no arguments for considering monovariant curves (Fig. 6) to be less correct than $\pm 30°C$ (otherwise we had to admit serious errors in computing thermodynamical constants of such well examined minerals as kaolinite, pyrophyllite, quartz etc.) we have to postulate rather limited possibility of applying dehydration model for interpretation of common natural processes. Consequently, we have to conclude that not only $P_{H_2O} + T$ but, to large extent, also some other factors determine the trend of natural post-diagenetic processes.

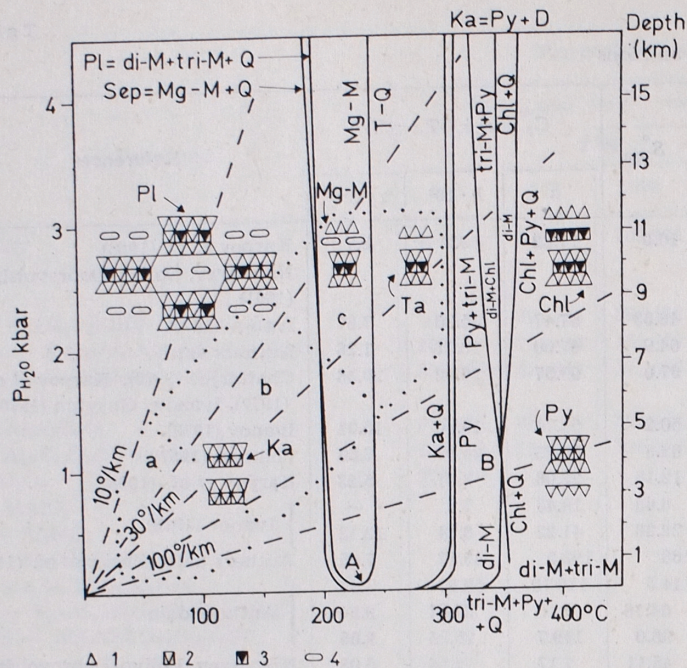Fig. 6. P_{H_2O} — T diagram showing phase relationships of clay minerals during their dehydration (dehydration model)

A, B — non-variant points: a — P_{H_2O}-T-fields of early catagenesis, b — ditto for late diagenesis, c — for metagenesis (after Logvinenko, 1968). S y m b o l s o f p h a s e s: Pl — palygorskite, di—M — dioctahedral montmorillonite, tri—M — trioctahedral montmorillonite, Mg—M — magnesian montmorillonite, Sep — sepiolite, Q — quartz, Ka — kaolinite, Py — pyrophyllite, D — diaspore, Chl — chlorite, T — talc. S t r u c t u r a l f r a g m e n t s: 1 — Si—O tetrahedra, 2 — octahedra of dioctahedral structures, 3 — octahedra of trioctahedral ones, 4 — exchange cations and water molecules

Fig. 7. P_{H_2O}—T—$lg(a_{Na^+}/a_{H^+})$ — diagram showing dehydration-ionic phase relationships of silicates under hydrothermal conditions

a — general block diagram, b — fragment of diagram showing decrease of Al-montmorillonite field with increase of pressure. A — field of early katagenesis, B — field of late katagenesis, C — field of metagenesis (after Logvinenko, 1968). P h a s e s: Par — paragonite, Ab — albite, Bd — Al-montmorillonite (in particular — beidellite-like phase). Other symbols as in Figure 6. S t r u c t u r a l f r a g m e n t s: 1 — Si—O tetrahedra, 2 — octahedra, 3 — interlayer cations, 4 — exchange cations and water molecules, 5 — field of Al-montmorillonite, 6 — approximate limits of conditions of post-diagenetic alterations of rocks (after Logvinenko, 1968)

DEHYDRATION-IONIC MODEL

Qulitative arguments of the above statement result clearly from Figure 1, showing decrease of stability fields of clay minerals in various chemically different hydrothermal environments, resembling the natural ones. It was interesting to obtain quantitative data, based on precise thermodynamical parameters, for the systems presented qualitatively in Figure 1. So e.g. quantitative calculations for the system K_2O — Al_2O_3 — SiO_2 — H_2O are presented by Zharikov et al. (1972). Moreover, valuable experimental and theoretical quantitative data for K, Na-bearing systems were reported by Ivanov and Gusynin (1970), Ivanov (1970) and by Hemley and Jones (1964). The present authors attempted to examine in detail relatively low-temperature equilibria in the system Na_2O — Al_2O_3 — SiO_2 — H_2O, first of all under stability conditions of clay minerals. This problem was discussed more in detail by Kotov (1973, 1974). The quantitative data obtained are presented in generalized form in block-diagram
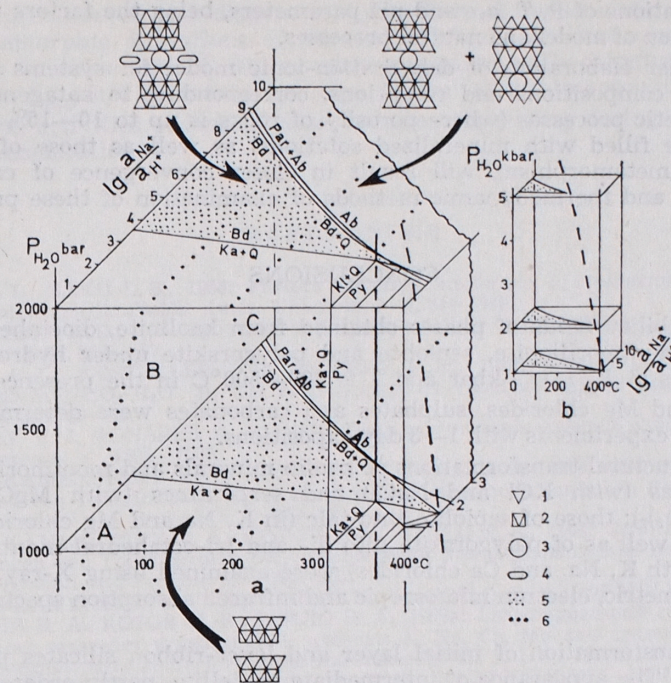
(Fig. 7a). As follows from these data, the association kaolinite + silica is really stable up to comparatively high temperatures ($T \sim 325°C$) if NaCl concentrations (more precisely — the values of $lg(a_{Na^+}/a_{H^+})$ are low. However, if the value of this logarithm exceeds approximately 2.3 (at $P_{H_2O} = 2$ kbar) the temperature range of stability of this association considerably decreases. This is due to appearance of Na, Al-montmorillonite (more precisely — of Na-beidellitic phase) observed in some experiments (Fig. 1). Moreover, careful inspection of Figure 7a indicates that the increase of $lg(a_{Na^+}/a_{H^+})$ value results in decrease of thermal stability range of Na, Al-montmorillonite which decomposes into albite or paragonite + albite. Figure 7b illustrates general decrease of stability field of this montmorillonite with increasing P_{H_2O}. Definite mechanism of structural transformation of the above mentioned phases can be deduced by means of earlier discussed structural-crystallochemical criteria. On the other hand, thermodynamic data allow to find real values

and variations of P, T, a_{I^+} and pH parameters, being the factors used for comparison of model and natural processes.

Further elaboration of dehydration-ionic model for systems of more complex compositions and conditions, corresponding to katagenetic and metagenetic processes (where porosity of rocks is up to 10—15% and the pores are filled with mineralized solutions) as well as those of hydrothermal metamorphism, will result in closer convergence of crystallochemical and thermodynamic methods of examination of these processes.

CONCLUSIONS

1. Stability fields of phases obtained from kaolinite, dioctahedral Al, Mg, Fe-montmorillonite, sepiolite and palygorskite under hydrothermal conditions at $P_{H_2O} = 1$ kbar and $T = 200—500°C$ in the presence of Na, K, Ca and Mg chlorides, sulphates and carbonates were determined by means of experiments with 1—3 day expositions.

2. Structural transformations of kaolin minerals and montmorillonoids into micas (with KCl and NaCl) and serpentines (with $MgCO_3$ and $CaMg(CO_3)_2$); those of sepiolite into talc (in K, Na and Mg chloride solutions) as well as of palygorskite into di- and tri-octahedral montmorillonoids (with K, Na, and Ca chlorides) were examined using X-ray, microdiffractometric, electron microscopic and infrared absorption spectroscopic methods.

3. Transformation of initial layer and layer-ribbon silicates proceeds in stages. The appearance of intermediate beidellite, partly ordered mica-montmorillonite and chlorite-montmorillonite, Al, Mg-serpentines, uniaxal hexagonal modification of anorthite, Mg-montmorillonite (after sepiolite) and of other phases was observed. It was shown that stability range of mixed-layer compounds is very typical for intermediate stages of alteration process of initial layer and pseudolayer phases into final products. This phenomenon is closely related with transformation process of structural changes of layer silicates.

4. A characteristic feature of transformation is the inheritance of structural pattern of initial minerals by the new-formed ones. However, contrary to topotaxial solid phase reactions, transformation processes are characterized not only by structural inheritance in solid phase (preservation of individual layers or of their spatial configurations) but also by synthesis of new compounds in vapour phase at the expense of this part of altered substance which, because of structural limitations, cannot participate in solid phase transformations (e.g. fide Fig. 2).

5. The obtained experimental data are valuable for interpretation of definite reactions between clay minerals. In general, such reactions cannot be foreseen a priori because of complicated multi-component composition of systems in study.

6. Dehydration and dehydration-ionic models of hydrothermal alteration processes of layer and pseudolayer silicates are discussed. P-T-X-pH parameters of some experimentally checked reactions were computed by means of thermodynamic methods. Such procedure allows to overpass the limits which are due to the influence of kinetics, time and other factors on their correct interpretation.

7. This approach is very important in application of experimental data for interpretation of post-diagenetic, hydrothermal metasomatic and contact-metamorphic alterations of minerals. Dehydration-ionic model was found to be more suitable since, when compared with dehydration one (based on P_{H_2O} and T parameters only), it also takes into account the role of pH and activities of ions in water solutions operating during reactions under consideration.

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KRYSTALOCHEMIA I TERMODYNAMIKA TRANSFORMACJI STRUKTURALNYCH NIEKTÓRYCH KRZEMIANÓW WARSTWOWYCH W WARUNKACH HYDROTERMALNYCH

Streszczenie

W pracy przedstawiono i omówiono wyniki badań doświadczalnych nad transformacją niektórych krzemianów warstwowych w warunkach hydrotermalnych.

Wyznaczono pola trwałości faz otrzymanych z kaolinitu, Al, Mg, Fe-montmorillonitu dioktaedrycznego, sepiolitu i pałygorskitu przy $P_{H_2O} = 1$ kbar, $T = 200—500°C$ w roztworach chlorków, siarczanów i węglanów K, Na, Ca i Mg, przy ekspozycji 1—3 doby.

Metodami rentgenowskimi, mikrodyfraktometrycznymi, elektronomikroskopowymi i spektroskopowymi w podczerwieni zbadano przebieg transformacji strukturalnych minerałów grupy kaolinitu i montmorillonitu w hydromiki (w obecności KCl i NaCl) i w serpentyny (z MgCO$_3$ i donitu w hydromiki (w obecności KCl i NaCl) i w serpentyny (z MgCO$_3$ i dolomitem), sepiolitu w talk (w środowisku chlorków K, Na i Mg), jak również pałygorskitu w di- i trioktaedryczne montmorillonitoidy (w obecności chlorków K, Na i Ca).

Transformacja krzemianów warstwowych i warstwowo-wstęgowych przebiega przez różne stadia pośrednie. W produktach przeobrażenia minerałów grupy kaolinitu stwierdzono powstawanie fazy beidellitowej, częściowo uporządkowanych przerostów mieszano-pakietowych, mikowo-montmorillonitoidowych, uporządkowanych przerostów mikowo-montmorillonitoidowych i chlorytowo-montmorillonitoidowych, (Al, Mg)-serpentynów, heksagonalnej warstwowej modyfikacji anortytu, a po sepiolicie — Mg-montmorillonitu i in.

Charakterystyczną cechą transformacji jest dziedziczenie przez nowo-powstałe fazy cech minerałów wyjściowych. W przeciwieństwie jednak do topotaktycznych reakcji w fazie stałej, procesy transformacji przebiegają nie tylko z zachowaniem poszczególnych pakietów i ich przestrzennego ułożenia, lecz również zachodzi synteza nowych związków w fazie gazowej. Odbywa się to kosztem tej części hydrotermalnie zmienionego substratu, która ze względów krystalochemicznych nie może uczestniczyć w transformacji fazy stałej.

Omówiono dwa modele procesu przemiany hydrotermalnej krzemianów warstwowych i pseudowarstwowych: dehydratacyjny i dehydratacyjno-jonowy. Metodami termodynamicznymi obliczono parametry P-T-X-pH kilku zbadanych doświadczalnie reakcji. Podejście termodynamiczne ma istotne znaczenie w zastosowaniu do interpretacji doświadczalnie stwierdzonych przemian minerałów: postdiagenetycznych, hydrotermalno-meta-somatycznych i kontaktowo-metamorficznych. Stwierdzono większą adekwatność modelu dehydratacyjno-jonowego w porównaniu z dehydratacyjnym, jako że poza ciśnieniem pary wodnej i temperaturą uwzględnia on również pH i aktywność jonów w roztworach wodnych, biorących udział w omawianych reakcjach.

OBJAŚNIENIA FIGUR

Fig. 1. Transformacje kaolinitu (A), dioktaedrycznego (Al, Mg, Fe)-montmorillonitu (B), pałygorskitu (C) i sepiolitu (D) w roztworach hydrotermalnych zawierających chlorki, siarczany i węglany K, Na, Ca i Mg (P_{H_2O} = 1000 kG/cm², T = = 200—500°C, t = 1—3 doby)
(szczegółowe objaśnienia faz podano w języku angielskim i rosyjskim)

Fig. 2. Schemat kolejności transformacji kaolinitu w mikę w środowisku hydrotermalnym zawierającym chlorki Na i K
a — kaolinit, b — pośrednia faza beidellito-podobna, c — częściowo uporządkowana mieszano-pakietowa faza mikowo-montmorillonit, d — mika stwarza się w wyniku odprowadzenia nadmiaru Al i Si w fazę gazową, e — mika pochodzenia transformacyjnego powstała w wyniku przekształcenia w fazie stałej częściowo uporządkowanej fazy mieszano-pakietowej
1 — czworościany Si-O, 2 — czworościany (Si, Al)-O, 3 — ośmiościany, 4 — kationy międzypakietowe, 5 — kationy wymienne i drobiny wody, 6 — nadmiar Al i Si wynoszony po przeprowadzeniu reakcji w fazę gazową

Fig. 3. Schemat kolejności transformacji pałygorskitu w roztworach hydrotermalnych zawierających KCl
a — pałygorskit, b — nowo utworzone montmorillonity trioktaedryczne, c — nowo utworzone montmorillonity dioktaedryczne, d — mika potasowa. 1 — czworościany Si-O, 2 — czworościany (Si, Al)-O, 3, 4 — ośmiościany, 5 — potas, 6 — kationy wymienne i drobiny wody

Fig. 4. Schemat transformacji minerałów kaolinitowych w warunkach hydrotermalnych w (Al, Mg)-serpentyny w obecności domieszki MgCO₃ (rzut struktur na płaszczyznę ac)
A — dickit, B — nakryt, C i D — nowo powstałe (Al, Mg)-serpentyny, w których orientacja ośmiościanów w przyległych pakietach jest identyczna jak w minerałach wyjściowych. 1 — czworościany Si-O, 2 — czworościany (Si, Al)-O, 3 — ośmiościany Al-OH, 4 — ośmiościany (Al, Mg)

Fig. 5. Schematy transformacji kaolinitu w warunkach hydrotermalnych w obecności CaCl₂, MgCl₂ i CaMg(CO₃)₂
A — schemat transformacji kaolinitu w obecności chlorków Ca i Mg, B — to samo, z domieszką dolomitu. Oznaczenia faz: Ka — kaolinit, Bd — faza beidellito-podobna, Rc — rektoryt, Ts — tosudyt, An — anortyt trójskośny, An^H — heksagonalna warstwowa modyfikacja anortytu, (Al, Mg)-serp — (Al, Mg)-serpentyn glinowo-magnezowy (7 Å), Chl — chloryt (14 Å). Objaśnienia symboli 1—6 patrz fig. 2

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КРИСТАЛЛОХИМИЯ И ТЕРМОДИНАМИКА СТРУКТУРНЫХ ПРЕОБРАЗОВАНИЙ НЕКОТОРЫХ СЛОИСТЫХ СИЛИКАТОВ В ГИДРОТЕРМАЛЬНЫХ УСЛОВИЯХ

Резюме

В работе представлено и преанализировано результаты экспериментальных исследований структурных преобразований некоторых слоистых силикатов в гидротермальных условиях.

Выявлено поля синтеза фаз полученных из каолинита, диоктаэдрического (Al, Mg, Fe)-монтмориллонита, сепиолита и палыгорскита при P_{H_2O} = 1 кбар, T = 200—500°С и экспозиции 1—3 сут. в присутствии K, Na, Ca, Mg-хлоридных, сульфатных и карбонатных добавок.

Методами рентгеновской дифрактометрии, электронной микроскопии с микродифракцией, ИК-спектроскопии изучены структурные преобразования каолиновых минералов и монтмориллонидов в гидрослюды (с KCl и NaCl) и (Al, Mg)-серпентины (с MgCO₃ и CaMg(CO₃)₂), сепиолита — в тальк (в K, Na, Mg-хлоридных средах), палыгорскита — в монтмориллоноиды ди- и триоктаэдрического типов, (с добавками K, Na, Ca-хлоридов).

Установлено стадийное преобразование исходных слоистых и слоисто-ленточных минералов, проявляющееся в синтезе по каолиновым минералам промежуточной бейделлитоподобной фазы, частично упорядоченных слюда-монтмориллонитовых, упорядоченных слюда-монтмориллонитовых и хлорит-монтмориллонитовых образований, (Al, Mg)-серпентинов, однослойного гексагонального аналога анортита, по сепиолиту — Mg-монтмориллонита и т.д.

Главной чертой трансформационных реакций является унаследование структурой новообразований важнейших структурных черт исходных минералов. Однако в отличие от топотаксических твердофазовых реакций трансформационные включают структурную преемственность как в твердой фазе (унаследование отдельных плоских сеток или их объемных кон-

фигураций и др.), так и синтез новообразований в паровой фазе за счет той части изменяющегося материала, которая в силу структурно-кристаллохимических ограничений не может участвовать в механизме собственно твердофазовых преобразований.

Рассмотрены дегидратационная и дегидратационно-ионная модели процессов гидротермальных преобразований слоистых и псевдослоистых силикатов. На примере некоторых конкретных реакций, выявленных экспериментально, далее, с помощью термохимических методов рассчитаны минимальные P-T-X-pH- параметры протекания реакций с целью снятия ограничений, которые накладывают кинетические факторы, фактор времени и др. на их корректное представление. Последнее имеет важное значение для перенесения данных экспериментов на аналогичные процессы постдиагенетических, гидротермально-метасоматических и контактово-метаморфических изменений минералов при интерпретации последних. При этом выявлены преимущества дегидрационно-ионной модели, т.к. она в отличие от дегидратационной модели учитывает влияние на реакции не только P_{H_2O} и $T°$ параметров, но и pH гидротермальных сред и активности ионов в водных растворах.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Фазовые преобразования каолинита, диоктаэдрического (Al, Mg, Fe)-монтмориллонита, палыгорскита и сепиолита в K, Na, Ca, Mg-хлоридных сульфатных и карбонатных гидротермальных условиях ($P_{H_2O} = 1000$ кг/см², $T = 200 -- 500°C$, t — 3 сут.)

Преобразования: А — каолинита, В — монтмориллонита, С — палыгорскита, Д — сепиолита. Фазы: 1 — каолинит, 2 — разупорядоченный каолинит, 3 — упорядоченный смешаннослойный пирофиллит-монтмориллонит, 4 — гидральсит, 5 — андалузит, 6 — пирофиллит, 7 — бейделлитоподобная фаза, 8 — частично упорядоченная смешаннослойная K-слюда-монтмориллонитовая фаза, 9 — мусковит, 10 — частично упорядоченная смешаннослойная Na-слюдамонтмориллонитовая фаза, 11 — парагонит, 12 — тосудит, 13 — ректорит, 14 — однослойный гексагональный аналог анортита, 15 — калсилит, 16 — кальцит, 17 — нозеан, 18 — частично упорядоченная смешаннослойная хлорит-монтмориллонитовая фаза, 19 — 14 Å-хлорит, 20 — тальк, 21 — кварц, 22 — ангидрит, 23 — маргарит, 24 — триклинный анортит, 25 — лейцит, 26 — гексагональный натродавин, 27 — анальцим, 28 — нефелин, 29 — магнезит, 30 — (Al, Mg)-серпентин, 31 — форстерит, 32 — брусит, 33 — кальцит, 34 — доломит, 35 — Al-диоктаэдрический монтмориллонит, 36 — (Al, Mg, Fe)-диоктаэдрический монтмориллонит, 37 — триоктаэдрический монтмориллонит, 38 — олигоклаз, 39 — калевый полевой шпат, 40 — фенгит, 41 — вермикулит, 42 — кристобалит, 43 — волластонит, 44 — палыгорскит, 45 — тремолит, 46 — сепиолит, 47 — Mg-монтмориллонит

Фиг. 2. Схема последовательности срруктурных преобразований каолинита в слюду в K, Na-хлоридных гидротермальных условиях

а — каолинит, b — промежуточная бейделлитоподобная фаза, с — частично упорядоченная смешаннослойная слюда-монтмориллонитовая фаза, d — слюда, сформированная за счет выноса Al-Si-материала в паровую фазу, e — слюда трансформационного генезиса за счет твердофазового преобразования структуры частично упорядоченной смешаннослойной фазы, 1 — Si-O — тетраэдры, 2 — (Si, Al)-O — тетраэдры, 3 — октаэдры, 4 — межпакетные катионы, 5 — обменные катионы и молекулы воды, 6 — (Al, Si) — материал, выносимый за счет растворения в паровую фазу

Фиг. 3. Схема последовательности структурных преобразований палыгорскита в гидротермальных K-хлоридных условиях

а — исходный палыгорскит, b — новообразованные три- и с — диоктаэдрический монтмориллониты, d — K-слюда, 1 — Si-O-тетраэдры, 2 — (Si, Al)-O-тетраэдры, 3 — ди- и 4 — триоктаэдры, 5 — калий, 6 — обменные катионы и молекулы воды

Фиг. 4. Схема структурных преобразований каолинитовых минералов в гидротермальных условиях в (Al, Mg)-серпентины в присутствии добавки MgCO₃ (проекция структур на плоскость ac)

А — диккит, В — накрит, С и D — новообразованные (Al, Mg) — серпентины, в структуре которых ориентировка октаэдров смежных пакетов сохраняется той же, что и в исходных материалах, 1 — Si-O — тетраэдры, 2 — (Si, Al)-O — тетраэдры, 3 — Al-OH — октаэдры, 4 — (Al, Mg) — октаэдры

Фиг. 5. Сопоставление схем структурных преобразований каолинита в гидротермальных условиях в присутствии добавок CaCl₂, MgCl₂ и CaMg(CO₃)₂

А — схема преобразований каолинита с добавками CaCl₂ и MgCl₂, В — тоже с добавкой доломита. Обозначения фаз: Ка — каолинит, Bd — бейделлитоподобная фаза, Rc — ректорит, Ts — тосудит, Anᴴ — однослойный гексагональный аналог анортита, Anᵀ — триклинный анортит, (Al, Mg)-serp — 7 Å, (Al, Mg) — серпентин, Chl — 14 Å — хлорит. Остальные обозначения (1—6) см. на фиг. 2

Фиг. 6. $P_{H_2O} — T$ диаграмма, иллюстрирующая фазовые взаимоотношения глинистых минералов при их дегидратации (дегидратационная модель)

А, В — нонвариантные точки: а — $P_{H_2O}—T$ — поля начального и В — позднего катагенеза, С — метагенеза. Фазы: Pl — палыгорскит; di-M — диоктаэдрический, tri-M — триоктаэдрический, Mg-M — магниевый монтмориллониты; Sep — сепиолит; Q — кварц; Ка — каолинит; Pyr — пирофиллит, D — диаспор; Chl — хлорит; Ta — тальк. Фрагменты структур: 1 — Si-O — тетраэдры, 2 — октаэдры ди- и 3 — триоктаэдрических структур; 4 — обменные катионы и молекулы воды

Фиг. 7. $P_{H_2O}—T—\lg(a_{Na^+}/a_{H^+})$ — диаграмма, иллюстрирующая дегидратационные фазовые взаимоотношения силикатов в гидротермальных условиях

а — общая блок-диаграмма, b — фрагмент диаграммы, иллюстрирующий сокращение поля Al-монтмориллонита с увеличением давления, А — поля начального, В — позднего катагенеза и С — метагенеза (по Логвиненко 1968). Фазы: Par — парагонит, Ab — альбит, Bd — Al — монтмориллонит (в частности, бейделлитоподобная фаза), остальные обозначения см. на фиг. 6. Фрагменты структур: 1 — Si-O — тетраэдры, 2 — октаэдры, 3 — межпакетные катионы, 4 — обменные катионы и молекулы воды, 5 — поле Al-монтмориллонита, 6 — примерные границы условий постдиагенетических изменений пород