With compliments V. Frank-Kamenetskii 16-X-73

Mineral. Soc. *Japan*. Spec. Pap. **1**, 88~97 (1971) [Proc. IMA–IAGOD Meetings '70, **IMA Vol.**]

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.

Polytypic modifications of newly formed micas depend upon the structure of the initial material: from kaolinite, mica 1M prevails; from dickite-mica $2M_1$; 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 sanidine, and with Na and Ca chlorides to trioctahedral montmorillonite and plagioclase. In the presence of $MgCl_2$ 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, $T\sim325°$, 22–140 hr) and substituted by Mg-montmorillonite; palygorskite under the same conditions is substituted by montmorillonite, then ($\sim500°$) 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 decomposition of sepiolite and palygorskite are marked (~250–$300°$). From sepiolite in the presence of Ca chlorides Mg montmorillonite→talc+Ca-amphibole are formed; with $MgCl_2$-Mg montmorillonite→talc+pyroxene. From palygorskite with $CaCl_2$ 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 ($\sim250°$) and to di- and trioctahedral montmorillonite ($\sim300°$). Further, under $T=400$–$450°$ talc is formed after sepiolite and plagioclase, chlorite+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.

* Regime of X-ray investigation: CuKα; Ni-filtr; 35 kv; 24 mA; 1°/1200; RC = 1–2 sec.

Introduction

In the present article are compared the essential features of structural succession that are typical for structural-typomorphous[1] alteration under hydrothermal conditions of kaolinite group (kandites, montmorillonoids, smektites) 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 Turomginsk deposit, USSR, sepiolite from Karamasar, USSR and palygorskite from Pamir, USSR. The samples were held under constant $P_{H_2O}=1$–2 kb, $T=200$–650°C conditions in a reactor with a cold lick (Tuttle apparatus type[2]) 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,[3] 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.*

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,[11] 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 diffractogramms of all layered phase which take a part in reactions, this can be seen in the conservation of the position of reflections hkO (h, k–0; 1, 2, 3 . . . ; h, k, h+k–even) and in essential alteration of the position of reflections 001 and hkl (for example—the experiments with KCl and $CaCl_2$—(Figs. 2, 3). Small variations of parameter b ($\Delta b\pm0.06$ Å), that is fixed by changing of maximum 060, show that the movement of structure in the basal plane is insignificantly small. It is interesting to compare the sequenses of formation of new phases, between the system in which kaolinite minerals were treated under hydrothermal conditions with addition of $CaCl_2$ 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—7Å (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 7Å phase was examined by electronomicrography 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 conditions[11] 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

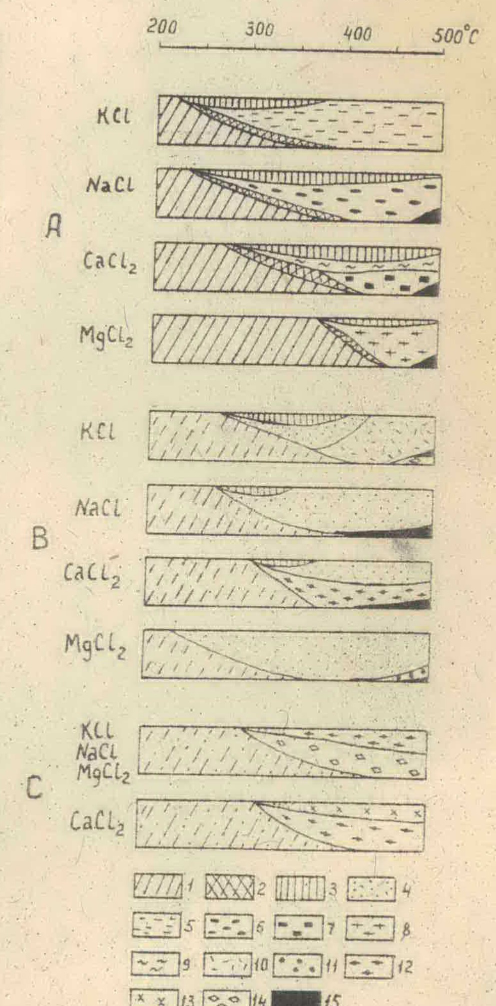

Fig. 1. Phases formed from kaolinite (A), palygorskite (B) and sepiolite (C) under hydrothermal conditions with additions of chlorides ($P_{H_2O}=1$ kbar, 200–500 C, 22–44 hours).

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) SiO_2; 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.