

GI69-1-1

PHASE TRANSFORMATIONS IN SEPIOLITE AND PALYGORSKITE AT DIFFERENT PRESSURES UNDER HYDROTHERMAL CONDITIONS

V. A. Frank-Kamenetskiy, N. V. Kotov and G. N. Klochkova

Leningrad State University

Sepiolite and palygorskite are layer-chain silicates composed of pyroxene-type chains connected by oxygen bridges (Fig.1A,B) /1,2/. In palygorskite the chains are double and in sepiolite, triple pyroxene chains.

The behavior of these structurally similar minerals under hydrothermal conditions, at elevated temperatures and pressures, is of interest in connection with investigations of structural transformations in the principal components of sediments /3,4/.

Starting materials . The samples used in the investigation were palygorskite from the Pamirs /5/ and sepiolite from Karamazar /6/. The chemical composition of these minerals is shown in Table 1.

Table 1

The crystallochemical formula of palygorskite was calculated on the basis of anion $(Si_8O_{20})^{8-}$:

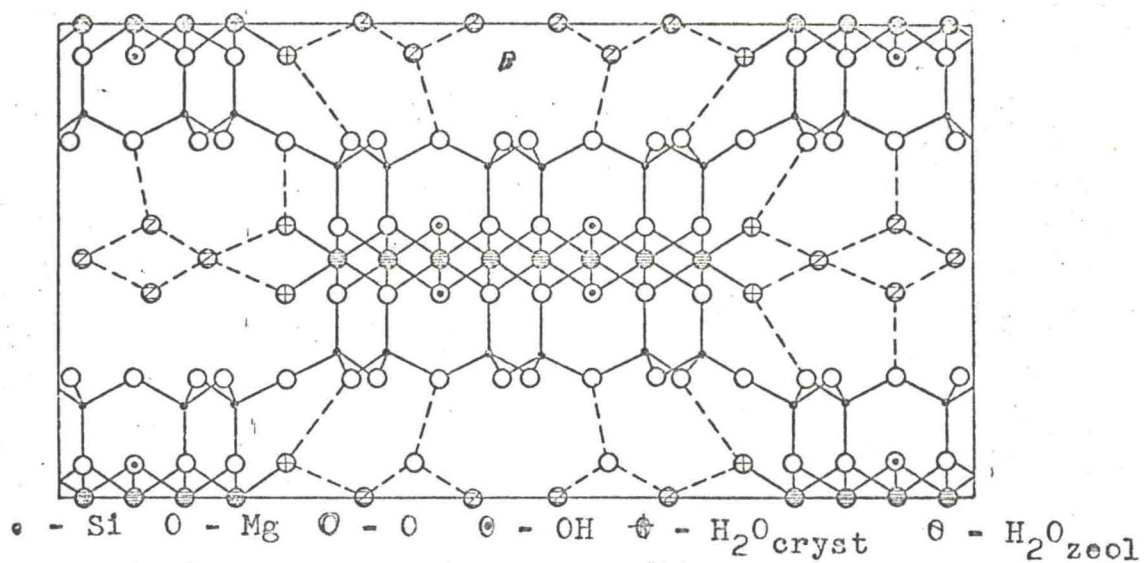
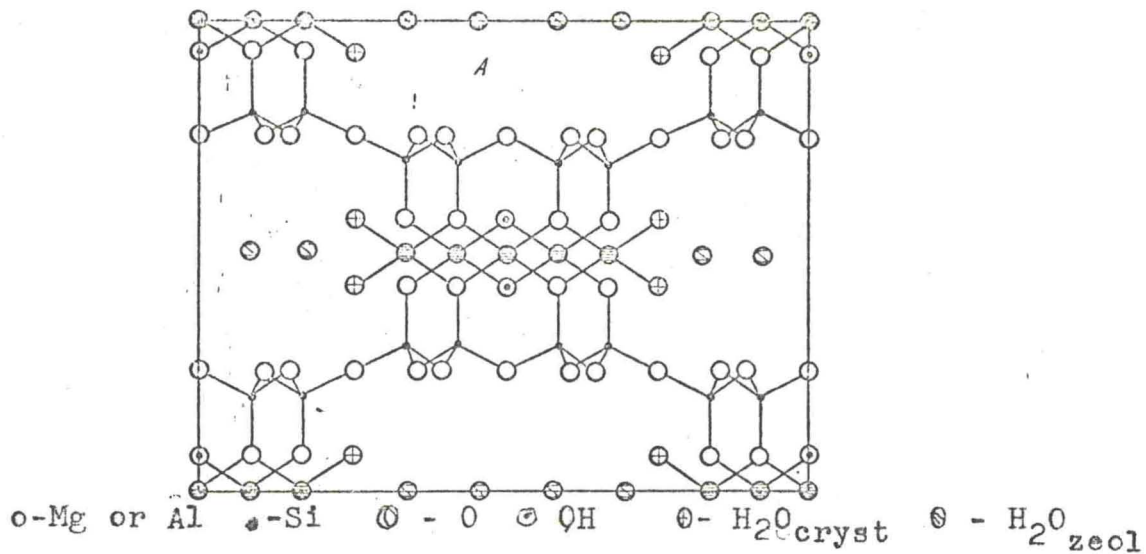
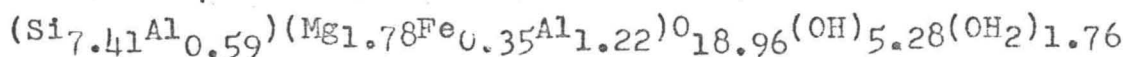
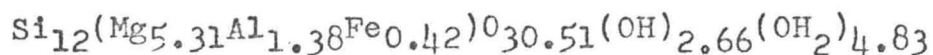


Fig.1. A-unit cell of palygorskite projected on (001) - A

B-unit cell of sepiolite projected on (100)



and of sepiolite, on the basis of anion $(\text{Si}_{12}\text{O}_{30})^{12-}$:



Water content was determined from weight loss curves on derivatograms /5,6/.

Experimental method. The samples were subjected to hydrostatic pressure ($P_{\text{H}_2\text{O}} = 800, 1400, 2000 \text{ kg/cm}^2$) in cold seal pressure vessels of the Tuttle type /7/. The charges were sealed in platinum capsules, heated at temperatures from 100 to 700°C, and quenched under identical conditions for both minerals. The x-ray diffraction data were obtained on diffractometer DRON-1, and in part ^{of} diffractometer URS-50 I, ~~using~~ ^{using} filtered copper radiation. The diffractometer traces were recorded under exactly the same conditions in all experiments.

Fig.1

EXPERIMENTAL DATA

The diffractometer traces of the experimental products are shown in Figs. 2 and 3. The crystal structures of palygorskite and sepiolite in the pressure interval from 800 to 2000 ~~kg~~^{kg}/cm² and temperature range from 100 to 300°C remain unchanged. This is shown by the very close similarity of the traces of sepiolite (Fig. 2^A, a-d) and of palygorskite

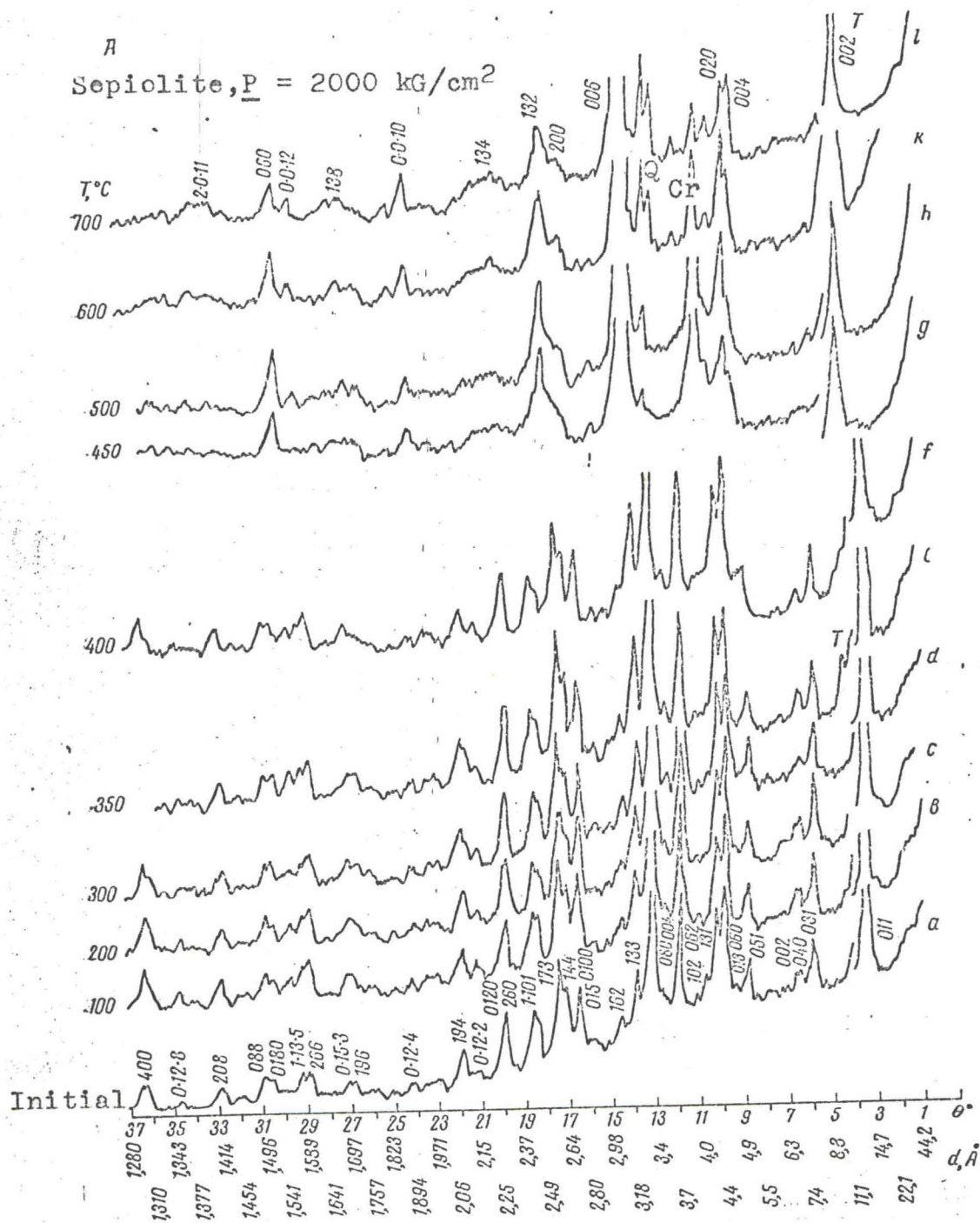
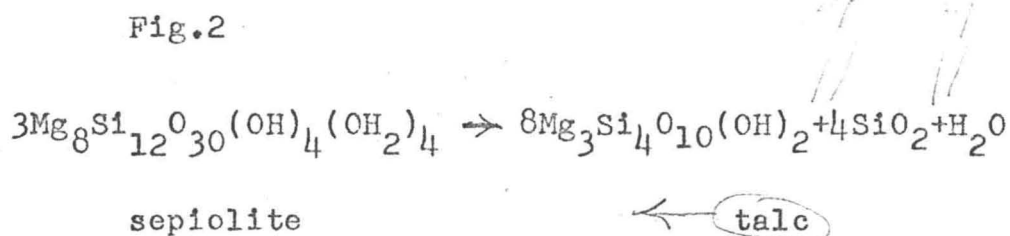


Fig.2. Diffractometer traces of sepiolite (A) and palygorskite (B) under water vapor pressure of 2000 kg/cm^2 , T 100 to 700°C , 22 - 48 hour runs

T - talc; Cr - cristobalite; Q - quartz; initial n.c. - palygorskite freed of calcite; M - montmorillonite; M-X - mixed layer phase - montmorillonite-chlorite; Cor - cordierite

(Fig.2B, a', b', c', a, d. At 350°C, under hydrothermal conditions, sepiolite changes to talc (Fig.2A, e) and palygorskite, to montmorillonite (Fig.2B, e), and further transformations of these minerals must be considered separately. As can be seen from the data of Table 2, the characteristics of the diffractometer traces become clearer and clearer as the duration of run is increased.

Sepiolite. The formation of talc at the expense of sepiolite can be represented by the following equation, in which the idealized formulas of the minerals are used:



As can be seen from Fig.2A, d, B, d the silica released in this reaction appears as cristobalite (reflection 4.04 Å).

Fig. 2B

At $T = 350^\circ\text{C}$ talc is represented by its hydrated variety, as indicated by the increase in the interplanar distance d_{002} to 9.7 Å. This value of d is the same as d_{001} in non-expandable montmorillonite; however, experiments with dioctahedral montmorillonite (from Askangel', Georgian SSR) show that expandable montmorillonite remains stable up to a temperature

Experimental Results

Pressure, kG/cm ²	Temperature, °C	Time, hours	Products
			<u>Sepiolite</u>
2000	100	22	Near initial charge
	200	48	" " "
	300	24	" " "
	350	48	Appearance of hydrous talc
	400	22	" " "
	450	24	" " "
	500	22	No sepiolite; unoriented microcrystalline talc; cristobalite
	600	24	Talc, cristobalite, quartz
			Talc, oriented on 001; less cristobalite; more quartz; appearance of mullite
			" " "
1400	300	22	Near initial charge
	400	22	Appearance of hydrous talc
	400	120	Less sepiolite; hydrous talc
	500	22	Talc, cristobalite
	600	22	Oriented talc, cristobalite, quartz, mullite
	650	22	Same
800	300	48	Near initial charge
	400	22	Appearance of hydrous talc
	350	120	Sepiolite, hydrous talc
	400	120	" " "
	500	22	" " "
	650	22	Talc, cristobalite, quartz Talc, cristobalite, quartz, mullite " " "
2000	100	22	
	200	48	
	300	23	
	350	48	
	400	22	
	450	24	
	500	22	
	550	22	
	600	24	
	700	5	
1400	300	22	<u>Palygorskite</u>
	400	22	Near initial charge
	400	120	" " "
	500	22	" " "
	550	22	Appearance of montmorillonite
	650	22	More montmorillonite
800	300	48	Same
	400	22	Montmorillonite, cristobalite, quartz
	350	120	Mixed-layer phase: montmorillonite+chlorite, quartz, traces of cordierite and talc
	400	120	Chlorite; sharp increase in quartz content; traces of talc
			Cordierite, talc, quartz
			Near initial charge
		Appearance of montmorillonite	
		Montmorillonite, cristobalite	
		Montmorillonite, quartz	
		Montmorillonite+chlorite, quartz	
		Montmorillonite+chlorite, quartz, talc, cordierite	
		Same	
		Near initial charge	
		Montmorillonite, palygorskite	
		" "	
		" "	

Table ²~~X~~ cont.

500	22
550	22
600	22
650	22

Montmorillonite, palygorskite, quartz
 Montmorillonite+chlorite; quartz
 Montmorillonite+chlorite, talc, cordie-
 rite, quartz
 Same

of 480°C . With increase in temperature (from 350 to 700°C) d_{002} of talc gradually changes from 9.7 to 9.4 A.

Table 2

Although talc begins to form at $\sim 325^{\circ}\text{C}$ at all pressures, the course of its crystallization is dependent on both P and T . In the interval between 400 and 500°C there is an increase in the content of small talc crystals in the charge, as indicated by increase in the intensity of all

Fig.3

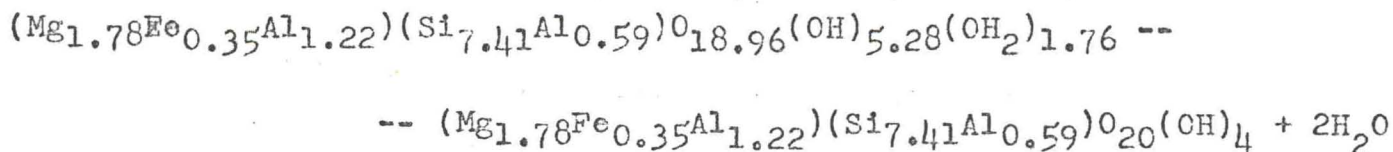
of its reflections on the diffractometer trace. At temperatures between 500 and 700°C only the crystals lying on their basal pinacoids increase in size, for the diffraction patterns show increase in the intensity of the $00l$ reflections only. At higher water vapor pressures talc crystallizes more rapidly but the size of the crystals increases more slowly than at lower pressures.

With increase in $P_{\text{H}_2\text{O}}$, in 22-48 hour runs, sepiolite decomposes completely at lower temperatures, and this explains earlier appearance of cristobalite in the charges. The content of cristobalite reaches a maximum at 500°C and $P_{\text{H}_2\text{O}} = 2000 \text{ kg/cm}^2$. Beginning with 600°C cristobalite is transformed into quartz, and judging by weak 3.41 and 2.29 A reflections,

mullite appears in the charge. Transformation of cristobalite into quartz reaches maximum intensity at the highest pressure (2000 kg/cm^2).

Palygorskite. In 22 to 48 hour runs decomposition of palygorskite is completed sooner at high pressures, although, as in the case of sepiolite, the process begins at 325°C .* Beginning with a temperature of 325°C , in the entire temperature range, palygorskite was transformed into montmorillonite, whose appearance is indicated on the diffractometer traces by reflection $d_{001} = 14.7 \text{ \AA}$ (Fig. 2B, e, f, d). In samples saturated with glycerine d_{001} increased to 18 \AA (Fig. 3A, a, b, c), and after annealing at 600°C , decreased to 9.9 \AA (Fig. 3B, a, b, c).

The montmorillonite formed from palygorskite is dioctahedral with $d_{060} = 1.485 \text{ \AA}$ (Fig. 2B, d). The transformation may be represented by equation:

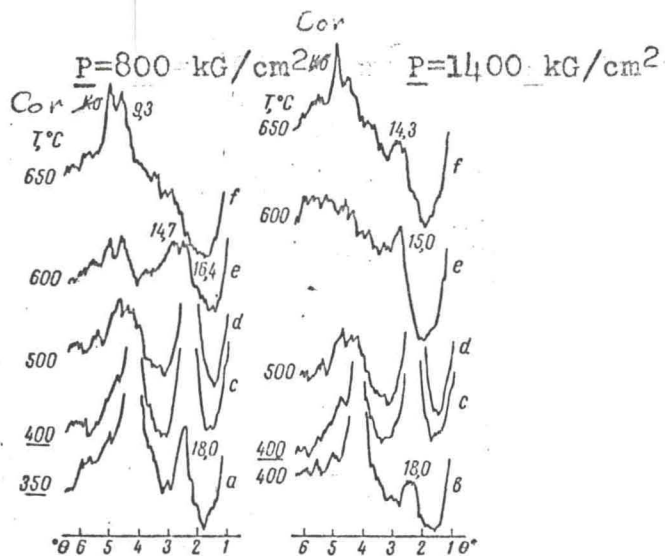


Beginning at 500°C , under water vapor pressure, montmorillonite

* In the experiments at $100\text{--}200^\circ\text{C}$ (Fig. 2B, b', c') palygorskite with admixed calcite was used, but in the experiments at higher temperatures (Fig. 2B, d-1) only palygorskite freed of calcite by washing in 5% HCl (Fig. 2B, a) was used.

A

Palygorskite treated with glycerine



B

Palygorskite heated at 600°C

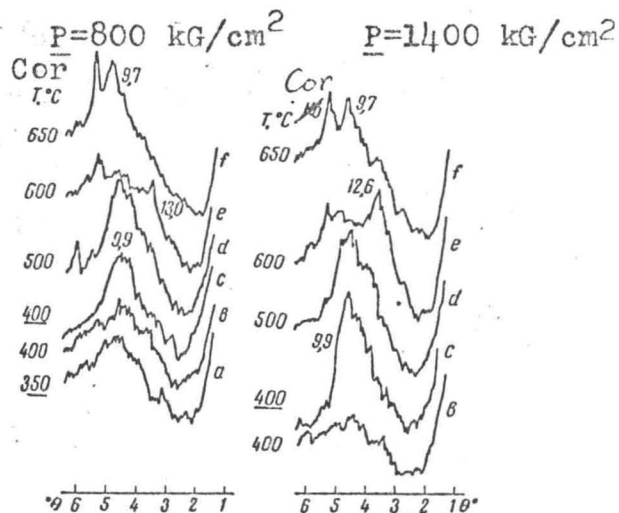


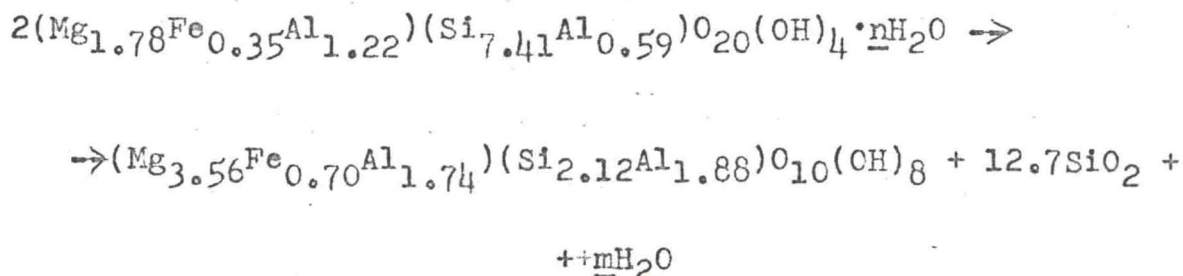
Fig.3. Parts of diffractograms of the phases developed in palygorskite sample at $P_{H_2O} = 800$ and 1400 kg/cm^2 and $T = 350$ to 650°C after 22-48 hour runs; A - sample treated with glycerine after experiment; B - sample heated at atmospheric pressure for 2 hours at 600°C

gradually changes to chlorite, forming with it a disordered mixed layer structure (Fig. 3A and B: at temperatures above 400°C reflection with $d \sim 14 \text{ \AA}$ is no longer shifted towards $\sim 18 \text{ \AA}$ in montmorillonite saturated with glycerine, and does not decrease sharply to 9.9 Å in montmorillonite heated for 2 hours at 600°C). The transformation of montmorillonite to chlorite at $P_{\text{H}_2\text{O}} = 1400 \text{ kg/cm}^2$ is shown in Fig. 4. The diagram shows change in the value of d_{100} in untreated montmorillonite (a), montmorillonite saturated with glycerine (b), and montmorillonite heated for 2 hours at 600°C (c).

The formation of disordered mixed layer montmorillonite-chlorite structure begins at point A (500°C, 1400 kg/cm²). At 650°C

Fig. 4

the structure becomes strictly non-expandable. If, instead of the mixed layer phase, chlorite is taken as the end member in the montmorillonite - chlorite transformation, the transformation may be represented by equation:



The silica released in this reaction crystallizes as quartz,

whose reflection^s appear on the diffraction traces of samples heated above 450°C (Fig.2B,h,k,l).

The dependence of the montmorillonite-chlorite transformation on pressure can be traced by the appearance of the quartz reflexes on the diffractometer traces, for release of silica from the montmorillonite structure is the first sign of its destruction. The content of quartz in the charge increases with chlorite content. At high

Fig.5

pressures, as shown by the diffractograms, the process of formation of chlorite is intensified.

At a temperature of 600-700°C and $P_{H_2O} = 800 - 2000 \text{ kg/cm}^2$, high temperature minerals, cordierite and talc, are formed. Their reflections are marked on the diffraction traces (Fig.2B, k,l). Talc forms from palygorskite at a higher temperature than from sepiolite (600°C). In the case of palygorskite three intermediate phases form in the course of

structural transformation: montmorillonite, disordered mixed-layer phase (montmorillonite + chlorite) and chlorite, but in the case of sepiolite there is only the final phase - talc.

Stability fields of the phases. Using the data of Table 2, we constructed a schematic $P_{\text{H}_2\text{O}}-T$ diagrams (Fig. 5A,B) showing stability fields of the starting and some intermediate phases. The upper temperature limit of stability is the same for sepiolite and palygorskite, $\sim 325^\circ\text{C}$. At higher temperatures (up to $T = 700^\circ\text{C}$) sepiolite is transformed into talc, and palygorskite is first transformed into montmorillonite and then (at 500°C) into a mixed-layer montmorillonite+chlorite phase, followed by chlorite. Above 600°C cordierite and talc are the products of transformation of palygorskite. Pressure has little effect on the phase boundaries, except for the cordierite boundary, which shifts into the region of lower temperatures at lower pressures.

SUMMARY

1. Sepiolite and palygorskite are stable under hydrothermal conditions ($P_{\text{H}_2\text{O}} = 800 - 2000 \text{ kg/cm}^2$) at temperatures below $\sim 325^\circ\text{C}$.
2. At higher temperatures, and in the same pressure range, sepiolite undergoes the following transformation: sepiolite $\xrightarrow{325^\circ\text{C}}$

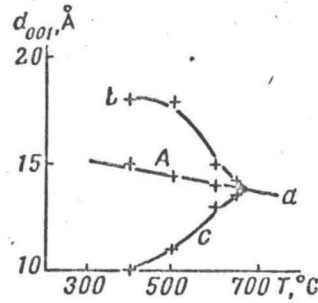


Fig.4. Variation in d_{001} of montmorillonite formed from palygorskite

a - montmorillonites obtained at $p_{H_2O} = 1400 \text{ kg/cm}^2$ and $400-600^\circ\text{C}$; b - same, saturated with glycerin; c - same heated for 2 hours at 600°C under atmospheric pressure. Crosses are experimental points

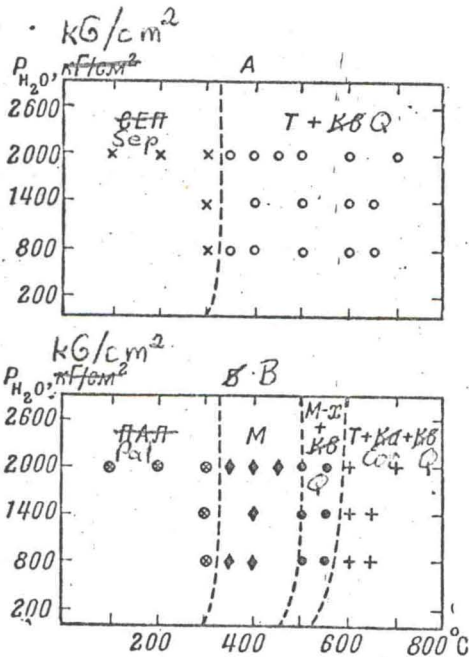
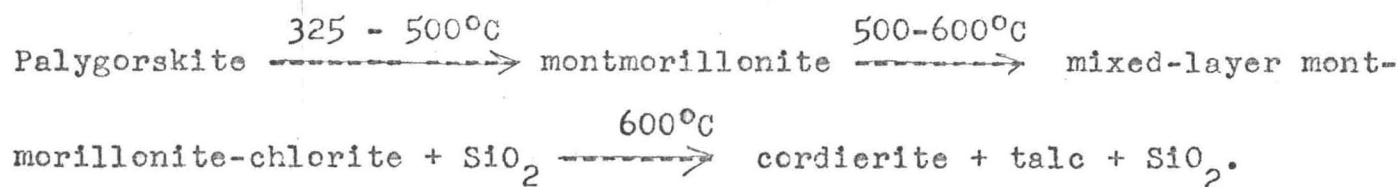


Fig.5. $P_{H_2O} - T$ diagrams of stability fields of sepiolite (A), palygorskite (B) and some phases formed from them
 Sep - sepiolite; T+Q - talc + quartz;
 Pal - palygorskite; M - montmorillonite;
 M-X - disordered mixed layer montmorillonite-chlorite phase + quartz; T+Cor+Q - talc + cordierite + quartz. Interrupted lines - preliminary phase boundaries

→ talc + SiO₂. The transformation of palygorskite is more complex:



3. The difference in the phase transformations of sepiolite and palygorskite, two minerals with similar structure, is determined by the difference in their chemical composition.

REFERENCES

1. Brauner, K. and A. Preisinger, 1956. Structure of sepiolite. Miner. Petrogr. Mitt., №6, s.120.
2. Bradley, W.F., 1940. Structure of attapulgite. Amer. Mineralogist, №25, p.405.
3. Goylo, É.A., N.V. Kotov and V.A. Frank-Kamenetskiy, 1966. Èksperimental'noye issledovaniye vliyaniya stressa i gidrostaticheskogo davleniya pri razlichnykh temperaturakh na kristallicheskuyu strukturu kaolinita. ^{In:} ~~Vestnik~~ Fizicheskiye metody issledovaniya mineralov osadochnykh porod (EXPERIMENTAL INVESTIGATION OF THE EFFECT OF STRESS AND HYDROSTATIC PRESSURE AT DIFFERENT TEMPERATURES ON THE STRUCTURE OF KAOLINITE. PHYSICAL METHODS OF INVESTIGATION OF MINERALS OF SEDIMENTARY ROCKS). "Nauka", Moscow.
4. Frank-Kamenetzky, V.A., N.V. Kotov and E.A. Goylo, 1966. Strukturänderung von Tonmineralen unter verschiedenen thermodynamischen Bedingungen. Kristall. und Technik, ~~№1~~, ^{№1} ~~№1~~, №3, Berlin.
5. Klochkova, G.N., 1968a. K kharakteristike pamirskogo palygorskita (CHARACTERISTICS OF PALYGORSKITE FROM THE PAMIRS). Doklady Akad. Nauk Tadzh.SSR, №XI, No.8.

6. Klochkova, G.N., 1968b. Sepiolit iz Karamazara SEPIOLITE FROM KARAZAR). Doklady Akad, Nauk Tadzh. SSR, XI, No.9.
7. Tuttle, O.F., 1948. A new hydrothermal quenching apparatus. Amer. J. Sci., 46.

Received for publication

May 27, 1968