

formations with the contents of the admixture ( $R^+ + R^{++}$  in kaolinite  $\lesssim 1,2\%$ , in dickite  $\lesssim 0,015\%$ ) and, as a result from this, with the difference of alkalinescence of their water suspensions ( $pH = 8,2$  and  $6,5$  respectively). The latter circumstance, most probably, is connected with partial substitution of  $Al \rightarrow Si$  which produces an excess negative charge on the basal planes. Besides, here occurs the possibility of rising sorption of the protons, this leading to the increase of alkalinescence of suspensions. With kaolinite the possibility of sorption increases because of the larger surface area, connected with a higher dispersion of kaolinite. With ground minerals  $pH$  of the suspensions became even ( $6.8$  and

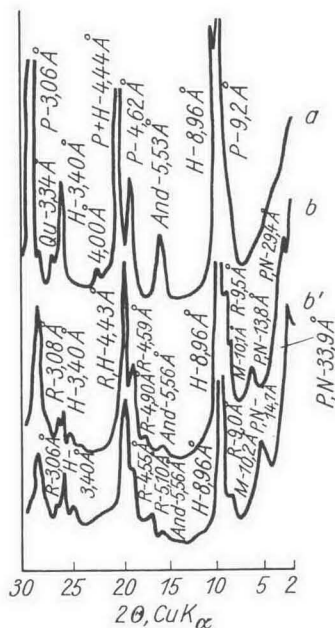


Fig. 1. X-ray diffraction patterns of transformation products of dickite (a) and kaolinite (b, b' - the right sample, but glycol treated) under hydrothermal conditions,  $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$ ,  $T = 450^\circ \text{C}$ ,  $t = 3$  days. Key: And - andalusite-like phase, H = hydralisite, Qu - quartz, R = random mixed-layer phase, P - pyrophyllite, M = mica, PN = partially nonrandom mixed-layer phase

$6.5$  respectively) the same as in filtrates of initial suspensions free from weighed particles ( $pH = 6.8$  and  $6.5$  respectively), thus emphasizing the significance of the last factor. Thus the higher contents of the admixture  $R^+ + R^{++}$  and the increasing alkalinescence of surroundings displace the process to the side of formation of aluminosilicate phases with  $Al^{IV} + Al^{VI}$ .

For more detailed revealing of the influence of the admixture cations the natural prozhanovski kaolinite (contents of the admixture  $R^+ + R^{++} \lesssim 1,2\%$ ) and the spectral-clean synthetic kaolinite ( $R^+ + R^{++} \lesssim 0,06\%$ ) were exposed to a hydrothermal process under  $T = 350^\circ \text{C}$ ,  $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$  in the course of 10 days. From natural kaolinite arose a partially ordered mixed-layer phase of pyrophyllite-beidellite type with  $Al^{IV} + Al^{VI}$  ( $d = 24.7 \text{ \AA} \xrightarrow{\text{glycol}} 29.4 \text{ \AA}$ ), but from synthetic kaolinite we did not observe any new growth (Fig. 2a, b).

Moreover, the spectral clean kaolinite remained unchanged in the runs with  $P_{H_2O} = 2000 \text{ kg} \cdot \text{cm}^{-2}$ ,  $T = 400^\circ \text{C}$  in the course of longest 30-days exposition (FRANK-KAMENETZKIJ, KOTOV, TOMASHENKO). From the comparison of the data of both kaolinites it is revealed that the presence of admixture  $R^+ + R^{++}$  lowers the upper limit of stability of kaolinite being stated by the occurrence of a newformed mixed-layer phase; the character of the latter shows that in this case a part of Al ions enters into tetrahedral positions.

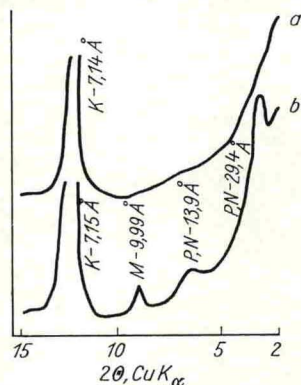


Fig. 2. Low-angle (part) of X-ray diffractograms of synthetic (a) and natural (b) kaolinites (glycol treated samples) after hydrothermal processing under  $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$ ,  $T = 350^\circ \text{C}$ ,  $t = 10$  days. Key: K = kaolinite, M = mica, PN = partially nonrandom mixed-layer phase

The following experiments were carried out with X-ray amorphous spectral-clean (admixture  $\leq 0.06\%$ ) Al-Si gels, with the composition  $\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:9$ ,  $2:8$  and  $3:7$ , that allowed to exclude the influence of admixtures on the synthesis of phases and revealed other factors controlling the formation of layer silicates and alumosilicates.

## 2.2. X-ray amorphous alumosilicate gels

In the runs with spectral-clean gels at  $P_{H_2O} = 2000 \text{ kg} \cdot \text{cm}^{-2}$  well crystallized three dimensional ordered kaolinite and pyrophyllite with  $\text{Al}^{\text{VI}}$  and poor crystallized beidellite and Al-chlorite with  $\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}}$  were formed (FRANK-KAMENETZKIJ; KOTOV, TOMASHENKO). The X-ray data showing the formation of beidellite from Al-Si gels of different composition are shown in Figure 3 A, B. In the runs at  $T = 300^\circ \text{C}$  (Fig. 3 B) and  $T = 350^\circ \text{C}$  (Fig. 3 A) in the course of 720 hours the maximum content of beidellite (the phase with  $\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}}$ ) is observed in the transformation products of the most siliceous gel ( $\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:9$ ) but in the transformation products of the gel, its composition corresponding to  $\text{Al}_2\text{O}_3:\text{SiO}_2 = 3:7$ , beidellite is not observed. In the products of synthesis of the latter gel a monomineral kaolinite is formed (Fig. 3 A, B, C). The reason why beidellite is formed from gels that do not correspond to its composition ought to be searched in the structure peculiarities of the latter. According to data of TAMELE in the fresh coprecipitated Al-Si gel, Al entered in fourfold coordination until its relative contents in the gel is small. In spite of the fact that we experimented with heated gels it appears that in this case too, the pro-