Al^{IV} and Al^{VI} in Transformation and Synthesis of Layer Silicates

perties of water suspensions of such type of gels confirms the regularity stated by these authors. So, with decrease of Al content in the gels, pH of water suspension (5.5 \rightarrow 5.6 \rightarrow 5.8) and the velocity of its coagulation in aqueous solutions of alcohol regularly increases. Thus, in experiments with chemical clean gels it is revealed that the formation of beidellite at T = 300-350 °C takes place more successfully from structurally prepared material (in that case rich in SiO₂ and consequently containing Al^{IV}) than from material which corresponds to its composition but less prepared structurally.



Fig. 3. Formation of beidellite from Al–Si gels under $P_{H_2O} = 2000 \text{ kg} \cdot \text{cm}^{-2}, t = 30 \text{ days}, T = 350 \text{ °C(A)}$ and 300 °C(B). The composition of starting mixtures (Al₂O₃:SiO₂): a = 1:9, b = 2:8, c = 3:7. Key: K = kaolinite, Bd = beidellite

At higher temperature (500 °C) and a pressure of 2 kb from siliceous gels pyrophyllite and hydralsite are formed. On the Figure 4A we see the results of transformation of gels of various Al–Si compositions with $P_{H_2O} = 2000 \text{ kg}$ $\times \text{ cm}^{-2}$, T = 500 °C with exposition times of 3 days. Pyrophyllite is the 1 Tc regular modification (Fig. 4A–a) similar to the nature of pyrophyllite described recently by BRINDLEY (BRINDLEY, WARDLE). Most successfully pyrophyllite is formed from the gel having the composition $Al_2O_3:SiO_2 = 1:4$, but when the contents of Al increase, there appears hydralsite. It was supposed that its structure was similar to pyrophyllite, but nearly half of Si in tetrahedral positions was substituted by Al (Roy, OSBORN).

However, the determination of the coordination of Al carried out by X-ray fluorescence methods, has shown that hydralsite is an Al silicate. Thus, it is settled that with the above conditions well crystallized phases with Al^{IV} are formed.

The same gels which had been submitted a hydrothermal influence in pure water at T = 500 °C but under a pressure of 1 kb, give essentially other results. As seen on the Figure 4B, in the experiments with $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$, T = 500 °C in the course of 3 days, from gels of pyrophyllite composition a random mixed-layer phase of pyrophyllite-beidellite type ($AI^{VI} + AI^{IV}$), cristobalite, hydralsite and a chlorite-like mineral ($AI^{IV} + AI^{VI}$) are formed. With the increase of the Al-contents in the gel the formation of a chlorite-like phase and hydralsite runs better. The chlorite-like phase is characterized by an unusual X-ray powder pattern in which the second basal reflection $d_{002} = 7$ Å has a very poor intensity. A similar phase obtained at analogous P-T conditions has been described recently for the first time (FONARJEV, BERHIN). The calculation shows that this phase must have very imperfect interlayers. According to the distribution of the intensities of basal reflections it more resembles vermiculite than chlorite, but similarly to chlorite it does not swell with glycol and does not



Fig. 4. Formation of pyrophyllite and Al-chlorite from Al-Si gels at T = 500 °C, t = 3 days and $P_{H_2O} = 2000 \text{ kg} \cdot \text{cm}^{-2}$ (A) and 1000 kg $\cdot \text{cm}^{-2}$ (B). The compositions of gels – a, b, c are analogous to that on Figure 3. Key: H – hydralsite, R = random mixed-layer phase, C – cristobalite, P – pyrophyllite, Chl – Al-chlorite

collapse when heated up to 650 °C. Thus the comparison of results of the experiments carried out with quite the same starting materials, but under different pressures, leads to the conclusion that with the increase of pressure from 1 to 2 kb friable structures disappear (imperfect Al-chlorite) and the principal formations were phases with sixfold Al coordination (pyrophyllite and hydralsite instead of mixed-layered pyrophyllite-beidellite phase and Al-chlorite). The preferred entrance of Al into octahedral positions can be connected with changes of the relation $r_k:r_a$ (FILATOV) as with changes of pH of aqueous solution with the increase of pressure in a contact zone Al-Si gel-H₂O.

According to the last datas and the results of experiments mentioned above the conducting role of pH (when the other parameters are held constant) in the synthesis of phases with hydrothermal conditions is more and more revealed. Therefore such runs should be carried out, which may allow to judge directly the influence of pH. In order to get such datas a series of runs was carried out with Al–Si gels of similar type under constant P–T, in hydrothermal solutions of NaCl, NaOH and NaCl + HCl, which contained an equal quantity of