



Fig. 5. Transformation of Al-Si gels in hydrothermal solutions of different alkalinescence. $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$, $T = 450^\circ\text{C}$, $t = 3$ days. Hydrothermal surroundings: A - 0,05 N (HCl + NaCl) pH (after run) ≈ 4 ; B - 0,05 N NaCl, $pH \approx 6$; C - 0,05 N NaOH, $pH \approx 10$. The composition of starting gels ($\text{Al}_2\text{O}_3:\text{SiO}_2$): a = 1:4, b = 1:3, c = 1:2. Key: H-hydralcite, P - pyrophyllite, R - random mixed-layer phase, Can - cancrinite, Ne - nepheline, Nos - nosean

Na (0,05 g/eq) but had different alkalescence. As seen on the Figures 5a, b, c the newly formed phases strongly differ from one another in dependence on the character of the hydrothermal surroundings. In acid solutions (pH in the interval 1.5–4) with $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$, $T = 450 \text{ }^\circ\text{C}$ in the course of 3 days there 1 Tc pyrophyllite (Al^{VI}) \pm hydralsite and andalusitelike phase were formed (Fig. 5A). In neutral surroundings the main newly formed phases are: random mixed-layer phase of pyrophyllite-beidellite type (Fig. 5b) with $Al^{IV} + Al^{VI}$ and hydralsite (Al^{VI}). In alkaline solutions the framework aluminosilicates nepheline, cancrinite, nosean are formed (Fig. 5c), possessing only Al^{IV} .

Thus, it is clear that the different structural positions of Al in newly formed phases seem to be the characteristic peculiarity of the processes taking place in neutral, acid and alkaline surroundings. The absence of layer phases in alkaline surroundings is not a considerable distinctive feature of the experiments described above, as it seems at first sight. The structural motive of Al, Si–O nets of cancrinite and particularly of nepheline considered perpendicular to the c^* axis or perpendicular to (111) for nosean, in a certain degree is similar to the structural motive of layer silicates, the structure of which can be transformed into them (KUBO, YAMAGUCHI, KASAHARA). The problem is to reveal the dimension of the construction units when a conversion from a layer phase to a framework one with alteration of alkalescence takes place. However, this question requires further investigations.

3. Discussion

Syntheses carried out under different P–T–X– pH conditions clearly show that the tendency of solid-phase transformations of layer silicates, and the process of crystallization of Al–Si gels essentially depend on the possibility of penetration of Al in the newly formed structures into Al^{IV} and Al^{VI} positions. This is connected with the character of Al coordination in the starting materials and with the chemism of the transformation process. It was found that this process is closely connected with pH of the surroundings. Therefore, for the judgement of the tendency of the transformations one may use the determination of pH of the suspensions, from which the synthesis is realized. The negative charge on a layer surface in clay minerals connected with a partial substitution $Si \leftarrow Al + \square$ leads to a sorption of protons and positive ions on them, thus increasing the alkalescence of the solution. With these factors the difference of pH of suspensions and the difference in the tendency of transformation of dickite and kaolinite, which differs by the contents of admixtures and by the values of pH of suspensions, may probably be explained.

A similar regularity may be observed with the crystallisation of gels. In gels containing a subdued quantity of alumina with higher value of pH of suspension. Al penetrates into tetrahedral positions of Al–Si structures in a higher degree and that is why beidellite is formed successfully from the gel the composition of which does not correspond to him.

In nature the hydrothermal solutions always in some degree are mineralized. According with this the processes of transformation in presence of such solutions may lead to a strong reduction of the limits of stability of layer silicates of Al. Both, in experiments (FRANK-KAMNETZKIJ, KOTOV, GOILO) and in nature (LOGVINENKO; DUNOYER DE SEGONZAC) kaolinite, when reacting with solutions,