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

Dedicated to Prof. H. Neels on his 60th birthday

The regularities of transformations of layer silicates under hydrothermal conditions have been examined. For solid phases reactions (transformation of Al–Si layer silicates, reactions in Al–Si gels) the main factors that control the formation of alumosilicates besides P–T-pH are the presence of admixtures of alkali and alkali-earth cations, likewise the presence of Al^{IV} in the starting materials. The increasing of T and decreasing of P also promotes the preferred formation of layer alumosilicates than silicates of Al. For the reactions that pass through the dissolution of components the leading factor (under P–T–X = const) is the pH of the surrounding. In acid surrounding silicates with Al^{VI} are formed and in alkaline conditions such phases, in which Al is an analog of silicon and supplies the tetrahedral positions. The results have significance for comprehend geological processes which take place in zones of hydrothermal alterations, of epigenesis and low-grade metamorphism likewise for comparison of experimental studies.

Исследованы закономерности преобразования слоистых силикатов в гидротермальных условиях. Для твёрдофазовых преобразований (трансформация слоистых силикатов Al, реакции в Al-Si гелях) главными факторами контролирующими формирование алюмосиликатов помимо P–T–pH являются присутствие примесей щелочных и щёлочноземельных катионов, а также присутствие Al^{IV} в исходных материалах. Увеличение температуры и давления также способствует преимущественному формированию слоистых алюмосиликатов. Для реакций проходящих через растворение компонентов ведущим фактором (при P–T–X = const) является pH среды. В кислых условиях формируются силикаты с Al^{VI} а в щелочных средах синтезируются фазы в которых Al является аналогом Si и занимает тетраэдрические позиции. Результаты имеют значение для понимания геологических процессов протекающих в зонах гидротермальной переработки, эпигенеза и начальных стадий метаморфизма, а также для сравнимости экспериментальных работ.

1. Introduction

The papers on hydrothermal synthesis in the systems K$_2$O, Na$_2$O–Al$_2$O$_3$–SiO$_2$–H$_2$O (Roy, Osborn; Jarikov, Ivanov, Dugikova, Shmonov, Fonarjov; Sand, Roy, Osborn) allowed to reveal a considerable quantity of alumosilicate phases, which have distinct structural differences for similar compositions. They are both typical polymorphs of Al$_2$SiO$_5$ composition (andalusite, sillimanite and kyanite) with various Al coordinations (Bragg, Claringbull) and layer hetero-

desmic phases with more complicated structures, with Al both in fourfold and in sixfold coordination, for example — mixed layer 1:1 pyrophyllite-beidellite (VJAHIREV, GOGISHVILY, MDIVNISHVILY), Al-corrensite (KOTOV, LEBEDEV, TARLAKOV), Al-chlorite (FONARJOV, BERHIN) and others. There are contradictory points of view about there stability and there field of synthesis, and at present this does not allow to make a definite conclusion on the conditions of formation of such phases.

It is known that the transformation by intermediate stages of kaolinite under higher P_{H_2O}–T parameters may pass either through the formation of the polar structure of beidellite with Al^{IV} and Al^{VI} and further through the transformation synthesis of mixed layer phases (FRANK-KAMENETZKIJ, KOTOV, GOILO) or through the formation of pyrophyllite and hydralsite (FRANK-KAMENETZKIJ, KOTOV, TOMASHENKO), if mixed layer phases cannot be stated. These different forms of transformation depend in principal upon Al being in tetrahedral and octahedral positions or only in octahedral positions of layer structures.

In this paper we report on attempts to investigate in details the conditions of formation of silicates with different coordination of Al. The results of the investigation may serve to understand the solid-phase structural transformations of phases in nature — in the processes of hydrothermal metamorphism and metasomatism.

The experiments were carried out in a reactor with a cold lick (KOTOV, KOPEIKIN) in tightly closed platinum ampullas, in the temperature interval 250 to 500 °C, $P_{H_2O} = 1000{-}2000$ kg · cm^{-2}, exposition 7—720 hours. As starting materials we used spectral pure gels (contents of the admixtures of alkalis and alkaline earths $R^+ + R^{++} \lesssim 0,06\%$) and natural kaolinite and dickite. The products of the experiments were investigated by X-ray methods. The coordination of Al in newly formed phases was regarded in accordance with data of structural studies (BROWN; BRAGG, CLARINGBULL). For the swelling phases the presence of Al in tetrahedral positions was determined by GREEN-KELLE's method.

2. Experimental part

2.1. Natural minerals

Kaolinite (Prosyanovskoie deposit, UkSSR) and dickite (Turominskoie deposit RSFSR) were subjected a hydrothermal process at $T = 450$ °C, $P_{H_2O} = 1000$ kg · cm^{-2} during 3 days. As seen on Figure 1, the new phases formed from these minerals have a marked difference. From dickite is formed (Fig. 1a) well crystallized pyrophyllite with Al^{VI} ($\pm$ andalusite-like phase and hydralsite), while from kaolinite is formed a random mixed-layer phase of the pyrophyllite-beidellite type with $Al^{VI} + Al^{IV}$, with the prevalence of pyrophyllites inter-packets intervals, and a partial nonrandom mixed-layer phase with d_{001} 29,4 Å $\xrightarrow{\text{glycol}}$ 33,9 Å and d_{002} 13.8 Å $\xrightarrow{\text{glycol}}$ 14.7 Å ($\pm$ andalusite-like phase, quartz and hydralsite). Thus, though experiments were carried out under identical conditions for both starting materials (both tubes in one reactor), kaolinite formed layer phases having a higher degree of tetrahedal Al → Si substitutions than those from dickite. The difference in these transformations cannot be explained by the fact that the starting minerals are different polytype modifications. It was thought to be possible to connect these differences in the trans-

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 alkalescence of their water suspensions (pH = 8,2 and 6,5 respectively). The latter circumstance, most probably, is connected with partial substitution of Al → 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 alkalescence 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
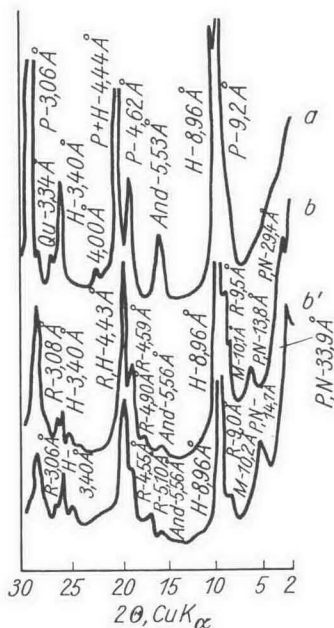

Fig. 1. X-ray diffraction patterns of transformation products of dickite (a) and kaolinite (b, b' — the right sample, but glycol treated) under hydrothermal conditions, P$_{H_2O}$ = 1000 kg · cm^{-2}, T = 450 °C, t = 3 days. Key: And — andalusite-like phase, H = hydralsite, Qu — quartz, R = random mixed-layer phase, P — pyrophyllite, M = mica, PN = partialy 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 alkalescence of surroundings displace the process to the side of formation of alumosilicate phases with Al^{IV} + Al^{VI}.

For more detailed revealing of the influence of the admixture cations the natural prosjanovski 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 °C, P$_{H_2O}$ = 1000 kg · 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 Å $\xrightarrow{glycol}$ 29.4 Å), 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 $P_{H_2O} = 2000 \text{ kg} \cdot \text{cm}^{-2}$, $T = 400\ °C$ in the coarse 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.
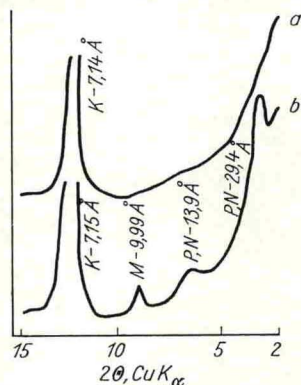

Fig. 2. Low-angle (part) of X-ray diffractograms of synthetic (a) and natural (b) kaolinites (glycol treated samples) after hydrothermal processing under $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$, $T = 350\ °C$, $t = 10$ days. Key: K = kaolinite, M = mica, PN = partialy nonrandom mixed-layer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

The following experiments were carried outh with X-ray amorphous spectral-clean (admixture $\leq 0.06\%$) Al–Si gels, with the composition $Al_2O_3 : SiO_2 = 1:9$, $2:8$ 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 Al^{VI} and poor crystallized beidellite and Al-chlorite with $Al^{VI} + Al^{IV}$ were formed (FRANK-KAMENETZKIJ; KOTOV, TOMASHENKO). The X-ray data showing the formation of beidellite from Ai–Si gels of different composition are shown in Figure 3A, B. In the runs at $T = 300\ °C$ (Fig. 3B) and $T = 350\ °C$ (Fig. 3A) in the course of 720 hours the maximum content of beidellite (the phase with $Al^{VI} + Al^{IV}$) is observed in the transformation products of the most siliceous gel ($Al_2O_3 : SiO_2 = 1:9$) but in the transformation products of the gel, its composition corresponding to $Al_2O_3 : SiO_2 = 3:7$, beidellite is not observed. In the products of synthesis of the latter gel a monomineral kaolinite is formed (Fig. 3A, 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-

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 SiO$_2$ and consequently containing Al^{IV}) than from material which corresponds to its composition but less prepared structurally.
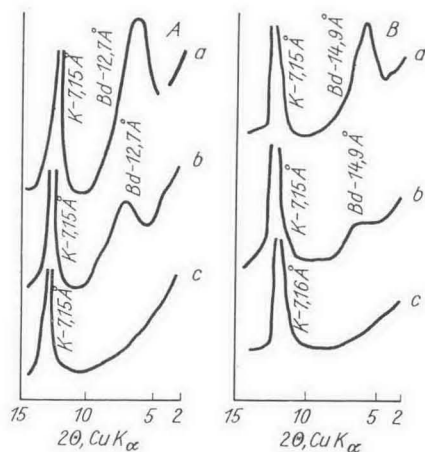

Fig. 3. Formation of beidellite from Al–Si gels under P$_{H_2O}$ = 2000 kg·cm^{-2}, t = 30 days, T = 350 °C(A) and 300 °C(B). The composition of starting mixtures (Al$_2$O$_3$:SiO$_2$): a = 1:9, b = 2:8, c = 3:7. Key: K = kaolinite, Bd = beidellite

At higher temperature (500 °C) and a pressure of 2 kb from siliceous gels pyrophyllite and hydralsite are formed. On the Figure 4 A we see the results of transformation of gels of various Al–Si compositions with P$_{H_2O}$ = 2000 kg × cm^{-2}, T = 500 °C with exposition times of 3 days. Pyrophyllite is the 1 Tc regular modification (Fig. 4 A—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$_2$O$_3$: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 4 B, in the experiments with P$_{H_2O}$ = 1000 kg·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 (Al^{VI} + Al^{IV}), cristobalite, hydralsite and a chlorite-like mineral (Al^{IV} + Al^{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
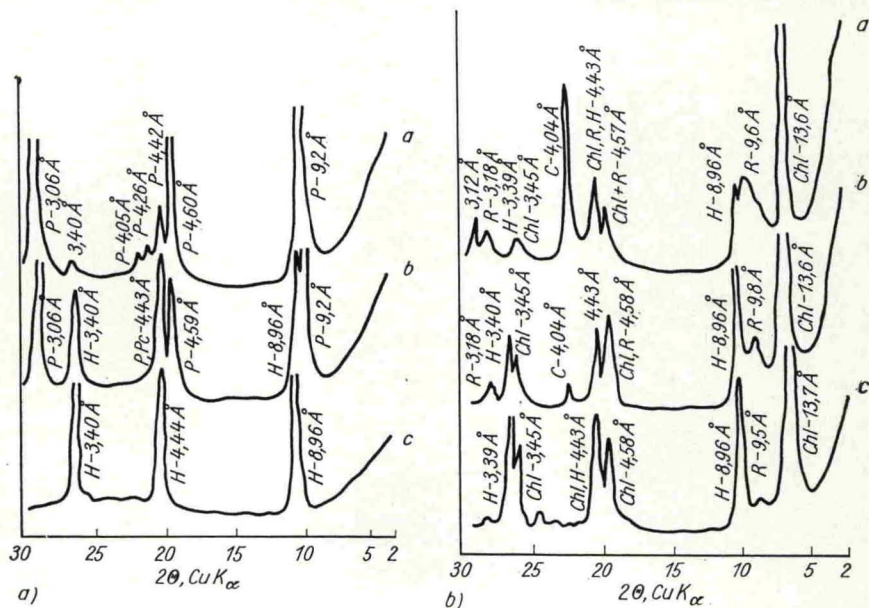

Fig. 4. Formation of pyrophyllite and Al-chlorite from Al–Si gels at $T = 500$ °C, $t = 3$ days and $P_{H_2O} = 2000$ kg · cm^{-2} (A) and 1000 kg · cm^{-2} (B). The compositions of gels — a, b, c are analogous to that on Figure 3. Key: H — hydralsite, R = random mixed-layer phase, C — cristobalite, 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-H$_2$O.

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
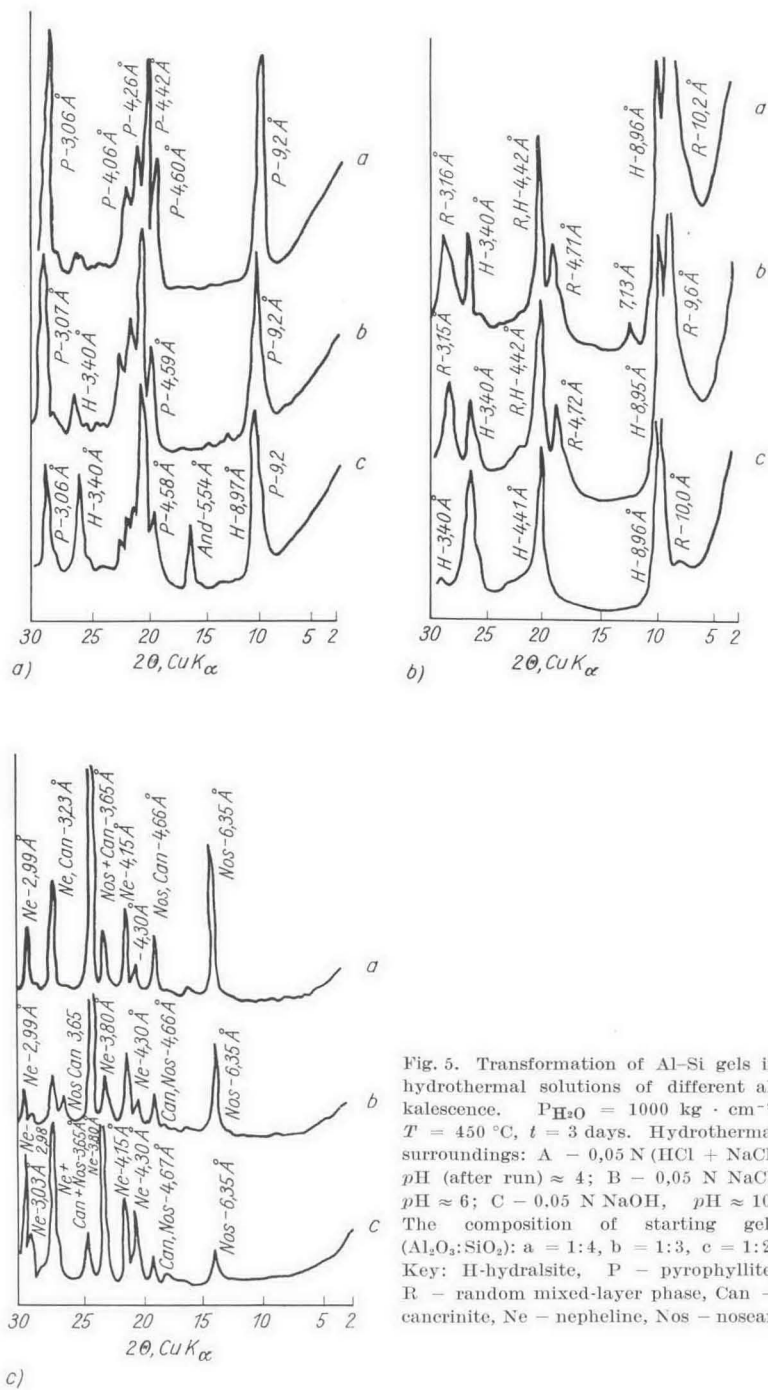
Fig. 5. Transformation of Al–Si gels in hydrothermal solutions of different alkalescence. P_{H_2O} = 1000 kg · cm^{-2}, T = 450 °C, t = 3 days. Hydrothermal surroundings: A — 0,05 N (HCl + NaCl) pH (after run) ≈ 4; B — 0,05 N NaCl, pH ≈ 6; C — 0.05 N NaOH, pH ≈ 10. The composition of starting gels (Al$_2$O$_3$:SiO$_2$): a = 1:4, b = 1:3, c = 1:2. Key: H-hydralsite, 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 $P_{H_2O} = 1000$ kg $\cdot$ cm^{-2}, $T = 450$ °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 alumosilicates 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^{IV} 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 $+$ $\boxminus$ 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,

rarely remains safe up to 200—250 °C (though the thermal limit of its stability at P$_{H_2O}$ 1—2 kb is about 375—390 °C), and pyrophyllite is spread considerable rarely than montmorillonoides and micas. Hence it follows that the experimental determinations of thermal limits of stability of layer silicates in "distilled" H$_2$O surroundings (ROY, OSBORN; FRANK-KAMENETZKIJ, KOTOV, TOMASHENKO; ALTHAUS) give the highest value of temperatures and can only be partially compared with geological processes taking place in "soiling" surroundings. The experiments and calculations carried out in consideration of the character and degree of mineralization of solutions and soiling of starting phases are of greatest value.

The fact that with an increasing pressure a tendency of transition of Al into octahedral position is observed, is most clearly confirmed by the behaviour of Al$_2$SiO$_5$ polymorphs. Among them disthen — the high pressure phase — has Al only in six-fold coordination; sillimanit — the high temperature phase (not high pressure) has 0,5 Al in tetrahedral and 0.5 Al in octahedral positions, and andalusite — the phase of moderate T and P has an intermediate coordination of Al (0.5 Al^{VI} + 0.5 Al^V) (BRAGG, CRARINGBULL). For phases, containing others cations exept Al, this rule is followed less strictly, but the most typical minerals of high pressures — jadeite, garnets — have only an octahedral Al. The in-
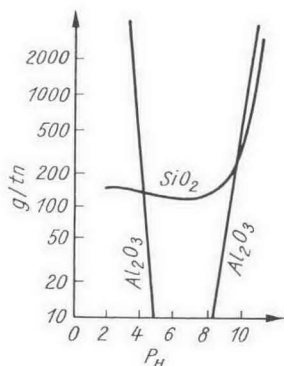

Fig. 6. Solubility of silica gel and aluminium hydroxide as a function of hydrogen ion concentration (CORRENS)

fluence of temperature is contrary to the effect of pressure. In both cases this influence is also connected with the change of relations $r_c : r_a$.

Taking into considerations the whole foresaid material, one may assume that the main factors controlling the formation and transformation of layer silicates and alumosilicates in solid-phase reactions, are the structure of starting materials, contents of admixture of alkaline earths cations, pressure, temperature and pH of surrounding.

In chemically aggressive surroundings (acid and alkaline) the part of process increases going through the solution of components. That is why the peculiarity of phase formation herewith must be examined in connection with the properties of solutions. So for example, the solubility of Al$_2$O$_3$ and SiO$_2$ gels increase (CORRENS) roughly with the increase of alkalescence of solutions (Fig. 6). Being amphoteric Al hydroxide with alkaline surroundings shows its acid properties (ALEKSEJEV) leading to the formation of well dissolved aluminates:

$Al(OH)_3 + NaOH \rightleftharpoons NaAlO_2 + 2 H_2O$. Al in that combination is in four-fold coordination (WILSON) and behaves itself as an analog of silicon. For Al–Si mixtures this is confirmed by our experiments with high P–T parameters, so far as with these conditions alumosilicates are formed but no silicates of Al. That the synthesis of framework alumosilicates passes through a liquid phase is testified by the fact that only in this case the products of experiments are mono-crystals measuring about 0,05 mm.

With acid conditions Al hydroxide shows the properties of a base and Al passes into solution, for example, by the reaction:

$$Al(OH)_3 + HCl \rightleftharpoons AlCl_3 + 2 H_2O \ .$$

In this case Al is the cation, similar to Mg and for it the six-fold coordination is characteristical.

Thus, in acid and alkaline solutions the tendency of syntheses is controlled by the behaviour of Al, which due to its amphoterity is the silicon analog with alkaline conditions, and Mg, Fe analog with acid conditions. This determines the formation of alumosilicates or silicates of Al in the process of synthesis.

4. Conclusions

1. For solid-phase reactions (transformations of Al–Si layer silicates, reactions in Al–Si gels) the main factors that control the formation of alumosilicates besides P–T-pH, are the presence of admixtures of alkaline and alkali-earth cations, likewise the presence of Al^{IV} in the starting materials. The last may be indirectly estimated by measuring pH of water suspension of starting minerals, so far as Al^{IV}, being the center of excess negative charge, favours the preferred sorption of H^+ on clay particles thus moving the pH of the solution to the alkaline region. The increase of temperature and decrease of pressure also promotes the preferred formation of layer alumosilicates, and not silicates of Al.

2. For the reactions that pass through the dissolution of components (acid and especially alkaline solution) the leading factor (with P–T–X = const.) it is the pH of surrounding which controlls the form of the existence of Al in solution, and finally its coordination in newly formed structures. In acid surroundings silicates with Al^{VI} are formed, and with alkaline conditions there are formed such phases in which Al is an analog of silicon and takes the tetrahedral positions.

3. The widespread findings in hydrothermal formations of dioctahedral mixed-layer phases with $Al^{VI} + Al^{IV}$ instead of kaolinite and pyrophyllite are explained by the fact that the stable existence of the latter at high $T-200$ to 400 °C — is possible only in neutral-acid surroundings, poor in alkaline and alkaline earth cations.

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