

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 considerably rarely than montmorillonoides and micas. Hence it follows that the experimental determinations of thermal limits of stability of layer silicates in “distilled” H_2O 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_2SiO_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 except Al, this rule is followed less strictly, but the most typical minerals of high pressures — jadeite, garnets — have only an octahedral Al. The in-

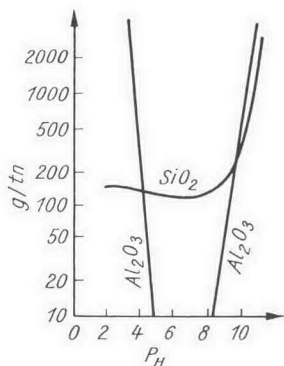


Fig. 6. Solubility of silica gel and aluminium hydroxide as a function of hydrogen ion concentration (CORRENS)

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_2O_3 and SiO_2 gels increase (CORRENS) roughly with the increase of alkalinescence of solutions (Fig. 6). Being amphoteric Al hydroxide with alkaline surroundings shows its acid properties (ALEKSEJEV) leading to the formation of well dissolved aluminates:

$\text{Al(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaAlO}_2 + 2 \text{H}_2\text{O}$. 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 aluminosilicates are formed but no silicates of Al. That the synthesis of framework aluminosilicates passes through a liquid phase is testified by the fact that only in this case the products of experiments are monocrystals 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:



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

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 aluminosilicates 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 aluminosilicates 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 aluminosilicates, 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 controls 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 $\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}}$ 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.

References

- ALEKSEJEV, V. N.: Course kachestvennogo chemicheskogo polumikroanaliza, Moscow Leningrad 1952, p. 207
 ALTHAUS, E.: N. Jb. Miner. Abh. **111**, (1) 74 (1969)
 BRAGG, L., CLARINGBULL, G. F.: Crystal structures of minerals, London 1965, p. 190
 BRINDLEY, G. W., WARDLE, R.: Amer. Mineralogist **55**, 1259 (1970)