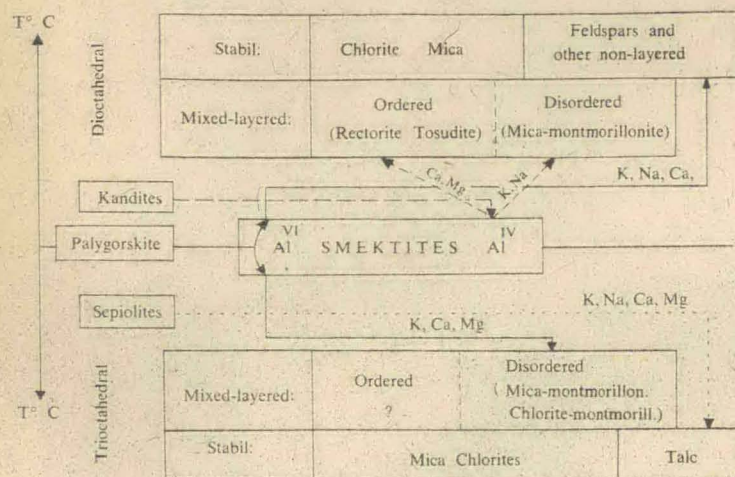


## Schematic Relations in the Transformation of Clay Minerals



from kaolinite (1T) mica with clearly prevalence of modification of 1M over 2M<sub>1</sub> is formed; mica with the prevalence of modification of 2M<sub>1</sub> over 1M is formed from dickite (2M<sub>1</sub>). In the examined transformations, the structure, as a whole, undergoes essential alteration from two-layered silicate to three-layered aluminosilicate, but the centres of ditrigons of tetrahedral nets of adjacent layers tend to keep the main layered nature; this shows that the three-dimensional nature of initial structure in newly formed materials is successive.

## Octahedral Layer

The above examples show a succession of structural features when transformation of crystalline products takes place without alteration of the character of population of octahedral positions. When K, Na, Ca are added the conservation of dioctahedral nature during the transformation of kaolinite minerals is noticed commonly, but when Mg is added dioctahedral nature increases, which requires special consideration. Small size of Mg-ion and a wide expansion of triocahedral micas, chlorites, montmorillonites, etc., rich in Mg, may give a clue in considering this problem.

Practically, in this case we have a pseudomorphous transformation of kaolinite to dioctahedral montmorillonite. As the duration is extended from 3 hrs. up to 70 hrs. and T from 400 up to 500°C, the montmorillonite transforms into ordered mixed-layered phase, 1:1 chlorite—montmorillonite.<sup>2,6,7</sup> The character of layered distribution was approximately established by means of one-dimensional Furje-synthesis after the 6 orders 001 for a specimen saturated with glycerol vapours and heated at 550°C (Fig. 6). The relation

of peaks of electron density shows dioctahedral nature of this mixed-layered structure, where Mg essentially enters into brucite layer and into interpacket intervals, but in a three-layered packets we have essentially dioctahedral structure. This conclusion confirms a small shrinkage—1 Å in c\* phase during its treatment with LiCl, heated and saturated with glycerol after Greenkelly.<sup>19</sup> In this way an ordered dioctahedral chlorite-montmorillonite is synthesised and this is close to the naturally occurring mixed-layered formation in Japan,<sup>20,21</sup> whose analog from Crimean alushite was investigated chrysollochemically<sup>22,23</sup> and called tosudite. It is conjectured that in some time under favourable conditions a dioctahedral layer in such structure can be transformed into a triocahedral one due to the migration of Mg from swelling montmorillonite intervals.

## Alteration of Kaolinite Structure during Transformation

In studying the phase transformation of kaolinite, it was noticed that the structure of kaolinite undergoes some regular alterations prior to the beginning of the formation of new phase (up to ~250°C with KCl or up to ~400°C with MgCl<sub>2</sub>) in 24 hours, and kaolinite is recrystallized partially and its structure improves. On diffractograms and electronmicrographs this can be seen as better development of 020-111, 021, 021, 130-131 reflections and as increase of numbers of crystallites having regular hexagonal morphology.

When temperature is reached to form any new phase in the presence of any cation addition, it is observed that ordered triclinic kaolinite changes to pseudo-monoclinic with disordered structure in the

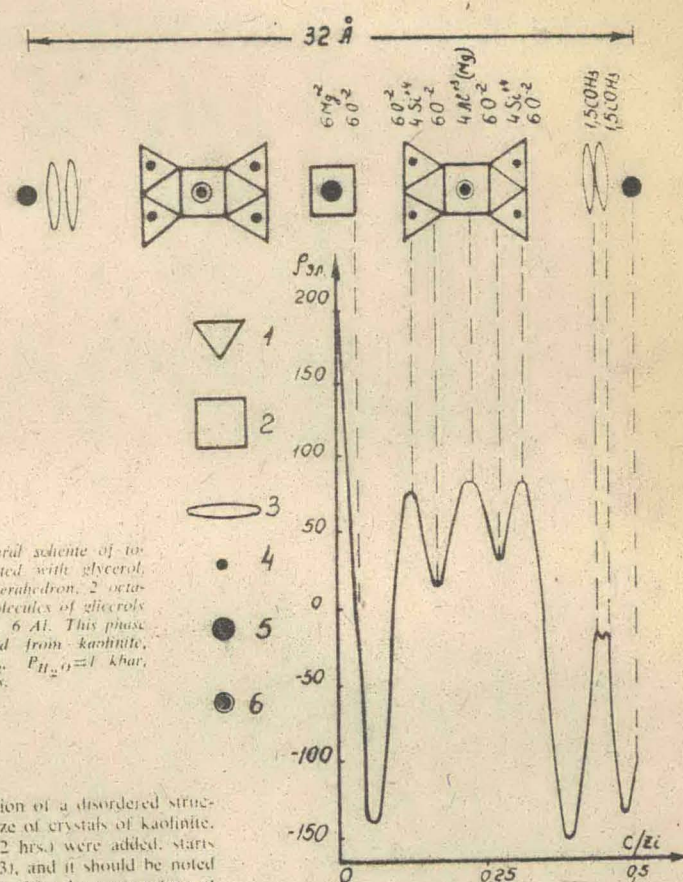


Fig. 6. Structural scheme of tosudite saturated with glycerol. Symbols: 1 tetrahedron, 2 octahedron, 3 molecules of glycerols, 4 Ca, 5 Mg, 6 Al. This phase is synthesised from kaolinite, with MgCl<sub>2</sub>, P<sub>H<sub>2</sub>O</sub> = 1 kbar, 450°C, 22 hrs.

basal plane (Fig. 1). Formation of a disordered structure and diminution of the size of crystals of kaolinite, when KCl and CaCl<sub>2</sub> (for 22 hrs.) were added, starts at about 250-300°C (Fig. 2, 3), and it should be noted that this is considerably lower than the temperature at which similar phenomena are observed under "pure" conditions *i.e.*, under the pressure of H<sub>2</sub>O-vapour only (~400°C) or with addition of MgCl<sub>2</sub> (~400°C). The worse crystallinity and disordering of the kaolinite structure under hydrothermal conditions with addition of K, Na, Ca, Mg chlorides is followed by the formation of new phases (montmorillonite, disordered mixed-layered phases). Similar structural changes of kaolinite (disordered in the basal plane) take place under the influence of stress pressure, whereas similar amount of hydrostatic pressure gives no effect up to 400°C at P<sub>H<sub>2</sub>O</sub> = 900 gk cm<sup>2</sup>, 22 hrs. Thus, stress and addition of cations lead to disordering of kaolinite structure. The initiation of disordering and the initial temperature of the formation of new phases are determined by the character of cations (Fig. 1). The process of disordering of layers observed here has a dislocation nature. Addition of cations stimulates deformation of the structure (shrinkage or expansion, normal to the base).

A different character of transformation of kaolinite structure, passing through the intermediate montmorillonite-like structure, when K, Na (right) and Ca, Mg (left) are added, is shown schematically in Fig. 7.

## Conditions for the Formation of Intermediate Mixed-Layer and Final Layer Structure

The presence of mixed-layered phases which are usually formed as intermediate forms in the course of structural alteration of clay minerals is inferred to the transformation character of the process as well as to the similar layered type of structures. As mentioned above, this process is essentially connected with the chemical nature of the surroundings. When kaolinite is treated in the presence of K, Na chlorides, the intermediate disordered mixed-layered structures of mica-