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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 aluminosilicates 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 aluminosilicates 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 твердофазовых преобразований (трансформация слоистых силикатов Al, реакции в Al-Si гелях) главными факторами контролирующими формирование алюмосиликатов помимо P-T-pH являются присутствие примесей щелочных и щелочноземельных 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 K₂O, Na₂O-Al₂O₃-SiO₂-H₂O (ROY, OSBORN; ЖАРИКОВ, ИВАНОВ, ДУГИКОВА, ШМОНОВ, ФОНАРЖОВ; SAND, ROY, OSBORN) allowed to reveal a considerable quantity of aluminosilicate phases, which have distinct structural differences for similar compositions. They are both typical polymorphs of Al₂SiO₅ 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 their stability and their 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, KOPEKIN) in tightly closed platinum ampullas, in the temperature interval 250 to 500 °C, $P_{H_2O} = 1000-2000 \text{ kg} \cdot \text{cm}^{-2}$, 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 (Prosyranovskoie deposit, UkSSR) and dickite (Turominskoie deposit RSFSR) were subjected a hydrothermal process at $T = 450 \text{ }^\circ\text{C}$, $P_{H_2O} = 1000 \text{ kg} \cdot \text{cm}^{-2}$ 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 interpackets intervals, and a partial nonrandom mixed-layer phase with $d_{001} 29,4 \text{ \AA} \xrightarrow{\text{glycol}} 33,9 \text{ \AA}$ and $d_{002} 13,8 \text{ \AA} \xrightarrow{\text{glycol}} 14,7 \text{ \AA}$ (\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 tetrahedral Al \rightarrow 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-