

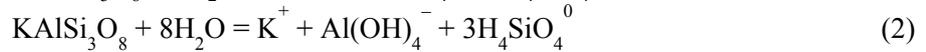
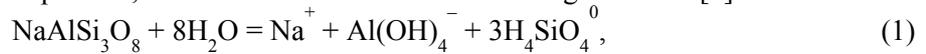
REACTION KINETICS OF ALBITE TO SANIDINE TRANSFORMATION WITH AND WITHOUT QUARTZ

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Initial minerals were crashed. Fractions with grain size 50–100 μ were obtained by sieving and cleaning ultrasonically from fine particles in water. Experiments were performed at 300°C and pH 9 in 0.1 *m* KHCO₃ solution in hermetic platinum capsules by quenching method. 2.5 mg of albite, 10 mg of sanidine, and 250 mg of quartz were in every ml of solution. Four series of experiments were performed using solid phases: 1) albite only, 2) albite and quartz, 3) albite and sanidine seeds, 4) albite, sanidine, and quartz.

Transformation reaction of albite to sanidine ($Ab \rightarrow San$) was followed by increase of sodium concentration in solution (m_{Na}) (fig.). Reaction $Ab \rightarrow San$ was run through primary albite dissolution and secondary sanidine precipitation, i.e. it is a difference of the following reactions [1]:



Permanent concentrations of Al and Si in time (see fig.) mean close rates of reactions (1) and (2). Both reaction rates (r_{Ab} and r_{San}) are described by the same equation [2]:

$$r = -kS[1 - (Q/K)^\sigma], \quad (3)$$

where k is rate constant ($k = 7 \times 10^{-8} \text{ mol m}^{-2} \text{ sec}^{-1}$), S is surface area of a mineral, Q and K are activity product and equilibrium constant of reaction ($K_{Ab} = 6.6 \times 10^{-13}$, $K_{San} = 1.6 \times 10^{-13}$), σ is coefficient ($\sigma = 0.83$). The quantity Q for reactions (1) и (2) has the expressions:

$$Q_{Ab} = a_{Na^+} a_{Al(OH)_4^-} a_{H_4SiO_4^0}^3, \quad (4)$$

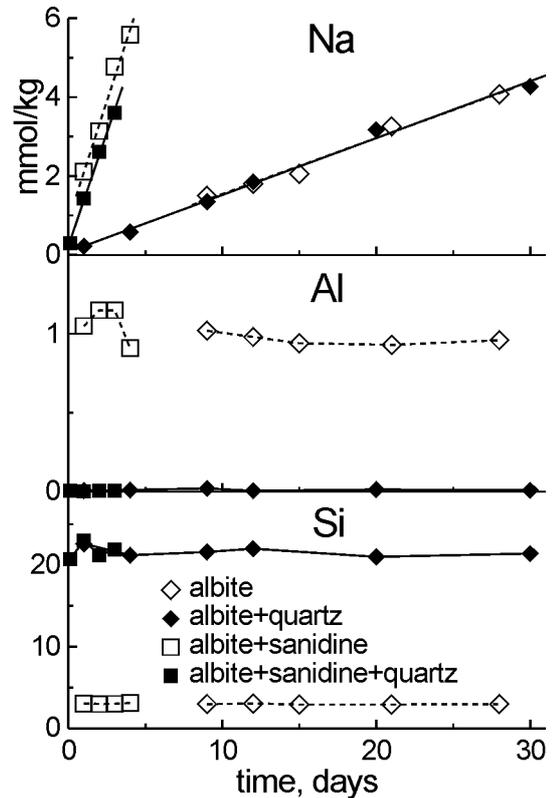
$$Q_{San} = a_{K^+} a_{Al(OH)_4^-} a_{H_4SiO_4^0}^3, \quad (5)$$

At first, congruent stage of albite dissolution according to reaction (1) took place. As soon as saturation of solution relative to sanidine was achieved ($Q_{San} \geq K_{San}$) incongruent stage began, i.e. reaction (2) (from the right to the left) was added to reaction (1). As a result of mutual influence of r_{Ab} and r_{San} through the activities of common aqueous species $Al(OH)_4^-$ and $H_4SiO_4^0$ in expressions (4) and (5), stationary state was achieved with close values of r_{Ab} and r_{San} [1].

In the presence of quartz, this state was established at considerably lower Al concentration in solution (m_{Al}) than in the absence of quartz (see fig.). It is explained by silica saturation of solution earlier than noticeable quantity of albite was dissolved. In the presence of high silica concentration, the quantity Q_{San} achieved value of K_{San} at $m_{Al} = 2\text{--}5 \text{ }\mu\text{mol/kg}$. As a result, initial congruent stage of albite dissolution was practically disappeared.

In the presence of sanidine seeds, slope m_{Na}/time raises (see fig.) that means increasing r_{Ab} . As this

Fig. Concentrations of Na, Al, and Si in 0.1 *m* KHCO₃ solution versus time as a result of transformation reaction of albite to sanidine (300°C, pH 9) with different composition of solid phases.



takes place, values of m_{Al} are diminished a little (see fig.). This means that reaction (1) proceeds farther from equilibrium where its rate is higher. In the presence of quartz, the scatter of m_{Al} values is considerably higher in experiments without seeds than with sanidine seeds. It is explained by formation of small sanidine nuclei in the bulk of solutions [1]. The nuclei pass through the filter and give additional contribution in solution analyses. In the presence of seeds, nuclei decrease in quantity leading to decreasing scatter of m_{Al} values.

A decrease of m_{Al} in experiments with quartz as compared to experiments without quartz does not change r_{Ab} (slopes m_{Na} /time on fig.). This was observed in experiments both with sanidine seeds and without them. Hence presented data definitely evidence the absence of influence of dissolved Al on dissolution rate of albite. However, some investigators note this influence on dissolution of some aluminosilicates: albite [3], potassium feldspar [4], kaolinite [5, 6]. Apparently, the effect of r slowing down ascribing to Al in fact is associated with precipitation of secondary minerals on active sites of primary mineral dissolution. As a result of blockade of these sites, dissolution of primary mineral decreases in rate. In particular, the evidence of this is the association of the effect with the beginning of secondary sanidine precipitation [1] and also the presence of single equation (3) for description of r_{Ab} and r_{San} . The latter can be interpreted as fulfillment of the principle of microscopic reversibility of two reactions [7]. The dissimilarity from usual approach is that the principle is fulfilled for dissolution and precipitation of not the same but distinct minerals [2]. This is possible when both reactions proceed on the same surface sites through formation and disruption of the same surface complex [7]. In reaction $Ab \rightarrow San$ this complex can be, as an example, $(H_3O)AlSi_3O_8$ [8].

Another question associated with the estimation of this effect is proper measurements of m_{Al} particular at low m_{Al} values. When pores of filter exceed minerals in size, the latter pass through the filter and give additional contribution in analyses of solution. This is observed at quartz dissolution (150°C) when fine particles were split out from quartz surface in the immediate process of dissolution [1], at albite dissolution (25°C) when fine crystals of Al hydroxide were formed as secondary mineral [9]. In this work (series albite+quartz), the formation of fine sanidine nuclei leads to pronounced increase in scatter of measured values of m_{Al} (see fig.). The data given in this paper demonstrate the complexity of unambiguous interpretation in studies where investigators evaluate the influence of dissolved Al on r but do not take into consideration concurrent influence of small amounts of secondary minerals and use filters with large pores.

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