

SHORT  
COMMUNICATIONS

# Kinetics of the Albite–Sanidine Transformation in the Presence or Absence of Quartz

V. G. Alekseev and L. S. Medvedeva

*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, Moscow, 119991 Russia*

*e-mail: alekseyev-v@geokhi.ru*

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## TECHNIQUE

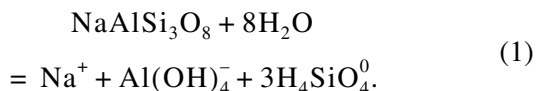
The experiments were conducted with fractions of low albite, intermediate sanidine, and  $\alpha$ -quartz crushed to 50–100  $\mu\text{m}$  [1]. The fractions were repeatedly rinsed with water in an ultrasonic bath to remove dust particles. The specific surface of albite and sanidine measured by the BET method is 0.11  $\text{m}^2/\text{g}$ . We performed four experimental series with different amounts of minerals (in mg) per 1 ml 0.1  $m$   $\text{KHCO}_3$ :

Series	Albite	Quartz	Sanidine
Albite	2.5	0	0
Albite + quartz	2.5	250	0
Albite + sanidine	2.5	0	10
Albite + sanidine + quartz	2.5	250	10

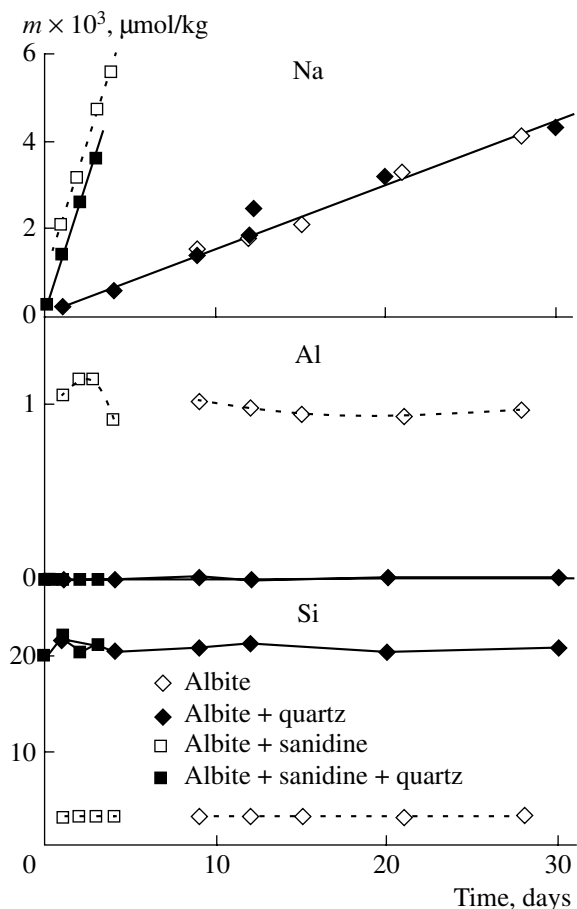
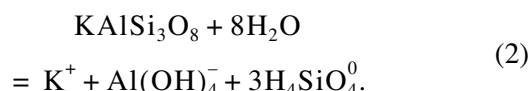
Experiments were conducted in platinum ampoules sealed by welding with an electric arc. Albite or its mixture with sanidine was placed at the bottom of the ampoule, and quartz was positioned near its top. The ampoules were heated in autoclaves at 300°C under saturated water vapor pressure for a specified time. Then autoclaves were quenched in cold water, the ampoules were opened, and the solution was filtered through 0.12- $\mu\text{m}$  membrane filter and analyzed by atomic absorption for Na and by AES-ICP for Al and Si. The values of pH determined potentiometrically and calculated for experimental temperature were close to 9 [1].

## RESULTS

In all experiments, the Na concentration in the solution increased with time, while those of Si and Al practically did not change but strongly varied in the experiments depending on the absence or presence of quartz (figure). In the absence of quartz, albite dissolution at the initial stage was congruent [1]:



As saturation of the solution with sanidine was reached, the latter began to precipitate (from right to left) simultaneously with reaction (1):



Change in the Na, Al, and Si concentrations in 0.1  $m$   $\text{KHCO}_3$  with time during albite-to-sanidine transformation (300°C, pH 9) at different compositions of the solid phases.

Since reactions (1) and (2) have similar stoichiometry in terms of Al and Si, the constant contents of these elements in the solution are explained by the similar rates of dissolution of the primary mineral and the precipitation of the secondary one. This indicates that the resulting albite–sanidine transformation ( $Ab \rightarrow San$ ) is the difference between reactions (1) and (2):



Since quartz dissolution is a more rapid process than the studied reaction, the solution reached quartz saturation in the presence of quartz before significant dissolution of albite. Under these conditions, the initial congruent stage is much briefer and is characterized by lower contents of dissolved elements (by a factor of ~200). When the content of dissolved Al reached 2–5  $\mu\text{mol/kg}$ , the activity product (quotient) of reaction (2)

$$Q_{San} = a_{\text{K}^+} a_{\text{Al(OH)}_4^-} a_{\text{H}_4\text{SiO}_4^0}^3 \quad (4)$$

reached the value of the equilibrium constant, since the solution already had high contents of K (0.1  $m$ ) and Si (0.022  $m$ ). As a result, sanidine began to precipitate from the very beginning of the reaction.

In the presence of sanidine seeds, the reaction  $Ab \rightarrow San$  proceeds significantly more rapidly, as can be seen from the increase in slope of the straight line in the  $m_{\text{Na}}$ –time plot (figure). This dependence was previously studied and has the form [1]:

$$r = 2.6 \times 10^{-8} (S_{Ab} S_{San})^{0.5}, \quad (5)$$

where  $r$  is the rate of  $Ab \rightarrow San$  reaction (mol/s), and  $S_{Ab}$  and  $S_{San}$  are the surface areas of albite and sanidine, respectively ( $\text{m}^2/\text{kg}$  solution). Following Eq. (5) at  $S_{Ab}$  and  $S_{San}$  of 0.28 and 1.1  $\text{m}^2/\text{kg}$  (albite + sanidine and albite + sanidine + quartz experimental series),  $r = 1.4 \times 10^{-8}$  mol/s. The value of  $r$  calculated from the slopes of the left-side straight lines in the  $m_{\text{Na}}$ –time diagram is the same.

In the absence of sanidine seeds, the rate of the  $Ab \rightarrow San$  reaction is almost one order of magnitude lower (right-side lines in the  $m_{\text{Na}}$ –time diagram). Under these conditions, sanidine precipitates on the albite surface as individual crystals, which grow inside the solution [1]. The  $S_{San}/S_{Ab}$  ratio calculated from Eq. (5) is 0.03. The kinetics of albite dissolution and sanidine precipitation under these conditions is described by the equations [2]:

$$r_{Ab} = -k S_{Ab} [1 - (Q_{Ab}/K_{Ab})^\sigma], \quad (6)$$

$$r_{San} = -k S_{San} [1 - (Q_{San}/K_{San})^\sigma], \quad (7)$$

where  $k = 7 \times 10^{-8}$  mol  $\text{m}^{-2}$   $\text{s}^{-1}$ ,  $\sigma = 0.83$ ,  $K_{Ab} = 6.6 \times 10^{-13}$ ,  $K_{San} = 1.6 \times 10^{-13}$ . According to the reaction (1), the activity product (quotient) of this reaction increases during the initial stage of albite dissolution:

$$Q_{Ab} = a_{\text{Na}^+} a_{\text{Al(OH)}_4^-} a_{\text{H}_4\text{SiO}_4^0}^3 \quad (8)$$

This causes a decrease in  $r_{Ab}$  according to the reaction (6). An increase in activities in the  $\text{Al(OH)}_4^-$  and  $\text{H}_4\text{SiO}_4^0$  solutions leads to an increase in  $Q_{San}$  [Eq. (4)], and, respectively,  $r_{San}$  according to Eq. (7). The increase in  $r_{San}$  leads to a decrease in  $Q_{San}$  and, respectively, in  $Q_{Ab}$ , which, in turn, causes an increase in  $r_{Ab}$ . This interdependence of  $r_{Ab}$  and  $r_{San}$  results in the rapid attainment of a quasistationary state with similar values of  $r_{Ab}$  and  $r_{San}$  [1]. When  $S_{San}$  is lower than  $S_{Ab}$ , such a state occurs under the near-equilibrium conditions for the reaction (1), when its rate is low. At high  $S_{San}$ , reaction (1) takes place under conditions remote from equilibrium, when its rate becomes higher. This reflects the influence of sanidine seeds on the rate of the  $Ab \rightarrow San$  reaction. Similar rates of the reactions (slope of the straight lines in the  $m_{\text{Na}}$ –time diagram) in the experimental series in the absence and presence of quartz indicate similar degrees of solution saturation under the quasistationary state. In the presence of seeds, the solution under a quasistationary state shows a lower degree of saturation than that in their absence. This is expressed in the lower Al contents (within the measurement error) in the experiments without sanidine seeds (figure). The scatter of  $m_{\text{Al}}$  in these experiments is significantly higher than in experiments with seeds. This is explained by the formation of a large number of small sanidine nuclei in the solution [1]. The nuclei partially pass through the filter, contributing additionally in the solution analyses. In the presence of seeds, the number of nuclei decreases, causing a decrease in the scatter of  $m_{\text{Al}}$ .

## DISCUSSION

Some investigators believe that dissolved Al retards the congruent dissolution of aluminosilicates: albite [3], K-feldspar [4], and kaolinite [5, 6]. In this work,  $m_{\text{Al}}$  was  $5 \times 10^{-6}$  in the presence of quartz and ~0.001, i.e. 200 times higher, in its absence. In spite of such a sharp difference in the Al content, the reaction rates (the slope of the straight lines in the  $m_{\text{Na}}$ –time diagram) are identical. This fact unambiguously indicates that dissolved Al has no influence on the rate of the  $Ab \rightarrow San$  reaction, and, hence, on the rate of congruent albite dissolution [reaction (1)]. This raises the question as to why in some cases Al affects the rate of mineral dissolution and in others not. We believe that the effect of rate lowering attributed to Al is actually governed by another factor, which is only occasionally correlated with Al. This factor is that the precipitation of secondary minerals occurs preferentially on the active dissolution sites of primary minerals. The blocking of these sites causes a decrease in the dissolution rate of the primary minerals. Such a phenomenon, in particular, was inferred from the long induction time between the congruent and incongruent (with the formation of sanidine as a secondary mineral) stages of albite dissolution [1]. This hypothesis is also supported

by the fact that the kinetics of albite dissolution and sanidine precipitation in the  $Ab \rightarrow San$  reaction is described by Eqs. (6) and (7), which are, in fact, the same equation. This can be interpreted as the fulfillment of principle of the microscopic-scale reversibility of these two reactions [7]. Unlike the usual approach, this principle is fulfilled for the dissolution and precipitation of different rather than the same minerals [2]. This is possible if the rates of both reactions are controlled by the dissolution or formation of the same surface complex. Such a common complex in the  $Ab \rightarrow San$  reaction can be, for example,  $(H_3O)AlSi_3O_8$  [8]. Since the surface complexes in the albite–analcime transformation are different (different Al/Si ratios of the minerals), no drastic lowering of the reaction was observed at the boundary between the congruent and incongruent stages [2].

Another problem in estimating the influence of dissolved Al on  $r$  is the correct measurement of its content, especially at low  $m_{Al}$ . If the size of pores in the filter is greater than grain sizes of the secondary minerals, they can pass through the filter, additionally contributing this component to the solution. This is seen from the scatter of  $m_{Al}$  in the albite + quartz series (figure). Albite dissolution (25°C, pH 5) was accompanied by the formation of Al hydroxide, which passed through the 0.45- $\mu m$  filter [9]. As a result, the measured Al content increased with time to 150  $\mu mol/kg$ . However, the same solutions passed additionally through a 0.1- $\mu m$  filter had a constant Al content of about 10  $\mu mol/kg$ . The  $SiO_2$  content in the solution after the dissolution of crushed quartz at 150°C and filtration through 0.12- $\mu m$  filter was four times higher than the equilibrium content; and that after filtration through 0.03- $\mu m$  filters was only two times higher [10]. In this case, the solutions were contributed to by primary minerals, whose small particles were detached from the surface during dissolution. The aforesaid data showed that the influence of dissolved Al on  $r$  cannot be unambiguously interpreted without allowance for the simultaneous influence of subordinate secondary minerals and pore size.

## CONCLUSIONS

The sanidine–albite transformation (300°C, pH 9) begins with the congruent dissolution of albite  $NaAlSi_3O_8$ . When the solution reaches equilibrium with respect to sanidine,  $KAlSi_3O_8$  starts to precipitate. In the presence of quartz, the solution reaches quartz saturation before significant dissolution of albite. As a result, albite dissolution and sanidine precipitation proceed at significantly lower Al content in the solution ( $5 \times 10^{-6} m$ ) than in the absence of quartz ( $10^{-3} m$ ), but with the same rate. Thus, the variations in the Al content in the solution by a factor of 200 do not affect the rate of the aluminosilicate dissolution ( $r$ ). The lowering effect of Al on  $r$  inferred by some authors is presumably related not to Al, but to the simultaneous precipitation of secondary minerals on the active dissolution sites of

the primary minerals. In addition, the Al content in the solution can be overestimated, if the grain size of the secondary minerals is lower than the pore size of the filter.

The reaction proceeds more rapidly in the presence of sanidine seeds than in their absence. This is explained by the mutual influence of the rates of the dissolution of primary mineral and the precipitation of the secondary mineral. The influence acts through the activity of aqueous species  $Al(OH)_4^-$  and  $H_4SiO_4^0$ , which are incorporated into the equations of rates for both reactions. As a result, the more intense sanidine precipitation on seeds leads to a shift of albite dissolution from equilibrium, and, respectively, an increase in the reaction rate.

## ACKNOWLEDGMENT

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