

Experimental investigation of the reaction: An-rich plagioclase + quartz + fluid = analcime-wairakite_{ss}

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ABSTRACT:

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The reaction An-rich plagioclase + quartz + fluid = analcime (NaAlSi₄O₁₂ · 2H₂O) – wairakite (CaAl₂Si₄O₁₂ · 2H₂O)_{ss} (solid solution series) has been studied experimentally in the temperature range 350-200°C. Distilled water or 0.1 M NaHCO₃ solution was used as fluid. All experiments have been performed under low silica activity. Due to the short duration of the experiments the reaction had not approached equilibrium and partly metastable phases were formed. Wairakite nucleated in the laumontite stability field in the system plagioclase-quartz-H₂O. Higher sodium activities led to the formation of mixed analcime-wairakite crystals or analcime crystals. The mechanism of zeolite formation seems to comprise topotaxial growth on the plagioclase surface caused by a dissolution-precipitation process. Some variations in the nucleation and growth kinetics were noticed which appear to be due to different physico-chemical conditions of zeolite formation.

Key words: Analcime-wairakite_{ss}, Hydrothermal synthesis, Plagioclase, Growth kinetics.

INTRODUCTION

Wairakite is one of the calcium bearing zeolites often appearing in active geothermal areas. It has been first recognised in the Wairakei hydrothermal area (STEINER, 1955). Its appearance is highly dependent on calcium, sodium, silica and carbonate (bicarbonate) activity in the system. The stability field of wairakite is also strongly influenced by temperature and pressure. Hydrothermal alteration of acidic, intermediate or basic volcanic rocks leads to the formation of wairakite or its sodium analogue. One of the formation paths comprises the following volcanic glass alteration: volcanic glass ⇒ clinoptilolite-mordenite ⇒ (analcime) ⇒ laumontite ⇒ wairakite (UTADA & *al.* 1999). Another path embraces the dissolution of plagioclase enriched in anorthite (GIANELLI & *al.* 1998). Both

processes are well known and have been investigated in the field in various areas. Wairakite was also yielded experimentally. The synthesis followed the path observed in the nature. In general zeolites belonging to the group wairakite-analcime_{ss} were typically exchange products of laumontite, heulandite, stilbite, lawsonite or products of a hydrothermal treatment of the oxide mixtures, gels or glasses (AMES & SAND 1958; COOMBS & *al.* 1959; KOIZUMI & ROY 1960; LIU 1970 1971; WIRSCHING 1981; GHOBARKAR 1985; FRANKE 1989; JOVE & HACKER 1997, WUST & AMBRUSTER 1999; GHOBARKAR & *al.* 1999). The process of wairakite formation through plagioclase dissolution was seldom presented (COOMBS & *al.* 1959; KOIZUMI & ROY 1960; LIU 1970).

COOMBS & *al.* (1959) pointed out the differences in the extension of the wairakite field stability in the sys-

tem anorthite - silica - water to be attributable to the form of silica in the starting material. Amorphous silica expanded the field towards higher temperature. COOMBS & *al.* (1959) used in their experiments only plagioclase with varying contents of anorthite. Through the entire range of the plagioclase composition no wairakite nucleation was observed. Even if the starting material was rich in anorthite, instead of wairakite the analcime appeared.

KOIZUMI & ROY (1960) used an oxide mixture of the composition: anorthite + 6 SiO₂ for the reaction. The results of the experiments provided information regarding the stability fields of both wairakite and anorthite, but the reaction did not approach equilibrium. LIOU (1970) pointed to the very slow conversion of anorthite into wairakite. The obtained products, after more than 40 days of run time, displayed overgrowths of wairakite crystals on corroded anorthite grains. The rate of the reaction was considerably enhanced by increasing the pressure up to 2 kb or even more. Under lower pressures ($P_{\text{fluid}} = 500$ bars) the reaction had not completed after two months.

A new discussion concerning nucleation and growth kinetics as well as the reaction mechanisms leading to wairakite formation was triggered by JOVE and HACKER (1997); they investigated experimentally the reaction laumontite \Rightarrow wairakite + H₂O, and noticed that the transformed high temperature sample contained two products: wairakite and a plagioclase-like phase. The plagioclase-like phase displayed a skeletal habit. Equilibrium stability fields for minerals in the system CaO-Al₂O₃-SiO₂-H₂O calculated on data presented by BERMAN (1988) and JOHNSON & *al.* (1992), as well as the experimentally determined stabilities by LIOU (1971) confirmed the presence of the reaction wairakite \Rightarrow anorthite + quartz at temperatures higher than 300°C. No reverse reactions were performed. Two mechanisms of wairakite formation were proposed. The prevailing mechanism under low temperature (<400°C) conditions was dissolution of the source material, transport within the fluid and finally precipitation of wairakite crystals. At higher temperature (>400°C) wairakite was formed due to topotaxial replacement of laumontite. The nucleation rate of wairakite was relatively slow compared to the growth rate.

The experiments being done until recently confirm the two paths of wairakite formation in the natural systems. The first one leads to wairakite formation through the dehydration reaction of the Ca-rich zeolites in the regime of increasing temperature. The second path follows the plagioclase decay process in the presence of quartz in the regime of decreasing temperature. Pure anorthite was usually used for the previous experiments, although natural wairakite can crystallise as a decay product of anorthite-rich plagioclase on hydrothermal conditions. Sodium

activity in the system seems to influence evidently the stability field of wairakite.

The aim of the present research work is to study experimentally this second path: that is the reaction: plagioclase + quartz + H₂O \Rightarrow wairakite. Ca-rich plagioclase and quartz crystals were used as the source material. The mole fraction of albite in the plagioclase was not higher than 0.4. The amount of quartz was kept at a relatively low level. A run time of only 30 days were chosen in order to observe the mechanism of zeolite formation before the reaction is completed. The temperature of the reaction was balanced within the range of the wairakite stability field established experimentally and confirmed throughout calculation (COOMBS & *al.* 1959; KOIZUMI & ROY 1960; LIOU 1971; KISELEVA & *al.* 1996; JOVE & HACKER 1997). Additionally runs were performed under higher sodium activity in the presence of HCO₃⁻ anions in the system, in order to compare the nucleation rate of wairakite, and its sodium analogue analcime, formed from the same source material.

EXPERIMENTAL PROCEDURES

All experiments were performed in vertically mounted cold seal pressure vessels (12 mm inner diameter and 240 mm inner length) with the cap nut at the bottom and with an external heating mantle. This arrangement gave rise to a thermal gradient of appr. 100°C between the top and the bottom of the used part of the reaction vessel. Four copper containers with 8 mm inner diameter and 20 mm inner length were fixed in the autoclave. The temperature in each container was measured in blind runs at 2 kbar using pressure tight welded shielded Ni-CrNi thermocouples, at the same time the temperature in an outside borehole was monitored. Each Cu-container was filled with starting material and solution in the proportion 1:10, placed in the cold seal vessel and heated in a furnace. Because of low redox potential dominating in the autoclave interior, no influence of copper from the container on the reaction kinetic had to be appraised. The temperature during the runs was monitored continuously. Eventually, the temperature of the reaction was extrapo-

	Oxides (wt %)
SiO ₂	53,136
Al ₂ O ₃	28,116
CaO	13,723
FeO	0,176
Na ₂ O	3,564
K ₂ O	0,259
NiO	0,016
TiO	0,029
Total	99,019

Table 1. Plagioclase compositions

RUN	T [°C] p [kbars]	Solution, pl:q ratio	Reaction products**	pH Solution***	Ca concentration in the solution*** [μg/ml]	Mean grain diameter [μm]	Nucleation (30 days) [crystal amount /10000μm ²]
1	350 1,9	H ₂ O pl : q = 1 : 2	leached pl	9,6	0,040	-	-
2	340 1,9	H ₂ O pl : q = 1 : 2	leached pl	9,6		-	-
3	325 1,9	H ₂ O pl : q = 1 : 2	leached pl	9,6		-	-
4	300 1,9	H ₂ O pl : q = 1 : 2	leached pl	9,6		-	-
5	250 1,8	H ₂ O pl : q = 1 : 2	leached pl	9,3		-	-
6	240 1,8	H ₂ O pl : q = 1 : 2	wa	9,3		8,2	64
7	225 1,8	H ₂ O pl : q = 1 : 2	leached pl	9,3		-	-
8	200 1,8	H ₂ O pl : q = 1 : 2	wa	9,3	0,020	5,7	84
9	350 1,6	0,1M NaHCO ₃ pl : q = 1 : 2	leached pl, zeo (can)	7,3	1,625	-	-
10	340 1,6	0,1M NaHCO ₃ pl : q = 1 : 2	leached pl, zeo (can)	7,3		-	-
11	325 1,6	0,1M NaHCO ₃ pl : q = 1 : 2	leached pl, zeo (can)	7,3		-	-
12	300 1,6	0,1M NaHCO ₃ pl : q = 1 : 2	leached pl, zeo (can)	7,3		-	-
13	250 1,5	0,1M NaHCO ₃ pl : q = 1 : 2	leached pl, zeo (can)	7,4		-	-
14	240 1,5	0,1M NaHCO ₃ pl : q = 1 : 2	an-wa	7,4		9,7	79
15	225 1,5	0,1M NaHCO ₃ pl : q = 1 : 2	leached pl	7,4		-	-
16	200 1,5	0,1M NaHCO ₃	an	7,4	1,900	0,7	8507
17	350 1,9	H ₂ O pl : q = 1 : 0,6	leached pl, zeo	7,4	0,400	-	-
18	340 1,9	H ₂ O pl : q = 1 : 0,6	leached pl	7,4		-	-
19	325 1,9	pl, q, H ₂ O pl : q = 1 : 0,6	an-wa	7,4		12,0	21
20	300 1,9	H ₂ O pl : q = 1 : 0,6	leached pl	7,4		-	-
21	250 1,8	H ₂ O pl : q = 1 : 0,6	leached pl, wa	7,3		3,4	350
22	240 1,8	H ₂ O pl : q = 1 : 0,6	leached pl, wa	7,3		2,8	323
23	225 1,8	H ₂ O pl : q = 1 : 0,6	leached pl	7,3		-	-
24	200 1,8	H ₂ O pl : q = 1 : 0,6	leached pl, wa	7,3	0,450	2,3	123
25	350 1,7	0,1M NaHCO ₃ pl : q = 1 : 0,6	leached pl, zeo (can)	7,5	1,375	-	-
26	340 1,7	0,1M NaHCO ₃ pl : q = 1 : 0,6	leached pl	7,5		-	-
27	325 1,7	0,1M NaHCO ₃ pl : q = 1 : 0,6	an, zeo (can)	7,5		6,2	273
28	300 1,7	0,1M NaHCO ₃ pl : q = 1 : 0,6	an	7,5		8,1	271
29	250 1,5	0,1M NaHCO ₃ pl : q = 1 : 0,6	leached pl, an	7,3		10,3	47
30	240 1,5	0,1M NaHCO ₃ pl : q = 1 : 0,6	an	7,3		9,0	72
31	225 1,5	0,1M NaHCO ₃ pl : q = 1 : 0,6	leached pl	7,3		-	-
32	200 1,5	0,1M NaHCO ₃ pl : q = 1 : 0,6	leached pl	7,3	1,480	-	-

* pl - plagioclase, q - quartz, pl : q - plagioclase quartz ratio,

** wa - wairakite, an - analcime, zeo (can) - zeolite (cancrinite?), leached pl - leached plagioclase

*** post reaction solution

Table 2. Experimental data

lated from the autoclave calibration curve. Water was used as the pressure medium.

The source material for the experiment, crystals of a basic plagioclase, was collected from Suwałki anorthosite massive (Table 1). Accurately selected plagioclase crystals, 2mm size and without any visible alteration phases, were mixed with quartz powder and distilled water or 0.1 M NaHCO₃ solution and maintained in the capsule. The ratio plagioclase/quartz varied within the range from 0.5 to 1.7. Amount of plagioclase crystals was almost the same in every run to ensure equal surface area during the reaction. The capsules were weighed before and after the run to check for leaks. The conditions of the runs, the capsules content as well as the reaction products, are presented in Table 2.

Products of the reaction were checked by means of optical microscopy, scanning electron microscopy, and semi-quantitative electron-probe microanalysis. Due to small amount of products in every run the X-ray powder diffractograms have not been taken. The composition of the post-reaction solution was checked for Ca and Si concentrations by means of the AAS method and the silicomolybdic acid method. Additionally the pH of the solution was determined.

RESULTS OF THE EXPERIMENT

Wairakite appeared as a reaction product in a number of runs, but the frequency of its presence cannot be easily correlated with the run conditions (Table 2). In the first series (runs number 1-8) wairakite crystallised occasionally at temperatures below 240°C. The crystal size varied from 4.2 μm to 15 μm (Text-fig. 1a). Assuming that the growth rate was more or less constant through the whole duration of the runs, the nucleation process seemed to be continuous, because the grains displayed a seriate range. At higher temperatures, above 240°C, the plagioclase was just leached, but no new zeolite-like phases were observed.

The next series maintained the same silica activity but the medium used was 0.1 M NaHCO₃ solution (Table 2; runs 9-16). The higher temperature runs (runs 9-13) displayed as reaction products needle like crystals aggregated randomly on the leached plagioclase surface. The needles are likely to be cancrinite (SŁABY 1999). Fine crystals with the composition of wairakite-analcime solid solution were formed below 240°C (Text-fig. 2.1-2.2). The crystals were attached to the plagioclase surface and grew in clusters or as single occurrence. Actually the crystals grew in small valleys appearing on the plagioclase surface due to the leaching process. Some parts of them are therefore hidden within the altered feldspar (Text-fig. 2.2). The

nucleation process seems to have taken place in the leached parts of plagioclase crystals. Not all of the plagioclase showed traces of leaching. Some of them are fresh without any signs of alteration. Some of them are leached, but no wairakite-analcime crystallisation process happened on their surface. The irregular pattern of the traces of leaching allows to conclude, that the reaction developed mainly due to the presence of surface defects. The nucleation rate for the crystals yielded in higher temperature runs (T=240°C) was slow comparing with the growth rate. On the contrary, the nucleation rate for the crystals appearing due to the reaction at lower temperatures (T=200°C) was high comparing with the growth rate (Table 2; Text-fig. 1a).

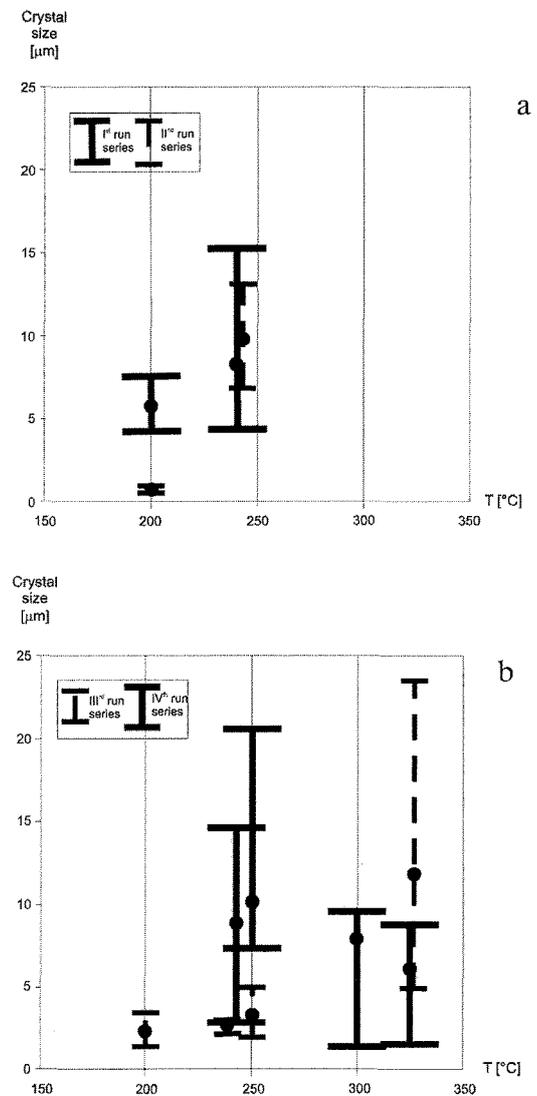


Fig. 1. Wairakite – analcime_{ss} grain size; the bars show the extension between maximum and minimum grain size, the point weighted average of mean diameter

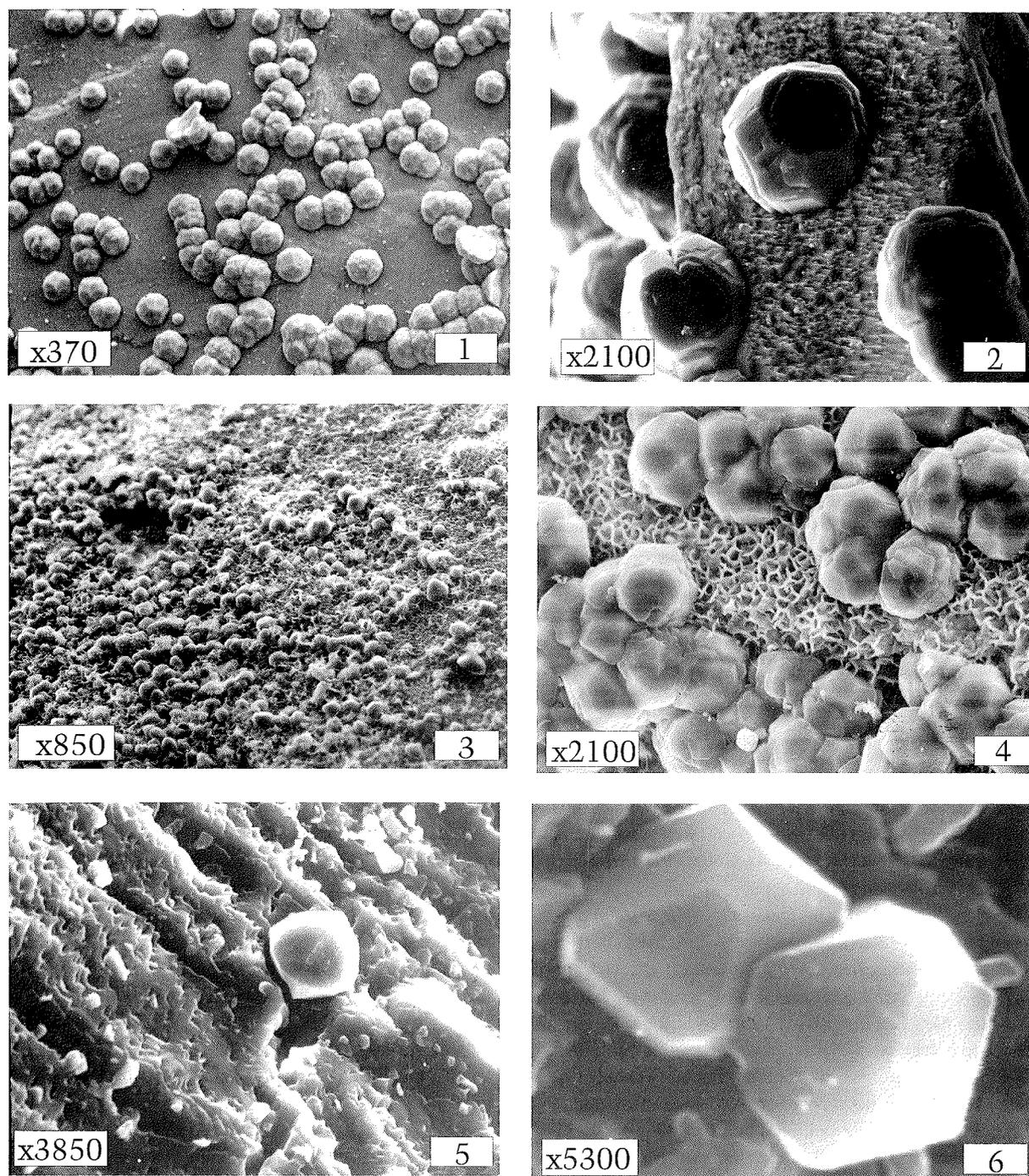


Fig. 2. SEM image of analcime - wairakite growing on the plagioclase surface: 1, 2 analcime- wairakite_{SS}, run 14; 3, wairakite, run 22; 4 analcime, run 27; 5,6 wairakite, run 21

The third series of runs comprised capsules with a lower quartz content (plagioclase/quartz ratio = 0.5-0.6) and distilled water (Table 2; runs 17-24). Products of the runs were generally wairakite, very seldom mixed analcime-wairakite crystals. Wairakite and wairakite-analcime usually started to nucleate below 325°C as single crystals

or as crystal clusters. Such crystals showed sometimes a very well shaped combination of cube {100} and deltoidicositetrahedron {211}. Crystals nucleated continuously and the range of their size is relatively wide (Text-fig. 1). The low temperature runs produced clusters of wairakite (Text-fig. 2.3). The wairakite is gathered in catenary

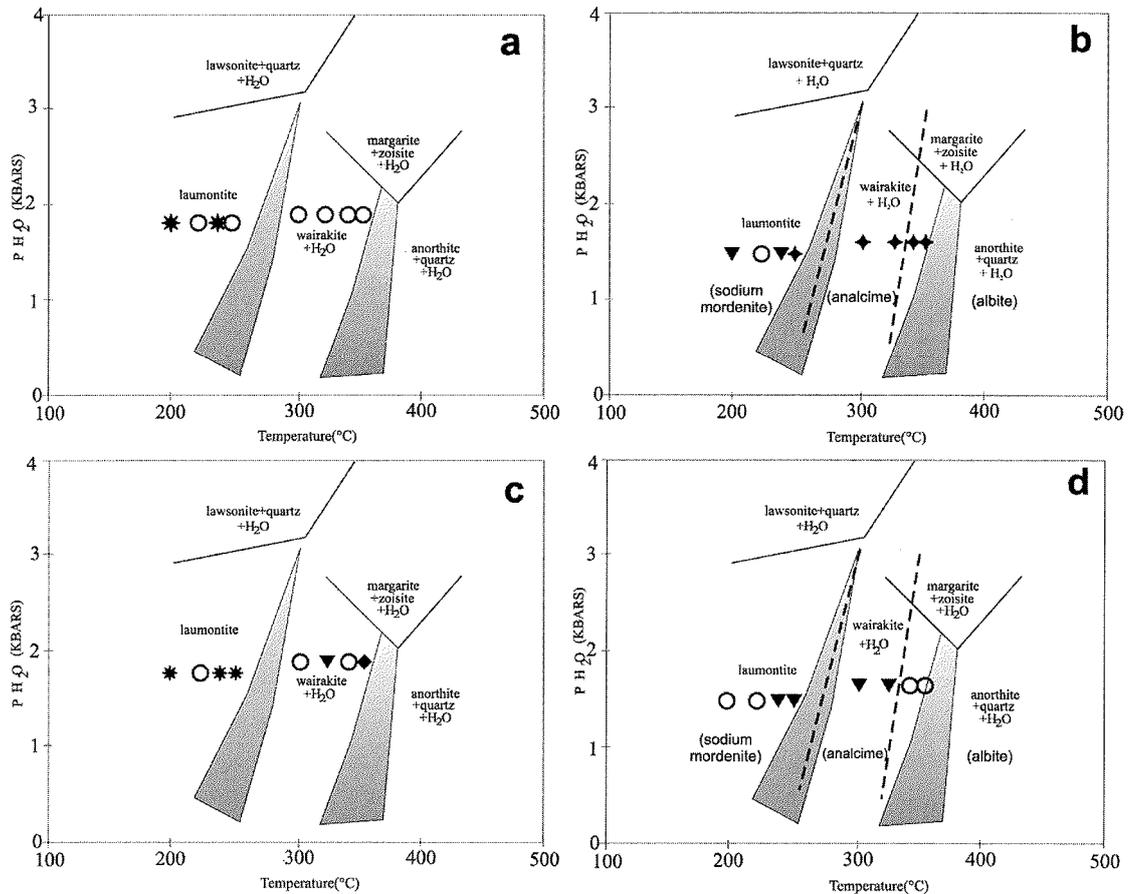


Fig. 3. Equilibrium stability fields for minerals in the calcium (a, c) and mixed calcium-sodium system (b, d) (based on COOMBS & *al.* 1959; LIOU 1971 and JOVE & HACKER 1997); symbols used: circle – leached plagioclase, triangle – analcime, diamond – needle shaped zeolite, asterisk – wairakite run series I, b) run series II, c) run series III, d) run series IV.

shaped aggregates on the cleavage plane or is covered uniformly on the plagioclase surface. The habit of the wairakite crystallised at lower temperature differs from that appearing as a higher temperature plagioclase alteration product. The crystals are rounded and usually suggest cubic symmetry. Their edges and faces are poor developed. Sometimes the combination of {111}, {010} and {100} could be recognised, which is attributed – according to GHOBARKAR (1985) and FRANKE (1989) – to a crystallisation process in the temperature range 200–270°C (Text-fig. 2.5, 2.6). Nucleation seemed to have taken place early in the experiment. Its frequency peaked at 250°C and falls rapidly down for higher and lower temperatures (Table 2, Text-fig. 1b).

Above 340°C needle-like crystals occur. The needle-shaped crystals as well as analcime-wairakite are accompanied by distinct tracks of plagioclase leaching. Though on almost all of the plagioclase crystals the leaching process was observed, the nucleation process of analcime-wairakite or needle-shaped zeolites were noticed only on

some of them. The frequency of zeolitic crystal appearance is much more higher than in the previous run series. The higher the temperature of the reaction the more seriate crystals of zeolite appear.

In the last run series the capsules were filled with the plagioclase + quartz powder (the ratio 1.7) and the 0.1 M NaHCO₃ solution (Table 2; run 25–32). Above the temperature 330°C on the leached surface of the plagioclase some rosettes of a zeolite-like mineral crystallised. Sporadically fine crystals of analcime appeared. The analcime crystals are poorly shaped. Mostly they display a skeletal morphology. In the range 330–300°C analcime appear more frequently (Table 2). Single crystals as well as aggregates are covering large parts of the surface of the plagioclase. (Text-fig. 1b and 2.4)

Run products at very low temperature (e.g. run 30) showed skeletal or poor shaped analcime on the leached plagioclase surface together with calcite. The frequency of analcime nucleation is lower than those observed within the temperature range 330–300°C. The growth rate is rel-

atively constant comparing with those observed for higher and lower temperature reaction products in the third series. In contrast the leaching process of the plagioclase is more advanced.

CONCLUDING REMARKS

Wairakite produced in the reaction plagioclase + quartz (the first and the third run series) appears mostly outside its stability field (Text-fig. 3a, b), indicating that equilibrium was not established. The reaction was controlled rather by kinetics than by thermodynamic equilibrium. It is also possible, that due to the use of quartz (instead of amorphous silica) the stability field of wairakite was shifted towards lower temperature (COOMBS & *al.* 1959). The plagioclase used in the present study contained both sodium and calcium; the presence of sodium does not impede wairakite formation, in the first run series in this mixed sodium-calcium system wairakite did nucleate. The crystals, however, appeared within the stability field of laumontite. Lower silica activities in the solution did not change the point of wairakite nucleation. The concentration of silica in the solution in the 1st run series approached the value of about 0.8 $\mu\text{g/ml}$. In the 3rd run series it was reduced to 0.22 $\mu\text{g/ml}$. In the wairakite stability field incidentally analcime-wairakite_{ss} crystal appears as a metastable phase.

Higher sodium activity in the system (the second and the fourth series) changes the reaction products. The reaction in the second run series does not seem to have approached equilibrium. It is very likely that the reaction is controlled by kinetics. Perhaps the fourth run series proceeded more closely to equilibrium. Sodium clearly hinders the decay of the albite particle. Although the decay of the anorthite particle is hence preferable, calcium-bearing wairakite did not nucleate in any of the two run series. Sodium bicarbonate added to the system induces crystallisation of cancrinite-like phase within the temperature range appropriate to the wairakite-analcime stability field (Text-fig. 3c, d). Analcime crystallises below its stability range. The lowering of the analcime nucleation temperature should be attributable to the form of silica present in the system. Although COOMBS & *al.* (1959) pointed to such possibility, the fourth run series brings some doubts about that conclusion. The runs performed under lower silica activity display analcime as a reaction product within its own stability field.

The formation of either analcime or wairakite, depends strictly on the composition and the structure of the starting material. All crystals of the initial plagioclase were carefully selected, grain after grain, and they did not display any visible defects. In spite of that fact the dissolu-

tion process of the plagioclase went differently. Under the same conditions not all grains were dissolved. Some energetically favourable places triggering the dissolution must have existed on the grains corners, edges or surfaces. Because the dissolution is better developed on the cleavage plane it is very probable that the valleys on the surface are formed due to dissolution starting from microcracks or structural defects. Lack of defects may be the reason that some of the plagioclase grains did not show any signs of alteration at all. The observation is consistent with the data given by TAYLOR & *al.* (2000). They suggest that the dissolution process of Ca-rich plagioclase under conditions far from equilibrium starts with etched pit formation at defect sites. Close to equilibrium the dissolution is more uniform across the crystal surface.

The nucleation process is closely associated to the alteration places of plagioclase. There was a variety of nucleation densities observed for different plagioclase crystals and the data presented in Table 2 refer to the crystals with the most numerous occurrences of analcimes/wairakites found. There were also samples of plagioclase crystals with no visible occurrences of analcimes/wairakites. Therefore it would be impractical to calculate the average nucleation rate as a parameter describing the process discussed in the present study. Nevertheless even the plagioclases with no nucleation contribute to the growth mechanism - liberating the material crystallizing afterwards as analcime or wairakite crystals.

An influence of the sodium concentration on the nucleation rate is not clearly visible, though sodium plays an important role in the aluminium transport in the solution (ANDERSON & BURNHAM 1983; DAVIS & LOBO 1992; DIAKONOV & *al.* 1994). On the contrary, the activity of silica in the system influences markedly the observed nucleation rate. The nucleation does not depend in a very clear way on the anion in the solution, though presence of carbonate accelerates the dissolution process, especially the release of Al from Ca-rich plagioclase structure, in neutral to near basic pH region (BERG & BANWART 2000).

Similarly to observations of JOVE and HACKER (1997) and WILKIN and BARNES (2000), the nucleation process started early in our experiments. In contrary to their conclusion, the nucleation in the higher temperature runs proceeded probably continuously during the experiment, producing usually a more seriate pattern of crystals. The mechanism of wairakite - analcime growth seems to obey the route of both the processes described by JOVE and HACKER (1997). The crystals are attached to the plagioclase surface and grow partly into the plagioclase. Though wairakite - analcime formation occur only on some plagioclase crystals, all the dissolved plagioclase contributes to the growth. The mechanism of growth embraces both replacement of the plagioclase by newly formed crystal

and dissolution, transport within the fluid and precipitation on the wairakite nuclei affixed on the feldspar surface. Plagioclase dissolution seems to be the reaction rate limiting process.

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