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Hydrothermal synthesis of albite: the effect of NaOH on obliquity

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SUMMARY. A series of albites was synthesized in the presence of aqueous NaOH fluids (concentration 0 to 4N NaOH, $P_{\text{fluid}} = 15\,000$ lb/in²) over the temperature range 300 to 500 °C. At fixed temperature–pressure conditions increasing NaOH concentration of the initial fluid can be correlated with decreasing obliquity of the albites.

EXPERIMENTAL studies of the alkali-feldspar system have outlined the effects of some physical and chemical parameters on the ordering of the alkali feldspars. MacKenzie (1957) synthesized albites in an intermediate structural state in the presence of excess water, Parsons (1968) studied the effects of potassium on the kinetics of the ordering process, and Martin (1969) outlined the effects of excess soda, alumina, and silica on the degree of ordering achieved in a fixed time. Martin noted that the degree of ordering achieved was probably some function of the $a\ \mathrm{Na}^+/a\ \mathrm{H}^+$ ratio. The degree of ordering achieved seemed to be a function of the alkalinity. In the present study a series of albites was synthesized in the presence of a range of NaOH concentrations in an attempt to delineate the relationship between the ordering mechanism and the pH of the environment.

Experimental method. The starting material was a dehydrated co-precipitated gel of $NaAlSi_3O_8$ composition made available by Dr. Ian Parsons. After drying at 110 °C about 20 mg. of gel together with a weighed amount of de-ionized water or sodium hydroxide solution (prepared by diluting British Drug House 4N NaOH solution with de-ionized water) was sealed in a $\frac{3}{4}$ in $\times \frac{3}{32}$ in external diameter gold capsule. The capsules were placed in contact with an Inconel-sheathed chromel–alumel thermocouple in a cold-seal pressure vessel. The internal thermocouple was calibrated against the boiling point of water, the melting point of zinc (419 °C), and the melting point of sodium chloride (801 °C). Temperatures were continuously recorded and maintained within ±5 °C of the desired value. Pressures were measured with a Budenburg gauge with periodic checks to ensure that the pressure was maintained within about 500 lb/in² of 15 000 lb/in².

Runs were brought to the desired conditions as quickly as possible and care was taken to prevent overshooting either temperature or pressure in the initial heating period. At the end of each run the pressure vessels were quenched with compressed air.

TABLE I. *Values of* $2\theta_{131}-2\theta_{1\bar{3}1}$ (Cu-$K\alpha$ *radiation) for an albite gel crystallizing in sealed gold capsules containing pure water or aqueous solutions of* NaOH. *All runs were at* P_{fluid} = 15 000 lb/in^2. Ab = albite, Anl = analcime, Q = quartz

Run no.	T	Duration in hours	Run products	$2\theta_{131}-2\theta_{1\bar{3}1}$	Initial fluid
534–1	500 °C	168	Ab+Anl	1·800	H_2O
489–5	500	333	Ab+Anl	1·694	H_2O
533–4	400	168	Ab+Anl tr.?	1·895	H_2O
521–3	400	772	Ab+Anl	1·690	H_2O
535–4	375	360	Ab+Anl	1·903	H_2O
524–1	375	772	Ab+Anl tr.	1·730	H_2O
495–1	350	191	Ab+Anl	1·882	H_2O
489–2	500	333	Ab+Anl	1·695	N/7 NaOH
476–1	400	140	Ab+Anl	1·748	N/7 NaOH
476–3	400	140	Ab+Anl	1·788	N/7 NaOH
477–4	400	166	Ab+Anl	1·740	N/7 NaOH
477–5	400	166	Ab+Anl	1·799	N/7 NaOH
534–4	500	168	Ab+Anl	1·684	N/2 NaOH
533–5	400	168	Ab+Anl	1·582	N/2 NaOH
535–3	375	360	Ab+Anl	1·453	N/2 NaOH
539–4	350	168	Ab+Anl	1·684	N/2 NaOH
536–3	325	360	Ab+Anl	1·788	N/2 NaOH
542–1	325	773	Ab+Anl tr.?	1·603	N/2 NaOH
534–2	500	168	Ab+Anl	1·707	1N NaOH
541–3	500	773	Ab+Anl	1·553	1N NaOH
518–2	400	144	Ab+Anl	1·379	1N NaOH
530–4	400	169	Ab	1·392	1N NaOH
526–4	375	334	Ab+Anl	1·337	1N NaOH
535–2	375	360	Ab+Anl	1·370	1N NaOH
523–1	375	771	Ab+Anl	1·325	1N NaOH
524–2	375	772	Ab+Anl	1·290	1N NaOH
527–4	350	334	Ab+Anl	1·409	1N NaOH
543–2	350	793	Ab+Anl	1·421	1N NaOH
536–1	325	360	Ab+Anl	1·569	1N NaOH
542–4	325	773	Ab+Anl	1·418	1N NaOH
513–3	425	332	Ab+Anl	1·359	4N NaOH
487–2	400	137	Ab+Anl	1·437	4N NaOH
487–4	400	137	Ab+Anl	1·469	4N NaOH
511–4*	400	331	Ab+Anl	1·382	4N NaOH
521–2	400	772	Ab+Anl	1·299	4N NaOH
523–2	375	771	Ab+Anl	1·306	4N NaOH
509–2	350	171	Ab+Anl	1·471	4N NaOH
495–3	350	191	Ab+Anl	1·419	4N NaOH
495–4	350	191	Ab+Anl	1·388	4N NaOH
527–2	350	334	Ab+Anl	1·284	4N NaOH
510–1	325	170	Ab+Anl	1·528	4N NaOH
510–2	325	170	Ab+Anl	1·538	4N NaOH
537–1	400	168	Ab+Anl	1·425	1N KOH
507–3	300	169	Anl+Ab	—	4N NaOH
483–3	400	331	Ab+Anl	1·37	4N NaOH

* Heated to 700° for 48 hrs and reduced to 400° for 331 hrs.

Smear mounts were prepared and the diffraction pattern scanned from 20°–45° 2θ (Ni filtered Cu-$K\alpha$ radiation). Six scans of the $2\theta_{131-1\bar{3}1}$ separation were made and the average separation determined at $\frac{2}{3}$ peak height. Instrumental conditions on the Philips diffractometer were scanning speed $\frac{1}{4}$°/minute, divergence slit 1°, receiving slit 0·1 mm, scatter slit 1°, chart speed 20 mm/min, and time constant 4 seconds. Duplicate smears agreed within ±0·005° 2θ.

Results. Table I includes data on runs that initially contained a gel of albite composition plus excess water or excess NaOH aqueous solution. The assemblage albite+analcime was observed in the temperature range 325–500 °C. Table II lists the data for runs containing SiO_2 in excess of the stoichiometric albite composition crystallizing in the presence of water or aqueous NaOH solutions. Only α-quartz and albite were observed. The presence of analcime or α-quartz was established by observations of at least the two strongest X-ray diffraction maxima.

TABLE II. *Values of* $2\theta_{131}-2\theta_{1\bar{3}1}$ (Cu-$K\alpha$ *radiation) for* $Ab_{90}Q_{10}$ (wt. %) *crystallizing in sealed gold capsules containing pure water or aqueous solutions of* NaOH. *All runs were at* $P_{\text{fluid}} = 15\,000$ lb/in²

Run no.	T	Duration in hours	Run products	$2\theta_{131}-2\theta_{1\bar{3}1}$	Initial fluid
533–2	400 °C	168	Ab+Q	1·873	H_2O
535–1	375	360	Ab+Q	1·863	H_2O
534–3	500	168	Ab+Q	1·631	N/2 NaOH
541–1	500	773	Ab+Q	1·433	N/2 NaOH
533–3	400	168	Ab+Q	1·545	N/2 NaOH
542–2	325	773	Ab+Q	1·401	N/2 NaOH
541–2	500	773	Ab+Q	1·490	1N NaOH
533–1	400	168	Ab+Q	1·351	1N NaOH
543–3	350	793	Ab+Q tr.	1·220	1N NaOH
536–4	325	360	Ab+Q	1·359	1N NaOH
542–3	325	773	Ab+Q	1·264	1N NaOH
518–3	400	144	Ab	1·341	4N NaOH
517–4	400	242	Ab+Q tr.	1·328	4N NaOH
522–1	400	772	Ab+Q	1·256	4N NaOH
519–2	375°	144	Ab	1·341	4N NaOH
520–1	350	144	Ab+Q tr.	1·311	4N NaOH

In general terms the obliquities (measurement of $2\theta_{131}-2\theta_{1\bar{3}1}$, for Cu-$K\alpha$ radiation, values of which are assumed to be a measure of the aluminum–silicon order–disorder) appear to decrease with time as observed for end-member albite by MacKenzie (1957) and potassium-bearing compositions by Parsons (1968). The addition of NaOH to both stoichiometric albite gels and albite+silica results in large decreases in obliquity values for runs of less than one week duration. There are systematic and measurable decreases in obliquities for runs up to 772 hours duration. The lowest obliquity values obtained are similar to those observed for runs on the $NaAlSi_3O_8$–$Na_2Si_2O_5$ join by Martin (1969).

Effect of NaOH *concentration.* It is helpful to separate the effect of concentration of components, temperature, and time when describing the effect of fluid composition on obliquity. From fig. 1 it is apparent that an increase in NaOH concentration correlates with a decrease in obliquity for runs of the same duration at a given temperature and pressure. It would appear that the higher concentrations of NaOH either accelerate the ordering process or result in a lower 'equilibrium' obliquity value. It is likely that the optimum initial concentration of NaOH for this temperature and pressure is probably about 1N NaOH. It should be noted that no attempt was made to determine the fluid composition after the runs were completed—all compositions refer to starting conditions.

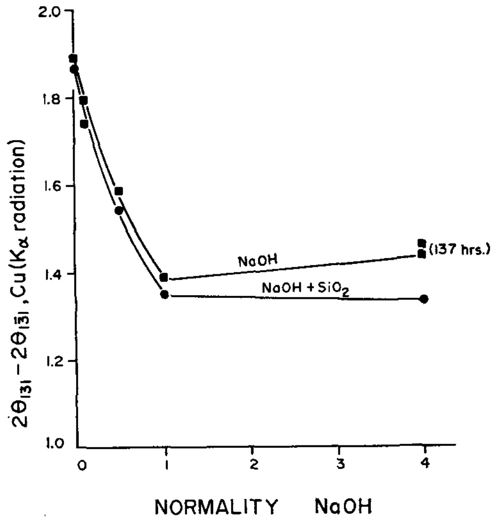
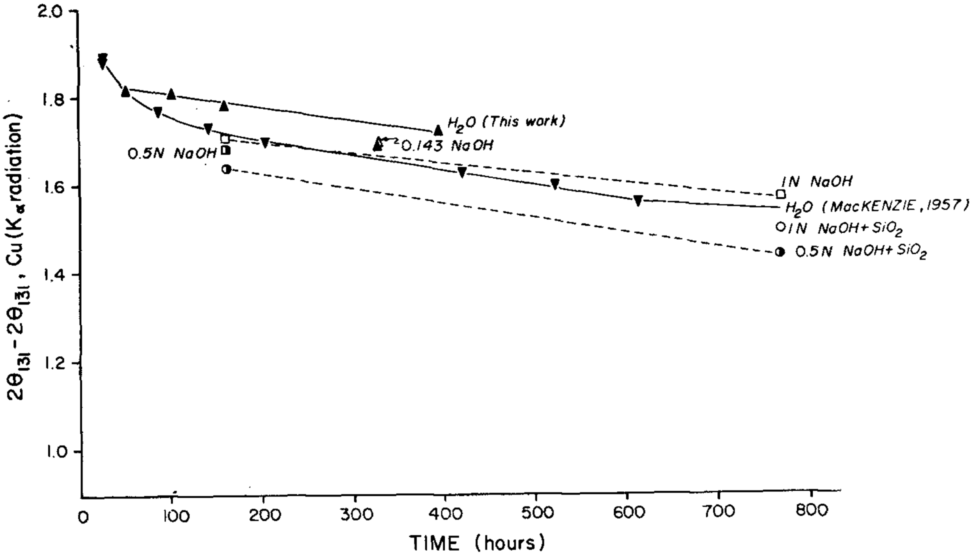
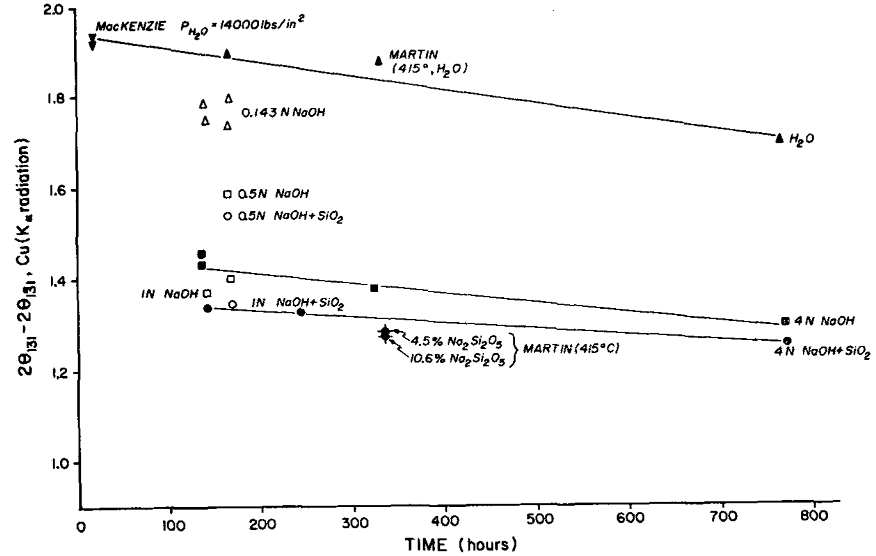


FIG. 1. Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ of albite with NaOH concentration. Duration of runs approximately 168 hrs. at 400 °C, $P_{\text{fluid}} = 15\,000$ lb/in², presence or absence of excess SiO_2 in starting composition is indicated on the curve.

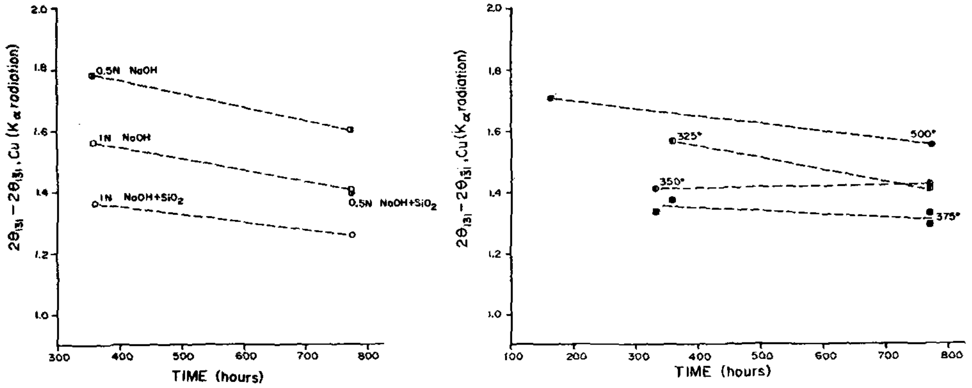
It has been previously determined that the duration of a run is an important factor in experiments describing the obliquity of stoichiometric compositions (MacKenzie, 1957; Parsons, 1968). Duration of the runs was found to be an important consideration in runs involving NaOH. Figs. 2, 3, 4 illustrate the interrelation of NaOH concentration, presence or absence of excess SiO_2, and run duration for three temperatures. At 500 °C the obliquity–time curve for 1N NaOH solutions is approximately 0·1° 2θ lower than the curve for water alone, and the curve for 0·5N NaOH+ excess SiO_2 is in turn about 0·1° 2θ lower. Within experimental error these curves all have the same slope. The curve determined by MacKenzie (1957) is included for comparison and again has the same slope although his starting material was a glass of albite composition. It should be noted that at 500 °C both 0·5N and 1N NaOH solutions have the same effect on obliquity indicating that the optimum NaOH concentration is less than 0·5N. At 500 °C a decrease in obliquity is promoted by increased NaOH concentration and the presence of excess SiO_2.





FIGS. 2 and 3: FIG. 2 (top). Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with duration of crystallization 500 °C, P_{fluid} = 15 000 lb/in^2. The curve from MacKenzie (1957) is included for comparison. The author is indebted to Dr. Ian Parsons for the three points on the Ab_{H_2O} curve at 48, 108, and 402 hours. FIG. 3 (bottom). Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with duration of crystallization 400 °C, P_{fluid} = 15 000 lb/in^2. Points for excess H_2O, MacKenzie (1957), and for excess sodium disilicate, Martin (1969), are included for comparison.

At 400 °C (fig. 3) the same general pattern prevails except that the magnitude of the obliquity decrease is much greater. The addition of the 0·5N NaOH solution has resulted in a decrease of obliquity of 0·3° 2θ for runs of equal duration. At 400 °C the 1N and 4N NaOH solutions have the same effect on obliquity indicating that the optimum NaOH concentration is within that range. At this temperature the addition of NaOH promotes an obliquity change and the addition of excess SiO_2 has about the same effect as at 500 °C.



FIGS. 4 and 5: FIG. 4 (left). Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with duration of crystallization 325 °C, P_{fluid} = 15 000 lb/in². FIG. 5 (right). Change in $2\theta_{131}-2\theta_{1\bar{3}1}$ with duration of crystallization $P_{(\text{fluid} = 1\text{N NaOH})}$ = 15 000 lb/in², temperatures as marked on curves.

At 325 °C (fig. 4) the same general pattern is apparent except that the addition of excess SiO_2 results in a reduction of the obliquity by more than 0·2° 2θ. It is likely that the obliquity is still decreasing at a significant rate even after 772 hours and that an 'equilibrium' value has not been reached.

In an attempt to see if an 'equilibrium' value is reached, a series of runs were made with 1N NaOH concentration and a range of temperature (fig. 5). To a first approximation the curves for 500° and 325° appear to have a steeper slope (further from an 'equilibrium' value) than do the intermediate temperatures 350° and 375°. It seems that a longer time is required to reach an equilibrium obliquity at either high or low temperatures. It appears that there may be a relatively broad temperature interval that results in the same obliquity. This is a reflection of the 'trough' observed parallel to the pressure axis of pressure–temperature plots (Martin, 1969). The minimum for the obliquity is at a considerably lower temperature than for the albite–H_2O system (MacKenzie, 1957). The minimum obliquity 'trough' is approximately at 350 °C, similar to the observations of Martin for the $NaAlSi_3O_8$–$Na_2Si_2O_5$ join.

Discussion. MacKenzie's (1957) experiments in the $NaAlSi_3O_8$–H_2O system established the importance of time considerations in studying obliquity changes in albites. McConnell's and McKie's (1960) subsequent analysis of MacKenzie's data further evaluated the importance of rate considerations and recognized the existence of a smeared transformation in the albites. Although time limitations did not allow for a complete determination of the obliquity–time curves, it is desirable to conduct experiments of different time durations and to keep the time factor in mind for subsequent interpretation.

Aqueous solutions resulting from the dissolution of a natural ordered albite under supercritical conditions are non-stoichiometric and are moderately to strongly alkaline after quenching (Currie, 1968). Currie's experiments approximate a 'steady state' condition, and he states that after the first hour of the solution run the pH rarely changed more than 0·05 pH units. Under 'equilibrium' conditions it is likely that somewhat more alkaline conditions prevail. Between 400° and 600 °C at $P_{\text{fluid}} = 750$ to 3500 bars, the quench pH of all of Currie's runs on Amelia albite falls within the limits of 9·0 and 11·0 (fig. 6). For the temperature range 400° to 600 °C at $P_{\text{fluid}} = 1$ Kb the observed pH range was 9·5–9·85. Initial NaOH concentrations in the present study are considerably more alkaline than the solution experiments and indicate that strongly alkaline solutions promote a reduction in obliquity. Furthermore the reduction in obliquity can be correlated with an increase in initial NaOH concentration up to a limiting concentration, which may be different for each temperature–pressure condition (fig. 1). This correlation would be consistent with the reduction in obliquity being a rate process dependent on the availability of some ion or complex stabilized by the addition of NaOH to the system. The most likely species would be Na^+, OH^-, or a complex involving aluminum or silicon. If the ion or complex involved is one actually incorporated in the feldspar structure, a particular amount (as distinct from concentration of aqueous solution) would be necessary to produce the change in obliquity, i.e. if an aluminium deficiency or sodium excess is needed to produce a low obliquity, a fixed amount of the element would be needed to produce a particular obliquity. Duplicate runs involving different proportions of fluid resulted in nearly identical obliquities (Table III). Martin's experiments on the $NaAlSi_3O_8$–$Na_2Si_2O_5$ join also indicated that a wide compositional range results in the same obliquity.

TABLE III. *Value of* $2\theta_{131}-2\theta_{1\bar{3}1}$ Cu-*K*α *radiation for albite gels crystallizing in sealed gold capsules containing different wt. % of aqueous solutions of* 4N NaOH. *All runs were at* $P_{\text{fluid}} = 15\,000$ lb/in²

Run no.	T	Duration in hours	Run products	$2\theta_{131}-2\theta_{1\bar{3}1}$	Wt. % initial fluid
510–1	325 °C	170	Ab+Anl	1·528	7·4
510–2	325	170	Ab+Anl	1·538	17·0
495–3	350	191	Ab+Anl	1·419	10·9
495–4	350	191	Ab+Anl	1·388	18·4
487–2	400	137	Ab+Anl	1·437	22·0
487–4	400	137	Ab+Anl	1·469	10·9

As the NaOH concentration of the initial fluid is increased, lower obliquities are reached in experiments of the same duration, but it does not necessarily follow that lower 'equilibrium' obliquities are reached. If the addition of NaOH affects only the *rate*, it would be expected that the same degree of ordering will be reached over a wide range of NaOH concentrations with longer times required for dilute solutions.

A basic problem in proposing a mechanism for a crystallization or ordering process is the paucity of information on the predominant chemical species present at elevated temperature–pressure conditions, and so one falls back on extrapolation from very different conditions. When NaOH is added to the albite system, which species are involved in the reactions resulting in a decreased obliquity? Martin (1969) concluded that the obliquity could be correlated with the relative degree of dissociation of various sodium salts with the strongest electrolyte, NaCl, having no effect and the weakest, $Na_2Si_2O_5$, having the greatest effect. If the reduction in obliquity were simply a function of sodium concentration, then the obliquities should have been the same for all the sodium salts. This indicates that the anion and not the sodium is involved in the lowering of the obliquity.

In the present study runs on charges of composition $Ab_{90}(SiO_2)_{10}+H_2O$ did not result in lower obliquities than $Ab_{100}+H_2O$ indicating that excess SiO_2 alone is not sufficient. At temperatures below 400° ($P_{H_2O} = 15\,000$ lb/in^2), the addition of both sodium hydroxide and excess SiO_2 resulted in lower obliquities than NaOH alone. This may simply mean that at lower temperatures both sodium hydroxide and silica are involved in complex formation.

In Table I it was noted that the obliquity resulting from Run 537–1, 400 °C, 15 000 lb/in^2, 1N KOH was 1·425° 2θ as compared to Run 530–4 using 1N NaOH, which was 1·392° 2θ. The feldspar crystallizing in the run with 1N KOH was very nearly pure albite. According to Parsons (1968) the addition of potassium to the feldspar phase decreases the obliquity. The similarity of the two obliquities indicates that the hydroxyl ion and not the cation is the effective agent in lowering the obliquity and that the obliquity may be simply related to the pH of the environment. Additional runs for composition $Ab_{80}Or_{20}+1N$ KOH also resulted in a sodium feldspar with an intermediate obliquity.

If it is assumed that OH^- is involved in the reactions resulting in obliquity changes, then it may be helpful to develop a mechanism or model describing the role of OH^-. A number of studies have shown that the solubilities of many silicates are increased under alkaline conditions. For a summary of the quartz and corundum solubilities see Anderson and Burnham (1967). It may be that the changes in rates of reaction are simply due to increased solubility or it could be that OH^- stabilizes certain complexes. According to Hem (1970), $Al(H_2O)_6^{3+}$ is the predominant species in acidic solutions at 25 °C, while above neutral pH the predominant dissolved form of aluminium is the anion $[Al(OH)_4]^-$. Structurally these complexes are thought to represent octahedral and tetrahedral coordinations respectively. If we ignore the interference of such things as silica and soda, there is at least a possibility that a similar relationship will hold under supercritical conditions, i.e. tetrahedrally coordinated aluminum will be stabilized at higher pH values.

In Currie's (1968) 'steady state' experiments increased pressure resulted in more alkaline fluids with the most pronounced increase in alkalinity at higher temperatures. Increased pressure results in more alkaline quenched solutions and probably a more alkaline environment. If an alkaline environment promotes lower obliquity values, then we should expect a decreased obliquity with higher pressure and this is what was found by Martin (1969).

According to Barnes and Ernst (1963), there is a large decrease in the ionization of NaOH between 25 °C and supercritical conditions. Qualitatively we should expect the concentration of OH^- to be low at higher temperatures and, if obliquity is a function of OH^- concentration, we should expect obliquity to decrease with lower temperatures. For given temperature–pressure conditions we should also expect to find a limiting NaOH concentration that would be effective in reducing obliquity.

If platinum capsules are used, hydrogen formed by dissociation of water will diffuse through the walls of the capsule, fixing P_{O_2} at the H_2O buffer of the pressure container, Eugster (1957). With gold capsules, diffusion may be an important factor in long duration experiments and may result in time-dependent changes in obliquity. Commonly, observed differences in determined curves such as MacKenzie's (1957) curve and the curves determined in this study (fig. 2) are attributed to starting materials, porosity, etc., but these could well be due to changes in the composition of the bulk charges brought about by diffusion of hydrogen.

It is unlikely that the effect of hydroxyl on the crystallization and ordering of albite can be isolated or ascribed to a single mechanism. Probably it performs several interrelated functions. For example, if tetrahedrally coordinated aluminium complexes are stabilized at high pH values, then reaction rates at lower temperatures may be increased as a result of increased concentrations of aluminium (and silicon) in the fluid phase. This could result in the formation of the more highly-ordered forms of albite over a range of temperature.

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