"SOLUBILITY" OF ALBITE IN HYDROTHERMAL SOLUTIONS*

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Abstract

The apparent solubility of albite in pure water is determined over a limited range of temperatures at a pressure of 300 bars and compared with that of quartz. The solubilities are of the same order of magnitude suggesting that they both disintegrate or decompose according to the same mechanism. The greater "solubility" of quartz accounts for its first appearance and great persistence in natural hydrothermal solutions.

Both ions and silicate fragments result when albite is attacked under the experimental conditions used. The possibility that actual particles of silicate structures, ranging up to 1000 unit cells in size, might be transported through rocks is suggested.

An origin of certain clay minerals and the alumino-silicate fragments in shales is discussed.

Introduction

Geologists have been speculating since the earliest time concerning the manner in which materials are transported in or through rocks. The intriguing problems of the mechanism of metasomatism, granitization, vein-formation, and many others of this kind, challenge our imagination. In order to obtain a better insight into the mechanism of any of these processes, we need to formulate better or clearer ideas on

1. The solubility of silicates and other rock-forming material in hydrothermal solutions, and
2. The physical state in which material of this kind exists in these solutions.

Water is one of the most important components in most rock systems. We believe that the hydrogen ions of water are by far the most important of all elements in the earth's crust that affect geological processes. The purpose of this paper is to describe the behavior of albite in hydrothermal solutions—pure water heated to various temperatures under a pressure of 300 bars—and to speculate on the role played by hydrogen ions in this system.

Procedure

An albite crystal was suspended in a bomb filled with enough distilled water to give a pressure of 300 bars when heated to the desired temperature. The system was held at the desired temperature for approximately 100 hours. Samples of the fluid in the bomb were then isolated by a series of valves and tubes using a technique described by Frederickson and Cox (1953).

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To test the homogeneity of the fluid, one sequence of samples was siphoned from the bottom of the bomb and another from near the top of the solution chamber. The apparent solubilities of albite, under these conditions, is summarized by the curves in Fig. 1.

Samples of the fluids were evaporated on collodion supports and the products examined under an electron microscope (Fig. 2).

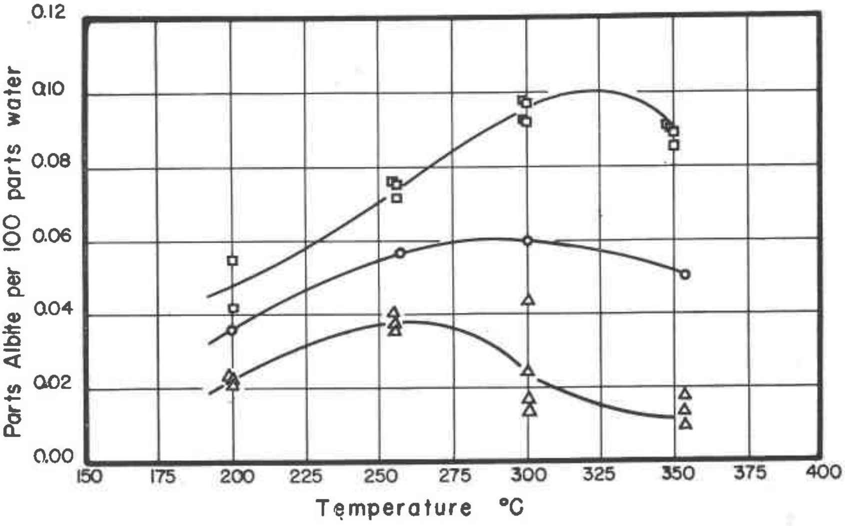

FIG. 1. Apparent solubility of albite in distilled water (pressure: 300 bars).
☐ Values for bottom of bomb
△ Values for top of bomb
○ Averages of above values

The solution was electrodialyzed. The apparatus consisted of two fritted glass, Gooch-type filtering crucibles immersed in a deep Petrie dish. Graphite electrodes were operated at a potential difference of approximately 40 volts. The amount of current passing through the system was measured by use of two copper strips connected in series and immersed in a 25 ml. beaker containing $CuSO_4$. The milliequivalents of copper transferred from one electrode to the other was taken as a measure of the current. The solution accumulated in the cathode chamber was periodically removed and analyzed with a flame photometer. The electrodialysis curve for the "albite" solution is shown in Fig. 4.

DISCUSSION

"Solubility" of Albite

The fluid in the bomb (see Fig. 1) is not homogeneous. The concentration of solids in the fluid is greater at the bottom of the bomb than at the

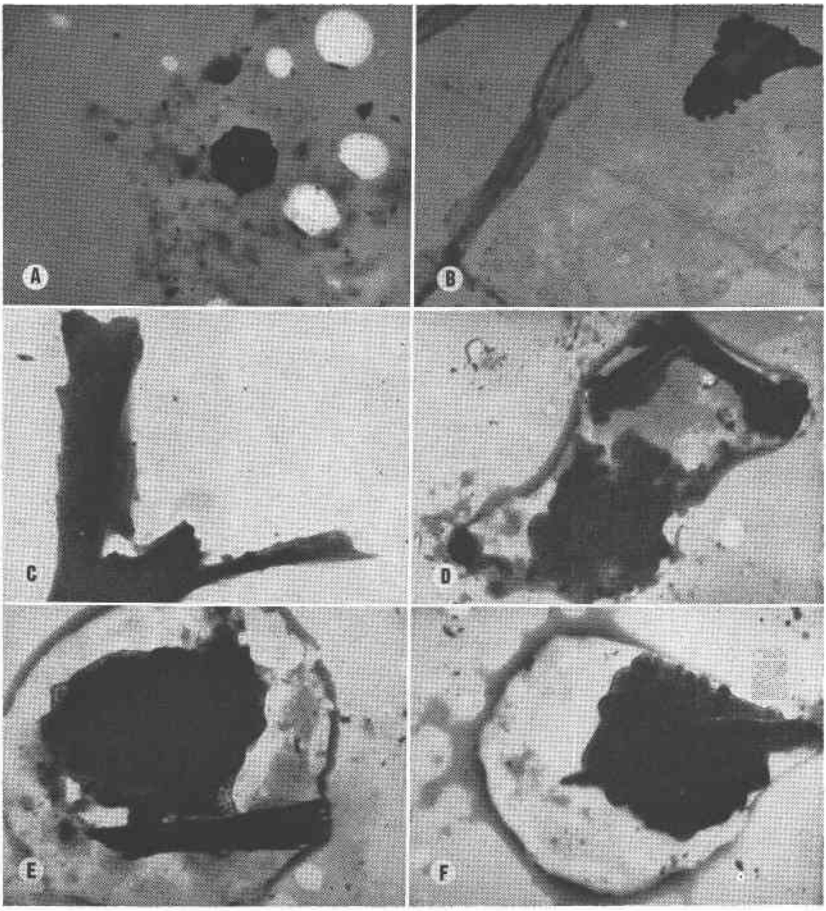

FIG. 2. Electron micrographs of "solutions" siphoned from the bottom of the bomb.

A. The comparatively large crystal with well-developed outlines is either an individual albite fragment or an aggregate of smaller albite fragments. Irregularities on the faces suggest a mosaic make-up. Smaller irregular albite granules can be seen scattered over the field. The small rod-like crystals are believed to be the zeolite detected by *x*-ray diffraction photographs.

B. Here the film of silica-alumina gel shows up clearly. It covers most of the field, and where broken, has curled and rolled back. The denser mass is composed of albite chunks and zeolite granules.

C. The alumina-silica gel has curled up into a series of rolls. These bear a striking resemblance to halloysite rolls or tubes. Only small changes in chemical composition and increased order within the film would be necessary to produce some of the clay minerals from this material. Perchance we have here visual evidence of the initial stages of at least one way of making a clay mineral: a sol formed during the decomposition and disintegration of the albite, gel and film formation by cross polymerization and, as seen top. This suggests that albite partially decomposes into fragments which settle toward the bottom of the bomb whereas smaller fragments or sols remain suspended in the fluid.

This conclusion is supported by the electron micrographic evidence (Fig. 2). Three products are seen:

1. Equant fragments,
2. A gel, and
3. Long fibrous and prismatic crystals.

X-ray diffraction work on these products indicates that the large, equant crystals are albite; the long, fibrous crystals are a zeolite of some kind, probably analcite.

The manner in which albite is thought to decompose is summarized in Fig. 3.

The large parent crystal contains many lineages, cracks and other crystal defects as well as a mosaic structure. After the crystal has been subjected to water at elevated temperatures and pressures, large fragments (0.1–5.0 microns) break away from the parent crystal to form the equant crystals seen in the electron micrographs (*A* and *B*, Fig. 2).

The increased solubility of the albite in water with an increase in temperature (at constant pressure) must be due to the increased activity of the hydrogen ions. The rapid increase of dissociation of water with increase in temperature results in a great increase in the number of hydrogen ions available to attack the crystals. Consequently, raising the temperature is equivalent to increasing the acidity (lowering the *p*H) of the solution.

Much of the material is reduced to particles having colloidal dimensions. When cooled, this material constitutes the gel which is the dark, mottled, gray, background material seen in most of the micrographs. Under the heat of the electron beam, the alumina-silica gel contracts, cracks, dries, and often rolls up (*B* and *C*, Fig. 2). The gel frequently shrinks into oval masses from which zeolite crystals grow.

The first zeolite to develop has a prismatic habit. If enough nutrient

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here, generation of a tube by shrinkage and rolling of the film.

D, E, and F. Each of these micrographs illustrate the types of residue formed from an evaporated droplet of solution from the bomb. Each contains (1) gelatinous, (2) granular, and (3) fibrous or columnar material, implying that the fluid part of the "solution" when first reduced to room temperature and pressure was still quite homogeneous in composition. The zeolites, as seen with the electron microscope, appear to lie on top of most of the granular masses and films and probably formed last from some of the silica-alumina gel and sodium ions during the evaporation of the droplet. The magnification of the electron photomicrographs is 10,000×.

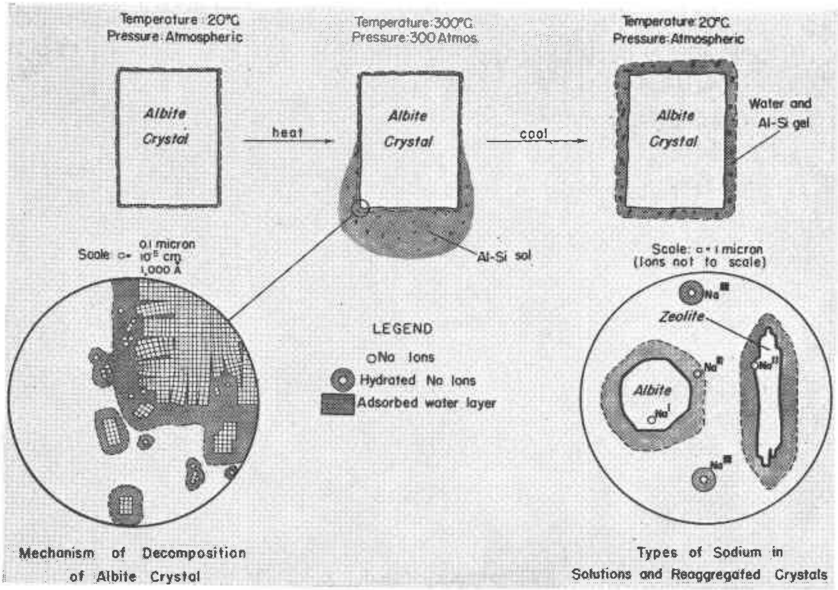

FIG. 3. Process and products of albite decomposition.

material is available, the crystals grow to a comparatively large size. The composition of the nutrient material apparently changes, or different temperature-pressure conditions cause a change in the crystal habit of the last zeolitic material to develop. The early zeolite crystals all have a long prismatic to a fibrous habit (*A*, *D*, *E*, and *F*, Fig. 2). At present, we are inclined to believe that all of the zeolite crystals grow only after the solution has been reduced to room temperature and pressure.

ELECTRODIALYSIS OF THE ALBITE "SOLUTION"

The amount of sodium transferred from the anodic to cathodic chamber is listed in Table 1 and plotted in the form of a curve in Fig. 4.

The electrodialysis experiments on the solutions taken from the bomb indicate that four different "kinds" of sodium exist. The occurrence of the sodium is indicated schematically in Fig. 3.

Large, hydrated sodium ions exist in solution (Type IIII). These are easily removed by dialysis. Extraction of this material produces the first part of the curve in Fig. 4. Increased current through the system now apparently causes a breakdown of some structure which results in a rapid release or a flood or "new" sodium. This sodium (Type III) is thought to occur as adsorbed ions around the albite fragments and on the zeolite

TABLE 1. ELECTRODIALYSIS DATA FOR THE ALBITE "SOLUTION"

Sample No.	Copper wt. change (grams)	Change in meq.	Current in meq. Cu/gm. product	Meq. Na found	Meq. Na/ Meq. Cu	Total current Meq./gm.
1	0.0010	0.0318	0.3225	0.055	1.730	0.3225
2	0.0010	0.0318	0.3225	0.079	2.484	0.6450
3	0.0035	0.1112	1.1278	0.069	0.625	1.7728
4	0.0008	0.0254	0.2576	0.020	0.787	2.0304
5	0.0005	0.0159	0.1613	0.005	0.314	2.1917
6	0.0011	0.0349	0.3540	0.005	0.143	2.5457
7	0.0054	0.1716	1.7404	0.030	0.175	4.2861
8	0.0020	0.0635	0.6440	0.015	0.236	4.9301
9	0.0018	0.0572	0.5801	0.000	0.000	5.5102
10	0.0038	0.1207	1.2241	0.003	0.025	6.7343
11	0.0027	0.0858	0.8702	0.007	0.082	7.6045
12	0.0078	0.2478	2.5132	0.000	0.000	10.1177

Initial volume of fluid: 250 ml.
Total amount of "dissolved" albite: 0.0986 gram.

crystals. The "structure" referred to above is the hydration shell adsorbed onto the albite crystal.

The first layers of this shell contain sodium ions arranged with a considerable degree of regularity and consequently can be considered to be fairly well crystallized. The removal of the sodium ions disrupts the shell which then assumes an ice structure (Frederickson, 1952) that has a lesser degree of crystallinity over a given distance from the crystal surface than did the one containing the sodium ions.

The breakdown of this layer progresses in a gradual manner as is indicated by the gradual change in slope of the dialysis curve.

The next flood of sodium is released rather abruptly and again is interpreted as being due to the breakdown of some structure; the zeolite. The amount of energy, epxressed in amount of current, necessary to break down this structure is, as would be expected, much larger than that required to wreck the less crystalline water hull.

The final, very sharp break in the curve is interpreted to mean that the remaining solid (albite) decomposes to release a small amount of sodium. The amount of sodium contained in the various postulated phases, some of which can be directly seen in the electron micrographs, is summarized in Table 2.

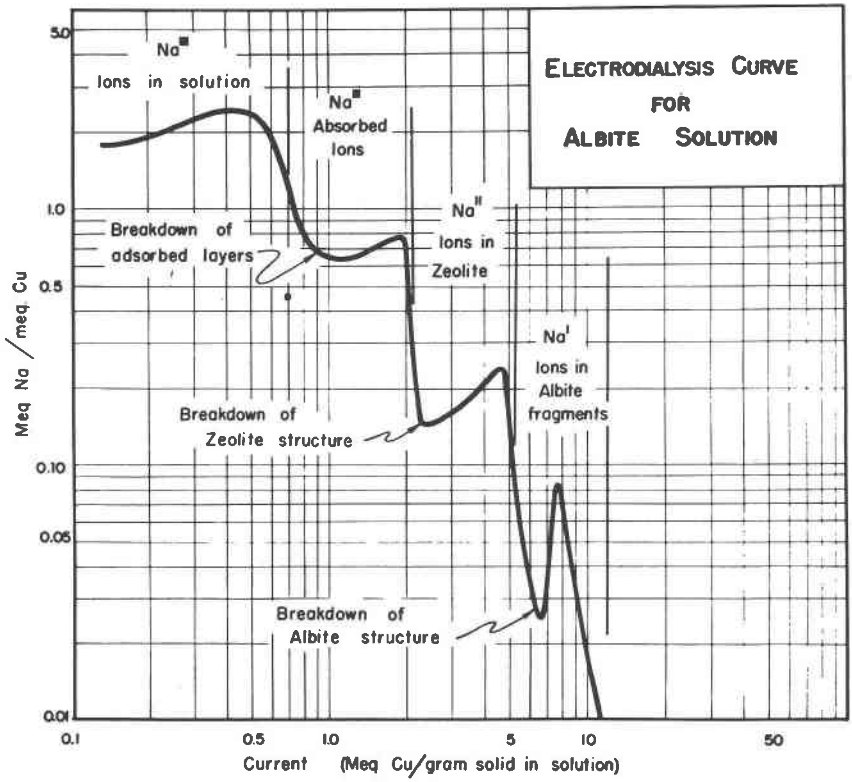

FIG. 4.

TABLE 2. AMOUNT OF SODIUM IN THE DIFFERENT PHASES IN THE ALBITE "SOLUTION"
(Calculated in per cent of the total sodium in the "solution")

Na IIII	Na III	Na II	Na I
Hydrated ions in solution 46 per cent	Ions in the zeolite 33 per cent	Ions in adsorbed water layer 18 per cent	Ions in albite fragments 3 per cent

All the various types of sodium will form a complex equilibrium. The rates at which these various equilibria will be established, however, will be considerably different; the rate at which the ions in true solution will reach an equilibrium with those adsorbed on the surface of the crystals will be very rapid. This will be in sharp contrast to the equilibrium between sodium Types I and II. The mechanism by which this equilibrium is reached was discussed in some detail by Frederickson (1952).

The dialysis procedure used here is relatively rapid; consequently equilibrium is not re-established after the first sodium is removed from the system. The current density, therefore, can be taken as a measure of how strongly the different kinds of sodium are held by the various phases.

SOME GEOLOGICAL IMPLICATIONS

Silicate Paragenesis

The most surprising fact about the behavior of albite in water heated to elevated temperatures under 300 bars pressure is that its apparent solubility is almost the same as that for quartz (Frederickson and Cox, 1953). This is certainly not what one would expect. The apparent solubility curves for albite (Fig. 1) are plotted with the earlier ones obtained in Fig. 5. Although our curves for quartz solubility are not exactly the same as ones previously published by other authors, the average curve representing an arithmetical mean between the curves for solutions siphoned from the bottom and the top of the bomb corresponds almost exactly with Kennedy's (1950) data. We therefore believe that our technique and results are essentially correct or at least of the correct order of magnitude.

The apparent solubility data for quartz and albite indicate that they

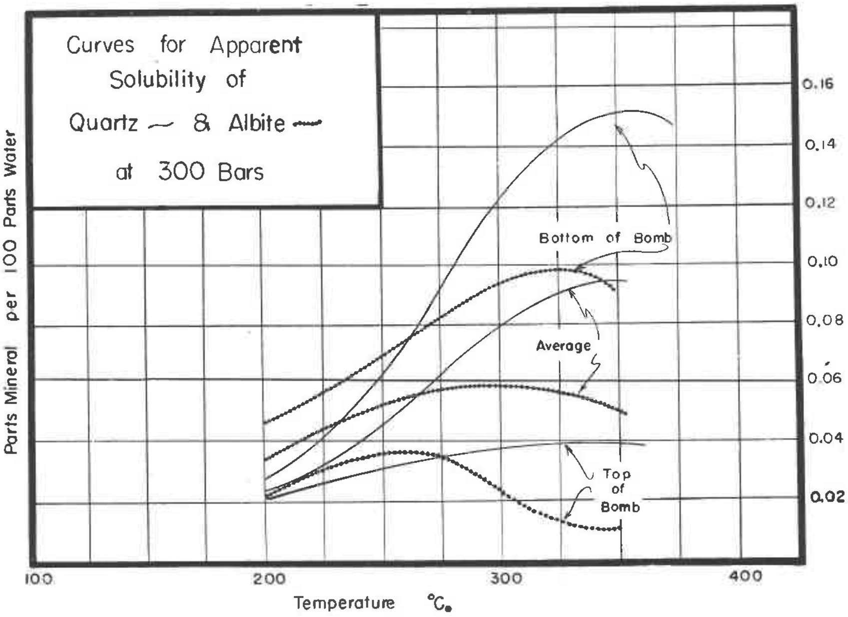

FIG. 5.

both decompose or disintegrate according to the same mechanism. The curves also indicate that quartz is appreciably more "soluble" and therefore should be selectively removed from rocks attacked by solutions of the kind used in these experiments. Not only will the quartz be selectively removed from the attacked rocks, but it will be retained in solution longer and consequently will travel farther than albite in a cooling system. Quartz should appear first in hydrothermal solutions and remain as the last component in such a system. These statements are in harmony with field observations.

The electron micrographs clearly indicate that the albite decomposes to yield both large fragments of albite and a gel material. The size of the albite fragments occurring in the "solution" can be directly measured; the largest so far seen is 5 microns in diameter, but by far the greatest percentage of these particles have a diameter closer to 0.5 micron or smaller. Some of the larger fragments may actually be aggregates of smaller ones.

In addition to these fragments, the gel material can be considered as particles of colloidal size. The large quantity of gel produced during the attack on the albite nutrient material suggests the possibility that matter can be transported in and through rocks as individual particles of considerably greater size than individual ions. Some of these particles may contain as many as 1000 unit cells of a silicate structure. The possibility of moving actual *particles* through rocks may help explain the manner in which certain preferred orientation develops in some tectonites as well as how local banding may develop by segregation (concretion and enrichment-of-the-most-stable-constituent principles of Eskola).

SIZE OF THE COLLOIDAL PARTICLES IN THE GEL

The physical state of the matter making up the gel has not been determined directly. The gel does not give an *x*-ray diffraction pattern that can be interpreted readily. Particles of albite and zeolite can be seen in the gel. These particles are so small that very little physical separation can be made with the means at our disposal; consequently the amount of the diffuse *x*-ray pattern contributed by the gel could not be assessed.*

Some idea concerning a possible size and shape of the colloidal particles can be indirectly deduced from electron micrographs of the surface of the parent albite crystal. Figure 6 is a chromium shadowed collodion replica of the surface of an albite crystal etched with distilled water at a maxi-

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* Standard supercentrifuge bowls require more solution than we obtain from our bombs. These small quantities, however, can be handled in an ultracentrifuge. Small-angle *x*-ray scattering experiments on the gel fraction should give useful information as to the average size of the gel particles and might also yield some information on particle shape.

mum temperature of 300° C and 300 bars pressure. The crystal has been differentially etched. Relatively large pits occur on the surface. The larger pits have rude crystal outlines; the triangular terminations are usually quite regular.

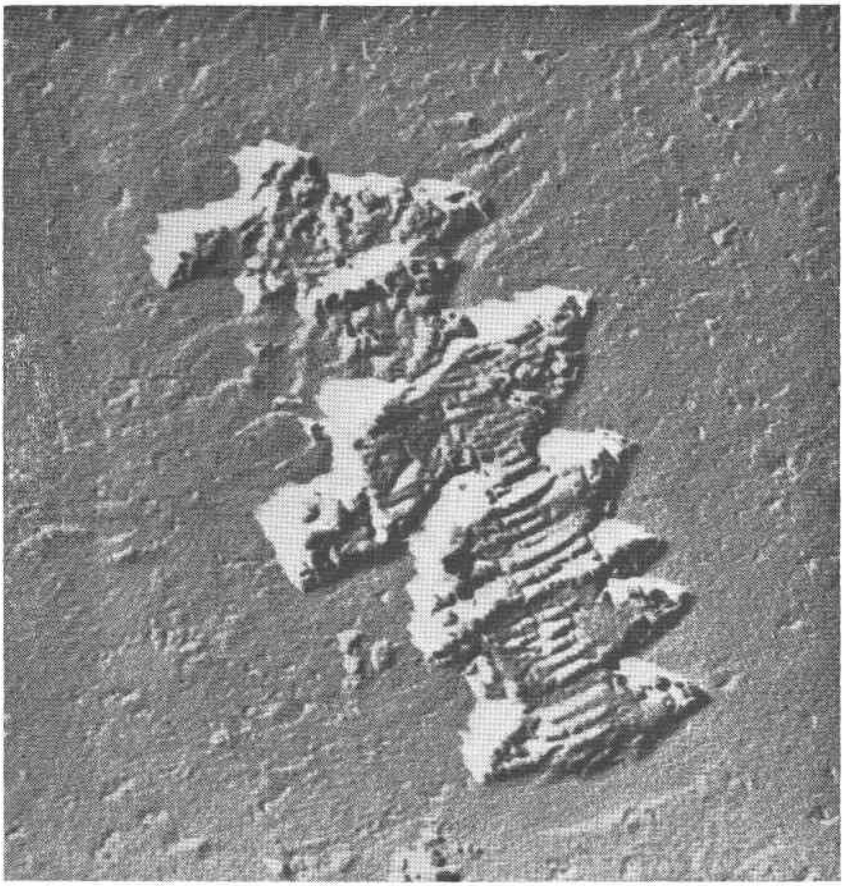

FIG. 6. Electron micrograph of a chromium shadowed collodion peel taken from the surface of an albite crystal etched with distilled water at a maximum temperature of 300° C and a pressure 300 bars. Magnification: 20,000 ×.

The most interesting features shown in Fig. 6 are the depressions within the small pits exhibiting the rude crystal outlines. It appears as if rods had been removed leaving a rod-shaped depression. The width of these rods is quite uniform and measures about 1 micron. The length of the depressions varies, but it appears as if the rods extended the full length of the crystal-shaped depression. These rods bear a striking resemblance to those of quartz (Frederickson 1953). We believe these to be the basic mosaic units contained in albite. Not enough work has been done to outline the role these rods-shaped crystallites play in gel formation. At present we believe that fragments of these rods constitute the albite fragments shown in Fig. 2. These are the mosaic units that spall off the crystal when it is attacked by the hydrothermal solutions. Both large (Fig. 2*A*) and small (Fig. 2*B*) albite fragments exist in the gel. This might be explained by assuming that albite fragments continue to spall off the parent albite crystal throughout the duration of the bomb run and that the first ones decompose almost completely to give rise to the gel. This would mean that the albite fragments shown in Fig. 2 represent mosaic units in various stages of disintegration. An argument of this kind, however, would mean that equilibrium had not been attained in the bomb and that the solubility value obtained should be a function of the duration of the bomb run. This is not the case.

The points in Fig. 1 show that the results can be closely reproduced. We therefore believe that equilibrium has been attained in the bomb. If this is accepted, some of the small crystallites must be stable in this environment.

The *x*-ray diffraction patterns of the albite fragments in the gel are quite diffuse. This can be interpreted to mean that the structure of these crystallites, although essentially the same as albite, has been greatly disturbed. This could easily result from the removal of the sodium ions. Inasmuch as albite can be considered as a coordinated network of SiO_4 and AlO_4 units slumped around the sodium ions which occcupy the interstices within the structure, a further distortion of the lattice would be expected if the sodium was removed. We believe that the lattice would actually expand (Frederickson, 1952) due to mutual repulsion of the negatively charged oxygen ions surrounding the possible sodium lattice sites. With this as a model, we visualize these fragments to be structurally similar to albite, but to also have a much larger unit cell and a different chemical composition. Particles in this condition should readily enter into chemical reactions because of their great specific surface and reactivity due to lattice distortion.

Marshall (1935) described particles found in the Putnam clay that closely resembled albite, but had slightly different indices of refraction indicating compositional changes. Bray (1937) described weathered mica products from which some of the potassium ions had been removed. The very small clay content of most shales (usually less than 5 per cent), indicates that alumino-silicate fragments, along with quartz particles, are the most important constituents of rocks of this kind. Much more work, however, must be done to establish the above presumptions as fact.

APPLICATION OF THESE RESULTS TO THE PROBLEM OF CLAY GENESIS

Experience indicates that clays can be formed in both weathering and diagenetic environments. The clays are frequently stated to be the weathering products of feldspars. Clays are essentially two-dimensional, layer-lattice structures in contrast to the three-dimensional feldspar frameworks. It is not possible to produce the clay-mineral structures from feldspar networks by a translation or displacement operation; one can be only formed from the other by a reconstructive type of transformation. What are the building blocks from which the clay structures are built? This work suggests at least two alternatives:

1. The small crystal fragments could be mortared together by aluminous or siliceous cements to form layer lattice minerals. Reaction of the cements with the fragments would produce a two-dimensional lattice and reaction products such as quartz and gibbsite. The complex layering of many clays and the common occurrence of excess silica some of which is known to exist as microcrystalline quartz, might be explained in this way.
2. The clays could be built up of the very small colloidal micelles of the gel products resulting from the decomposition of the feldspars.

Both of these possibilities are currently being tested.

ACKNOWLEDGMENTS

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