

DIFFERENTIAL SOLUTION OF PLAGIOCLASE IN SUPERCRITICAL WATER

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ABSTRACT

When plagioclase feldspar is held in H₂O at 500°C to 800°C at 2 kbar the albite components are removed in solution whereas the anorthite components remain as a relatively insoluble residue. Solution is so selective that the anorthite residuum typically forms a pseudomorph after the original plagioclase, preserving details of grain outline, cleavage and twinning. The volume deficiency of a pseudomorph is manifested by an intricate network of interconnecting channelways. Although albite is removed without apparent disruption of its parent plagioclase crystal, several lines of evidence indicate that the anorthite component also enters into solution but is immediately reprecipitated.

INTRODUCTION

This paper reports on a study of the mineralogical and compositional changes that occur as a result of differential solution of plagioclase feldspars in water in the range 500°C to 800°C at 2 kbar. The study is an outgrowth of earlier work on the hydrothermal leaching of natural granitic rocks at high temperatures (Adams, 1964) where it was found that dissolution is highly selective. Cores (0.9 cm in diameter) of granitic rock which had been leached of all traces of quartz and K feldspar, revealed that the plagioclase feldspar was attacked in an unexpected way. Crystals of intermediate plagioclase, rather than simply dissolving, retained their shape and changed in composition toward anorthite. A more detailed investigation of the behavior of plagioclase was undertaken, therefore, in order to better understand high-temperature hydrothermal reactions in natural rock systems.

The emphasis in this paper is on the mineralogical changes that occur when plagioclase reacts with water at high temperatures. Particular attention is paid to the significance of anorthite pseudomorphs after plagioclase and the implications regarding the mechanism of plagioclase dissolution. A better understanding of the solution chemistry requires further experimental work.

SOLUBILITY MEASUREMENTS

Few data have been published on the solubilities of the feldspars or other silicates at temperatures above 500°C, although a considerable amount of experimental work has been done on the solubility of quartz in

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TABLE 1. PLAGIOCLASE FELDSPARS USED IN HYDROTHERMAL EXPERIMENTS

Plagioclase	Location	% An	Remarks
Albite	Amelia Co., Va.	0	
Oligoclase	Mitchell Co., N. C.	26	
Andesine	Chelan Co., Wash.	37	Zoned from An ₂₈ to An ₄₂
Labradorite	Nain, Labrador	58	
Bytownite	Crystal Bay, Minn.	75	
Anorthite	Grass Valley, Calif.	96	

H₂O (see Anderson and Burnham, 1965, for a recent review). Morey and Hesselgesser (1951) measured the solubilities of albite and of microcline up to 500°C and 2000 bars. Schloemer (1962) determined the solubility of orthoclase, and orthoclase in the presence of quartz, at temperatures up to 550°C and pressures up to 1600 bars. Smith (1963, p. 241) calculated solubilities for alkali feldspar at higher temperatures and pressures using the data of Morey and Hesselgesser and assuming the applicability of the relation between solubility and temperature that holds for quartz. A recent paper by Currie (1968) on the solubility of albite at high temperatures is especially important and will be discussed in more detail later.

In the present study solubilities were measured by sealing a known amount of feldspar and water inside a gold capsule, placing this inside a 1.2 cm i.d. cold-seal bomb and determining the weight loss of the feldspar, following the general procedures used by Anderson and Burnham (1965). Temperatures were recorded using Pt-Pt (10% Rh) thermocouples which were calibrated to the melting point of NaCl (800.5°C). The monitoring point was a small well in the exterior of the bomb opposite the position of the charge. The thermal gradient along the charge was <1°C cm⁻¹. Heat was supplied by an external resistance furnace governed by a West SCR controller. Temperatures were continuously monitored by strip-chart recorder and are considered accurate to ±5°C. Pressures are considered accurate to ±50 bars.

Charges were prepared from cleavage fragments of natural feldspars (Table 1). The composition of the starting material and of the product was determined by measuring the refractive index of the glass made by fusing a portion of the feldspar, and then reading the percent anorthite from the curve of Schairer, *et al.*, (1956). Each product also was examined optically, and, where enough material was available, X-ray diffraction and electron microprobe analyses were made.

Based on the results of three runs with albite (An₀, Amelia Co., Va.) and three runs with anorthite (An₉₆, Grass Valley, Calif.) the apparent solubility of albite at 700°C and 2 kbar is approximately 3 times that of

the anorthite. Weighted averages for the apparent solubilities (in weight %) are:

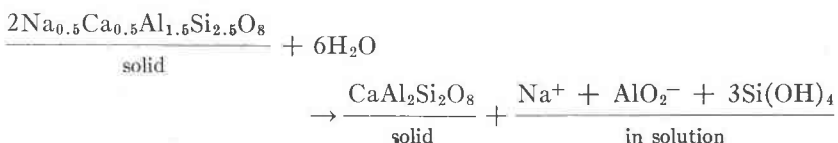
albite	$0.30 \pm 0.03\%$
anorthite	$0.09 \pm 0.03\%$

The runs ranged in duration from 48 to 456 hours without noticeable differential effects on the results. Although the assigned errors are large, these determinations will be useful in the subsequent discussion.

Recovery and analysis of the small amounts of fluids (1 to 2 ml) from a sealed-capsule run proved to be difficult. Inconsistent results from these analyses made it necessary to rely on determinations of the compositions of the solid residuums. Refractive index, X-ray diffraction, and microprobe analyses of the solid products revealed no departures from stoichiometry. However, analysis of the solid phase is relatively insensitive to small departures from stoichiometry since only 0.1 to 0.3 percent is removed in solution.

It is now known from the results of Currie (1968) that albite dissolves incongruently in water. Currie used a dynamic method that allowed him to collect approximately 1 liter of solution that had been brought into contact with albite. The mass of the material dissolved from Amelia albite at 700°C and 2 kb is in agreement with the present study. A study similar in detail to Currie's work on albite has not yet been made on anorthite. Preliminary work (Adams 1965, 1966) on the desilication of albite and anorthite showed that dissolution at 700°C in a dynamic system or under a 2.5°C cm⁻¹ gradient produced the reactions: albite→nepheline+(silica, in solution), and, anorthite→grossularite+(silica and alumina, in solution). Currie reported nepheline in runs with partial valve failures. By analogy with the behavior of albite in supercritical water, it seems probable that anorthite dissolves incongruently, also.

Measurements of the solubilities of intermediate plagioclases in water confirmed the results of the rock leaching experiments (Adams, 1964). Runs using intermediate plagioclases yielded the same apparent solubilities as for albite alone. For example, labradorite (An₅₈) has an apparent solubility of 0.29% ± 0.03% at 700°C and 2 kb. Dissolution of plagioclase is not congruent with respect to the original feldspar. The albite components are preferentially dissolved, leaving behind the anorthite as a solid phase. Dissolution *appears* to be congruent with respect to the albite end member following a reaction of the type:



Microprobe analyses of the starting plagioclase and of the solid product indicated that the components of albite entered the solution, for only stoichiometric anorthite remained as the solid phase. Analyses of the solids are useful here because there is a major composition change from plagioclase to anorthite. It is possible that the albite components reacted with the water at different speeds to yield an incongruent solution [as in the case for albite alone (Currie, 1968)]. However, any departures from albite stoichiometry were too small to be reflected in the analyses of the solid residuums. (See Table 2).

The anorthite component of plagioclase was dissolved only if the solution was undersaturated in the albite component. Thus, in excess water plagioclase first dissolves incongruently to produce albite components in

TABLE 2. ELECTRON MICROPROBE ANALYSES OF ANORTHITES

	1	2	3	4
SiO ₂	44.1	43.2	44.4	44.1
Al ₂ O ₃	37.2	36.7	36.7	36.7
CaO	19.2	20.1	19.3	19.3
Na ₂ O	<0.1	—	0.2	0.2
K ₂ O	<0.1	—	<0.1	<0.1

1. Anorthite residuum produced by reaction of labradorite with water at 700°C and 2 kbar.
2. Anorthite, synthetic (glass).
3. Anorthite, An₉₈, Grass Valley, Calif.
4. Anorthite, Grass Valley, Calif. after 10 hours in excess water at 700°C and 2 kbar.

solution and a crystal of anorthite; the anorthite crystal then is attacked, providing the solution is still unsaturated.

The presence of the albite components, of course, increases the activities of Al₂O₃ and SiO₂ in the solution, thereby depressing the solubility of anorthite. The extent of this effect was determined experimentally. Albite and anorthite were placed side-by-side (each in perforated capsules) with water, sealed inside a larger capsule, and held at 700°C and 2 kbar. In the presence of albite, the solubility of anorthite is depressed to <0.02 percent. The solubility of albite would be expected to be lowered simultaneously by the presence of the anorthite, however, this effect was too small to be detected in these experiments. The solubility of albite, therefore, is essentially unaffected by the presence of anorthite.

MINERALOGICAL EFFECTS OF DISSOLUTION

In the solubility measurements (using sealed capsules) plagioclase changed in composition toward the anorthite end member. Little change

could be seen, however, in a given plagioclase crystal unless the water/plagioclase ratio was high. With the volume of the capsule fixed at ~ 5 cm³ at STP, difficulty arose in trying to analyze the very small amounts of feldspar for compositional and crystallographic changes. A means was devised, therefore, to remove and replenish the water in a bomb while it was still hot, thereby allowing dissolution of several large plagioclase grains. In these experiments, which were conducted in the interval 500°C to 800°C, the charges were placed in unsealed gold capsules and the water was changed by opening a valve, allowing the pressure to drop, and then introducing fresh water by pump. No attempt was made to determine solubilities from runs in which pressure varied. This technique was useful, however, for observing the mineralogical changes.

The extraction of the albite component of intermediate or calcic plagioclase into solution is accomplished without destruction of the original plagioclase crystal. Typically the solid anorthite residuum occurs as a pseudomorph after the original plagioclase. The anorthite pseudomorph is riddled with holes and interconnecting channelways, although optical continuity indicates that it is a single crystal rather than an aggregate (Fig. 1). The openness of the anorthite crystal is proportional to the amount of albite component that has been removed. For example, the anorthite residuum that is produced by dissolving andesine is less than 50 percent of the original plagioclase volume. The anorthite, nevertheless, mimics the entire andesine grain, and this necessitates the construction of a very hollow pseudomorph. On the other hand, anorthite pseudomorphs after bytownite are less spongy, owing to the smaller loss of volume corresponding to the albite component. The preferential removal of albite from plagioclase containing less than about one third anorthite results in such a large loss of volume that the original grain collapses. The anorthite, then, collects as a powdery aggregate in the bottom of the capsule.

Solution works inward from the surfaces of grains, producing a "reverse" compositional zoning in the plagioclase. The boundary between the spongy anorthite shell and the undissolved plagioclase core may be sharp or gradational. The solution "front" which advances into a grain is controlled to a large extent by fractures and cleavages, which facilitate penetration of the solvent.

The anorthite product always had the same optical properties ($\beta = 1.585$, $2V_x \approx 80^\circ$) and X-ray diffraction pattern regardless of the composition of the starting plagioclase. The change in optical properties from the undissolved core to the partially dissolved rim of a single crystal, furthermore, was accompanied by an appropriate change (from core to rim) in the extinction angle (Fig. 2).

The rate at which solution proceeds in a run is strongly dependent on

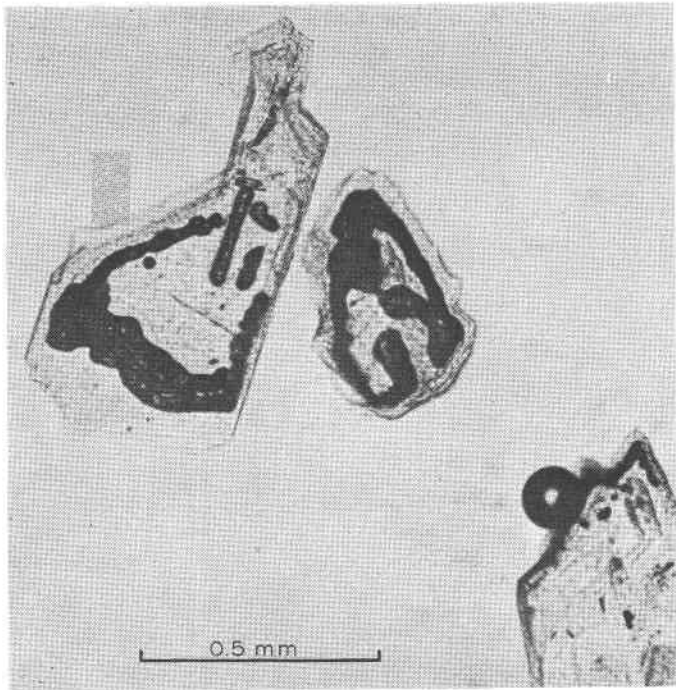


FIG. 1. Anorthite pseudomorphs after labradorite (An_{53}), produced by differential hydrothermal solution at 700°C at 2 kb. Crystals were removed from bomb, dried, and then placed in clove oil just prior to taking the photomicrograph. Dark areas are air bubbles being driven out of the spongy anorthite by the oil. Note bubble escaping at lower right. Sizes and shapes of labradorite crystals are preserved despite removal of albite component. Plane light.

the surface area of a given grain population, and therefore, on grain sizes and shapes. (Small, splinter-shaped grains, expectably, react faster with the water than a larger, equant grain does.) Furthermore, the anisotropy of an individual grain affects the rate of reaction. As a result, in a given time, fractured or strained crystals may react completely, whereas, more nearly isotropic grains of the same general size and shape may be entirely unchanged. This phenomenon at first caused difficulty in determining anything but the average compositions (by the glass refractive-index method) of the products of some runs. The difficulty was overcome by separating the reacted crystals from the incompletely reacted ones in a heavy-liquid density column. Although the anorthite product is typically spongy, the heavy liquid penetrates the pores and passageways, thereby allowing the anorthite (specific gravity = 2.76) to separate from the less-dense plagioclase (specific gravity 2.63–2.76).

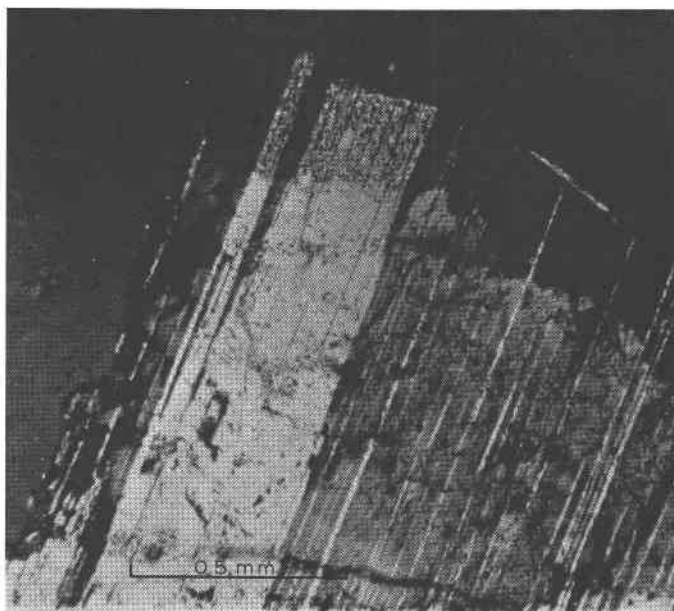


FIG. 2. Photomicrograph of thin section of partially dissolved crystal of andesine (An_{47}). Rim is porous anorthite, core is andesine. Twinning continues across andesine-anorthite boundary, but the extinction angle changes at the boundary for each twin lamella. Compositions determined by extinction normal to (010) were confirmed by electron microprobe analysis. Crossed polars.

DISSOLUTION MECHANISM

The dissolution of plagioclase crystals and the formation of an anorthite pseudomorph raises the question of the mechanism by which albite can be removed without apparently destroying the original plagioclase structure. One possibility is that the differential solution is due, at least in part, to compositional inhomogeneities in the plagioclase. Other possibilities are that the albite component of the plagioclase migrates, ion-for-ion, to the surface of the crystal through an essentially fixed (but pliable) crystal lattice, or, that the plagioclase structure is disrupted entirely and taken into solution, followed by the immediate reprecipitation of the anorthite as a pseudomorph.

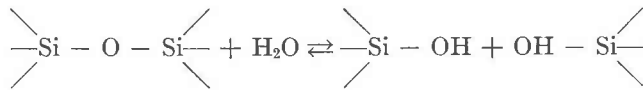
If the plagioclase consisted of a mosaic of sodic and calcic feldspar, each of which occupied discrete domains the size of a few unit cells, it might be possible to dissolve the sodic domains without destroying the anorthite-rich ones. Evidence of such compositional inhomogeneity exists in the peristerite range, $An_{5\pm 2}$ to $An_{17\pm 2}$, but even here the domains are not pure albite and anorthite but An_{0-6} and An_{20-35} (Ribbe, 1960).

Ribbe found that dry heating at 1000°C for a week homogenized the peristerites. It is unlikely that this homogeneous plagioclase would unmix rapidly in the presence of water at 700°C if an analogy can be drawn with homogenized alkali feldspars. Orville (1963) found that dry heated alkali feldspar of the composition $Ab_{56.4}Or_{43.6}$ did not unmix after hydrothermal treatment for 288 hours at 660°C and 2,000 bars H_2O .

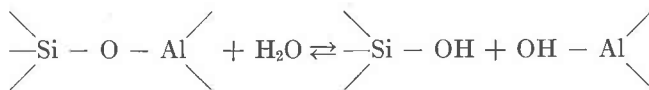
This suggested a means of testing the effect of compositional domains in the present study. Charges were prepared of peristerites that had been heated dry at 1000°C for one week. These homogenized feldspars, however, underwent differential solution in exactly the same way as the feldspars that had not been heated previously. The presence of discrete compositional domains is, therefore, not a prerequisite for differential solution of plagioclase.

A second test of the possible effect of compositional inhomogeneity was made by fusing labradorite (An_{58}) and partially dissolving the resulting glass. As in the runs with crystals, each bead was attacked from the outside inward and a crystalline anorthite product was formed. A notable difference exists, however, in that the anorthite is not spongy, but occurs as needle-shaped crystals oriented normal to the surface of the grain. Again, differential solution occurs in a homogeneous material of plagioclase composition.

Donnay, *et al.* (1959) and Wyart, *et al.* (1961), have stressed the idea that Si-O-Si and Al-O-Si bonds are readily broken and reformed in the presence of water at high temperatures. According to this hypothesis H^+ ions combine with the oxygen atoms which are shared by the tetrahedra, thus forming OH^- ions. SiO_3OH tetrahedra are created, but this leaves other incomplete tetrahedra which attract and combine with OH^- ions from the water to form more SiO_3OH tetrahedra. The process is considered reversible according to the reactions:



and



One of the significant aspects of this mechanism is that it provides a way for Si, Al and other cations to move through the crystal structure. Because the water acts only as a catalyst, and bonds are continually broken and reformed, the crystal structure need not be destroyed. Donnay,

et al. (1959), used this mechanism to explain the results of an experiment by Wyart and Sabatier (1958) in which an intergrowth of orthoclase and anorthite (the product) formed a pseudomorph after labradorite (the starting material) which had been held in an aqueous KCl solution at 500°C and 600 bars.

In ion-exchange experiments using alkali feldspars O'Neil and Taylor (1967) also formed pseudomorphs, but they concluded that the replacement mechanism involved solution and redeposition of the mineral phases. Their arguments are based on measurements of O^{18}/O^{16} ratios of the mineral and aqueous phases. It was found that the feldspar that had exchanged alkali ions with the surrounding alkali halide solution also had exchanged oxygen atoms, resulting in an equilibration of O^{18}/O^{16} in the feldspar with that of the solution.

The starting and product materials of three of the plagioclase runs (this study) also have been analyzed for O^{18}/O^{16} through the courtesy of Dr. J. R. O'Neil and Prof. H. P. Taylor at the California Institute of Technology. Labradorite (An_{58}), reacted to anorthite at 700°C and 2 kbar in an excess of water for 21, 48, and 80 hours, respectively, was used for the analyses. In each of the three runs, the value for δ

$$\left(\text{where } \delta = \left[\frac{(O^{18}/O^{16}) \text{ sample}}{(O^{18}/O^{16}) \text{ C.I.T. standard}} - 1 \right] \times 1000 \right)$$

for the anorthite product had moved approximately two-thirds of the way toward the δ value of the water. The labradorite gives $\delta = -17$ per mil, the water = -32 per mil and the three anorthite products = -27 per mil. Oxygen exchange between the plagioclase and the water during dissolution, therefore, had been substantial but not complete. A δ -shift of this magnitude appears to be consistent with the solution-redeposition mechanism, with perhaps some of the anorthite molecules remaining together to avoid complete oxygen exchange with the water, or with oxygen isotope exchange possibly occurring at a slower rate than the recrystallization.

To further investigate the dissolution mechanism and the significance of pseudomorphs, an attempt was made to differentially remove the anorthite component by placing plagioclase in 3N HCl at 1 atm between 25°C and 100°C. Pure albite is not noticeably affected by soaking in HCl for several hours, whereas anorthite is rapidly attacked. Labradorite, An_{58} (the same one used for hydrothermal runs) is also attacked, with the anorthite component apparently being preferentially removed. As in the hydrothermal experiments, differential solution works from the crystal surfaces inward, forming a shell of new material which is a pseudomorph

after the original feldspar. In HCl, however, the newly formed shell has a lower refractive index than the plagioclase core, and is relatively rich in the albite components. Further reaction with the strong acid clearly is incongruent with respect to plagioclase and with respect to the end members, and the solid-phase end product is silica gel.

The point of interest here is that even the silica gel forms a pseudomorph after the original plagioclase. For this reaction it is not possible to think in terms of a few bonds bridged by OH^- ions, and the movement of just cations. The plagioclase crystal has, necessarily, undergone a complete breakdown in order to liberate all of the sodium, calcium, aluminum and 60 percent of the oxygen from the framework structure. The insoluble residue of silica probably reprecipitates immediately, and its form is controlled by the shape of the solid structure on which it grows, as is shown by the pseudomorphs. The SiO_4 groups in the silica gel must be newly formed, for the most part, and be in new positions relative to those in the original plagioclase structure.

It is concluded that the high temperature dissolution of plagioclase in water entails a solution-redeposition mechanism, also. The liberation of sodium, aluminum, silicon and oxygen (in the proportions of the albite molecule) from a homogeneous plagioclase requires a complete dismantling of the crystal framework. The role of H^+ and OH^- ions in attacking the plagioclase structure is very possibly a large one, and the mechanism of breaking and bridging bonds, as discussed by Donnay *et al.* (1959), and Wyart *et al.* (1961), may apply to the question of how the silicate goes into solution. The construction of an anorthite pseudomorph after the plagioclase, however, does not appear to require an ion-exchange type of process.

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