

THE OXYGEN ISOTOPE AND CATION EXCHANGE CHEMISTRY OF FELDSPARS¹

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ABSTRACT

Cation exchange experiments between alkali and alkaline-earth feldspars and corresponding 2–3 molal aqueous chloride solutions were performed at a fluid pressure of one kilobar over the temperature range 350°–800°C. Oxygen isotope analyses of the exchanged feldspar indicate that essentially complete oxygen isotope equilibration between solution and feldspars accompanies the cation exchange. Oxygen isotope fractionations obtained this way were proved to be equilibrium fractionations by their agreement with those obtained by true isotope exchange reactions between synthetic feldspars and pure water.

The oxygen isotope fractionation factor (α) between alkali feldspar and water in the temperature range studied is given by the expression $10^3 \ln \alpha = 2.91 (10^6 T^{-2}) - 3.41$. No isotope fractionation was discernible between albite and potassium feldspar. However, the alkali feldspars were found to concentrate O^{18} relative to the alkaline-earth feldspars, indicating a relationship between the Al/Si ratio in feldspar and tendency to concentrate O^{18} . The plagioclase-water fractionation follows the equation: $10^3 \ln \alpha = (2.91 - 0.76\beta)(10^6 T^{-2}) - 3.41 - 0.41\beta$ where β is the An content of the plagioclase.

Observations made during the course of this work suggest that the mechanism of oxygen and cation exchange in these experiments involves fine-scale solution and redeposition in a fluid film at the interface between exchanged and unexchanged feldspar. A mechanism involving simple solid-state diffusion cannot explain the observed communication between the oxygen at the interfacial boundary and the solution.

INTRODUCTION

Because of their importance as rock-forming minerals and their interesting mineralogical and crystallographic characteristics, the feldspars are one of the most well-studied mineral groups. Oxygen isotope analyses have been made on natural feldspars from igneous and metamorphic rocks (Taylor and Epstein, 1962a, 1962b, 1963; Taylor *et al.*, 1963; Garlick and Epstein, 1966) and meteorites (Taylor *et al.*, 1965). These studies indicated that (1) feldspars exhibit systematic isotopic trends with respect to their coexisting minerals and in accord with changing geologic environments (that is, they are isotopically well behaved), (2) among the common silicates feldspars have a tendency exceeded only by quartz to concentrate O^{18} relative to their coexisting minerals, and (3) the alkali feldspars concentrate O^{18} with respect to alkaline-earth feldspars. In conjunction with the abundance and ubiquity of feldspars, these isotopic properties make them a promising mineral group for use

¹ Publications of the Division of Geological Sciences, California Institute of Technology, Contribution No. 1431.

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in oxygen isotope geothermometry and in the solution of other petrological problems.

Laboratory studies of the equilibrium oxygen isotope chemistry of feldspars permit quantitative interpretations to be given to the existing natural data. In addition, a study of the feldspars affords an opportunity to assess the importance of various parameters such as nature of the cation, aluminum to silicon ratio, and crystal structure, to the isotopic properties of silicates and oxygen-containing solids in general. With such information, minerals like the plagioclases, which form solid-solution series, can be treated isotopically in a straightforward manner. During the course of this work it was also possible to make observations on the rates of cation and oxygen isotope exchange. Knowledge of relative and absolute exchange rates of various minerals bears on the important problems of attainment of isotopic equilibrium and retention of the isotopic record in a mineral assemblage.

Because Wyart and Sabatier (1958) and Orville (1963) demonstrated silicon and aluminum mobilization during cation exchange between feldspars and alkali chloride solutions, it was thought that oxygen isotope exchange with the solution might also accompany these transformations. Inasmuch as oxygen isotope exchange between natural feldspars and water is sluggish, this induced exchange in alkali chloride solutions would permit equilibrium isotope data to be obtained in reasonable laboratory times. The discovered relationship between cation and O^{18} exchange gives insight into the mechanism of the water-mineral interaction.

EXPERIMENTAL PROCEDURE

The exchange experiments were done in sealed gold or platinum capsules using coldseal bombs and conventional hydrothermal apparatus. In all cases the fluid pressure was maintained at 1000 bars.¹ Temperature was monitored by a Chromel-Alumel thermocouple resting in a well on the outside of the bomb. By use of an automatic recorder, readings were taken at frequent intervals throughout each run and found to vary by only 2 to 3 degrees at the lower temperatures and no more than 5 degrees at the higher temperatures. In each run the silicate materials rested near the bottom of the gold capsules, directly adjacent to the thermocouple well. For the alkali feldspar experiments a typical charge consisted of 25 mg sodium feldspar, 42 mg KCl and 200 mg of water. The solutions were 2-3 molal in alkali chloride and were quite corrosive to the metal capsules above 600°C. In the case of the alkaline-earth feldspar runs, the chloride concentration of the solutions was about 4 molal (2 molal $CaCl_2$) and the length of the runs was severely limited by the corrosion problem. In some cases the capsules used in these latter experiments recrystallized with concomitant leaks in times shorter than that necessary for complete exchange to take place.

No exchange took place on quenching, as evidenced by the fact that the same results

¹ Calculations based on changes in molar volumes for isotope exchange reactions and an experiment by Hoering (1961) indicate that pressure effects on isotopic fractionation are negligible.

were obtained when experiments were carried out in small coldseal bombs (quenched in 2-3 minutes) or in a large coldseal (quenched in approximately ten minutes). After quench the capsules were weighed to check for leakage and then opened. The solids were washed in distilled water, rinsed in acetone, and dried at 110°C. After a small portion of the crystals was separated for X-ray and microscopic examination, the bulk of the product crystals (samples were often split for duplicate analysis) was reacted with fluorine gas according to the method of Baertschi and Silverman (1951) and Taylor and Epstein (1962a). The oxygen, liberated in 100 percent yield in this reaction, was converted to carbon dioxide which was analyzed for its isotopic content on a modified Nier 6", 60° sector isotope ratio mass spectrometer (McKinney *et al.*, 1950). The precision of a single analysis of this type is ± 0.2 per mil. Of the products, only the solids were analyzed for their oxygen isotopic composition. The isotopic compositions of the starting materials were known (waters were analyzed directly by the BrF_3 method of O'Neil and Epstein, 1966), and the $\text{O}^{18}/\text{O}^{16}$ ratio of the product solution, which contributed approximately 95 percent of the oxygen in the system, was calculated by material balance.

The sodium to potassium ratio in the alkali feldspars was determined by the 201 X-ray method using potassium bromate as internal standard and using the experimentally determined curve of Orville (1963). In the case of the alkaline-earth feldspars, emission spectrographic analysis, indices of refraction, and X-ray diffraction patterns provided sufficient evidence that phenomena were taking place that were directly analogous to the alkali feldspar experiments.

In order to facilitate cation and oxygen isotope exchange, the starting materials used in the equilibrium experiments were ultra-fine synthetic feldspars. Natural pegmatitic albite from Amelia, Virginia (an ordered, almost 100 percent sodium feldspar) was finely ground in an agate mortar. Those grains which "floated" in acetone (a few microns in average cross-section) were then reacted for a few days with a potassium chloride solution at 500°C, resulting in extremely fine synthetic sanidine. High albite starting material was prepared by reacting this sanidine with sodium chloride solution under the same conditions. Synthetic "celsian" was prepared in two different ways: (1) reacting natural anorthite (An_{98}) from Duke Island, southeastern Alaska with barium chloride solution at 600°C for a few days, and (2) crystallizing a glass of composition $\text{BaAl}_2\text{Si}_2\text{O}_8$ at 700°C in pure water. The glass was made from silica, alumina, and barium carbonate placed on a molybdenum tray and resistance-heated in a nitrogen atmosphere. The X-ray diffraction patterns (Fig. 1) of the materials prepared in both ways were identical.

The isotopic composition of the solutions used in the preparation of the synthetic feldspars was an important consideration bearing on the *modus operandi* used in this study. By mixing the appropriate amounts of O^{18} -enriched water and laboratory distilled water, a water (Water-2 of Tables 1 and 2) was prepared which had approximately the same isotopic composition as the working standard of the mass spectrometer. When the feldspars were prepared in this water, their resultant isotopic compositions were again approximately this same value. Exchange experiments performed with feldspar and solution, both of which have about the same isotopic composition as the working standard, have the following advantages: (1) precision and accuracy are markedly enhanced in a mass spectrometric analysis of a sample which has an isotopic composition near that of the standard, and (2) inasmuch as the feldspar-water fractionations vary only a few per mil from zero over the temperature range studied, the isotopic composition of the feldspar does not have to change very much to reach the equilibrium value.

At each temperature, the feldspar was equilibrated with two solutions that were identical except for isotopic composition. The two runs were commonly made simultaneously in the same large coldseal bomb; for those companion runs made in separate coldseal bombs,

conditions of time and temperature were made as alike as possible. As mentioned above, one of the solutions was of nearly the same isotopic composition as the feldspar. Thus the feldspar was initially almost in isotopic equilibrium with the solution. In the companion run, the isotopic composition of the solution was approximately 35 per mil different from the feldspar. Since all physical and chemical conditions were the same for the two runs, the feldspars exchange an equal fraction of the way to equilibrium during the time of the run. The extent of exchange is readily ascertained in the case of the starting materials with highly disparate isotopic compositions, because the equilibrium value can be roughly estimated and the initial distance from equilibrium is so great. The percent exchange so determined is then applied to data from the run where starting materials had isotopic compo-

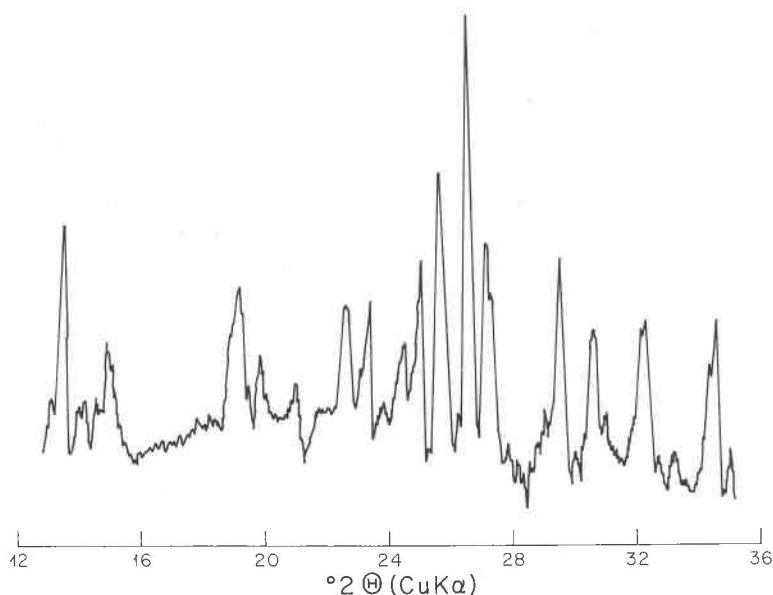


FIG. 1. X-ray diffraction pattern of synthetic $\text{BaAl}_2\text{Si}_2\text{O}_8$.

sitions such that the system was already close to equilibrium. This treatment results in an accurate determination of the equilibrium fractionation. In many of the runs, the extent of exchange was essentially 100 percent and so the same fractionation factors were commonly obtained from both of the companion runs. Only 72 percent exchange occurred in 524 hours at 350°C and in this case the method of graphical interpolation described by Northrop and Clayton (1966) was used to determine the equilibrium value at this temperature. The two methods described here are essentially the same, the former being a special case of the more general graphical interpolation technique.

When cation exchange is used as a means of promoting oxygen isotope exchange, the attainment of isotopic equilibrium cannot be demonstrated because there is the possibility that a kinetic fractionation might accompany the chemical reaction involved. The only unambiguous way to demonstrate isotopic equilibrium is to approach equilibrium from opposite directions in a true exchange reaction. In such a reaction only isotopes are exchanged and no new phases appear or disappear. Sodium and potassium feldspars apparently do not fractionate oxygen isotopes relative to one another (Taylor and Epstein, 1962b; Schwarcz,

1966) and thus this system approximates conditions of the ideal exchange reaction (that is, sodium and potassium feldspars have essentially identical isotopic properties). In order to resolve more fully this problem of demonstrating equilibrium when the cation exchange method is used, it was decided to perform true exchange reactions between synthetic feldspar and pure water and to apply the graphical interpolation technique to the results. Surprisingly, the synthetic feldspars underwent considerable exchange even at 500°C in 150 hours (61%). The equilibrium values obtained this way agree with those obtained by cation exchange at 500°, 600°, and 800°C (see Table 1). Thus, it is legitimate to infer that true equilibrium data are obtained at lower temperatures where only the cation exchange method was used.

DISCUSSION OF EXPERIMENTAL RESULTS

The results of runs made with the intention of securing equilibrium isotopic data are listed in Table 1 (alkali feldspars) and Table 2 (alkaline-earth feldspars). Where the entry in the "percent exchange" column is 100 percent the exchange reaction has gone to completion and the resultant equilibrium fractionation is given in per mil in the last column. For those cases where reaction was incomplete the method of graphical interpolation was used to obtain the equilibrium fractionation. Starting materials with the same description (*e.g.*, ultra-fine synthetic sanidine) are usually different preparations with different physical properties such that some of the rates of exchange which appear inconsistent are actually not. For example, at 350°C one synthetic sanidine preparation exchanged only 72 percent in 534 hours while another exchanged completely in 505 hours.

All of the salient features of these experiments are evident in the 500°C series of runs:

(1) The oxygen isotope data from runs made in pure water (true exchange reactions) agree with those utilizing cation exchange, demonstrating that equilibrium is attained in both sets of experiments.

(2) The interpolation method (not yet proved to be a valid procedure for all systems) yields fractionations in agreement with those where equilibration was complete.

(3) There is no detectable oxygen isotope fractionation between sodium and potassium feldspars. This observation concurs with the findings of Taylor and Epstein (1962b) and of Schwarcz (1966) who analyzed a number of natural coexisting sodium and potassium feldspars. Theoretically, any two oxygen-containing substances ought to fractionate oxygen isotopes with respect to one another. In this case, the fractionation is so small in the temperature range studied that it cannot be measured with present techniques and equipment. Of importance, however, is the conclusion that the univalent cation in alkali feldspars must not play a significant role in determining the isotopic properties of the mineral.

TABLE 1. O^{18} FRACTIONATION DATA FOR ALKALI FELDSPAR-WATER SYSTEM

Sample	Description	Water	Time (hrs.)	$10^3 \ln \alpha$	% Exchange ¹	$10^3 \ln \alpha_e$
<i>T = 800°C</i>						
181	Syn. san. (-100, +200) and pure water	7	48	- 8.84	54	—
183	Syn. san. (-100, +200) and pure water	4	48	+11.37	54	-1.29
243	Syn. san. (u.f.) and 3 m NaCl solution	3	40		100	-0.82
319	Syn. san. (-100, +200) and 2 m NaCl solution	2	12	- 2.83	85	—
320	Syn. san. (-100, +200) and 2 m NaCl solution	4	12	+ 2.84	85	-1.01
Average value						-1.04
<i>T = 600°C</i>						
162	Syn. san. (u.f.) and pure water	2	126	- 1.49	90	—
165	Syn. san. (u.f.) and pure water	4	126	+ 2.39	90	+0.59
309	Syn. san. (-200) and 3 m NaCl solution	2	48		100	+0.67
310	Syn. san. (-200) and 3 m NaCl solution	4	48		100	+0.37
Average value						+0.54
<i>T = 500°C</i>						
43	Nat. alb. (-200) and 3 m KCl solution	4	240		100	+1.57
94	Syn. san. (u.f.) and 3 m NaCl solution	2	26		100	+1.36
156	Syn. san. (u.f.) and pure water	2	149	- 6.83	61	—
157	Syn. san. (u.f.) and pure water	4	149	+ 7.91	61	+1.32
270	Syn. san. (u.f.) and 3 m NaCl solution	2	450		100	+1.53
281	Syn. san. (-200) and 3 m NaCl solution	4	288		100	+1.56
282	Syn. san. (-200) and 3 m NaCl solution	7	288		100	+1.59
283	Syn. alb. (-200) and 3 m KCl solution	4	288		100	+1.25
284	Syn. alb. (-200) and 3 m KCl solution	7	288		100	+1.92
Average value						+1.51
<i>T = 420°C</i>						
293	Syn. alb. (-200) and 3 m KCl solution	2	1050		100	+2.58
<i>T = 350°C</i>						
131	Syn. san. (u.f.) and 3 m NaCl solution	3	505		100	+4.04
217	Syn. san. (u.f.) and 3 m NaCl solution	3	524	+ 2.86	72	—
218	Syn. san. (u.f.) and 3 m NaCl solution	4	524	+ 9.83	72	—
217	Syn. san. (u.f.) and 3 m NaCl solution	7	524	- 1.87	72	+3.94
307	Syn. alb. (-200) and 3 m KCl solution	2	1120		100	+4.12
308	Syn. alb. (-200) and 3 m KCl solution	4	1120		100	+3.74
Average value						+4.00

$\delta_{\text{water}-2} = +1.16$ $\delta_{\text{water}-3} = -11.73$ $\delta_{\text{water}-4} = -35.96$ $\delta_{\text{water}-7} = +4.93$

Abbreviations:

San. = sanidine Syn. = synthetic (-100, +200) = mesh size α = measured fractionation factor
 m = molal Alb. = albite Nat. = natural u.f. = ultrafine α_e = equilibrium fractionation factor

¹ Values of 100 for the isolated experiments in which no companion runs were made are judged to represent essentially complete oxygen isotope exchange because they give the same α -value as do experiments in which equilibrium was approached from opposite directions. In all such cases 100 percent alkali exchange took place as well.

Considerable experimental problems were met in securing equilibrium data for the alkaline-earth feldspars. The noble metal corrosion problem previously mentioned prohibited long-term runs. This was particularly limiting in that the exchange rates are lower for these substances than for the alkali feldspars. The synthetic "celsian" yielded an X-ray pattern which was not the same as other published patterns for $\text{BaAl}_2\text{Si}_2\text{O}_8$ and because of this uncertainty was not used for partial exchange experiments. This material, however, when reacted with calcium chloride

TABLE 2. O^{18} FRACTIONATION DATA FOR ALKALINE EARTH FELDSPAR-WATER SYSTEM

Sample	Description	Water	Time (hrs.)	$10^3 \ln \alpha$	% Exchange	$10^3 \ln \alpha_0$
<i>T</i> = 800°C						
321	Syn. celsian (u.f.) and 2 m CaCl_2 solution	7	12			-2.60
<i>T</i> = 600°C						
215	Syn. anorthite (u.f.) and pure water	7	144		100	-0.76
253	Syn. celsian (u.f.) and 2 m CaCl_2 solution	4	144		100	-1.06
311	Anorthite glass (-200) and pure water	7	77		100	-1.04
312	Anorthite glass (-200) and pure water	4	77		100	-0.91
Average value						-0.94
<i>T</i> = 500°C						
258	Syn. celsian (u.f.) and 2 m CaCl_2 solution	7	254	-0.56	96	—
259	Syn. celsian (u.f.) and 2 m CaCl_2 solution	4	254	+1.15	96	-0.39
285	Syn. celsian (u.f.) and 2 m CaCl_2 solution	4	288	+4.27	88	—
286	Syn. celsian (u.f.) and 2 m CaCl_2 solution	7	288	-0.80	88	-0.18
Average value						-0.28
<i>T</i> = 420°C						
290	Syn. celsian (u.f.) and 2 m CaCl_2 solution	4	1050	+10.38	72	—
291	Syn. celsian (u.f.) and 2 m CaCl_2 solution	7	1050	-0.38	72	+0.11

Abbreviations same as in Table 1.

solutions, yielded good anorthite. Of interest is the fact that anorthite glass apparently crystallizes in isotopic equilibrium with water. This does not occur with silica glass (O'Neil, 1963) and may be a function of the rate of crystallization. The data for the alkaline-earth feldspars are not proved to be equilibrium data and only by analogy to the alkali-feldspar system (cation exchange runs) and their "reasonable" values are they considered meaningful.

That the alkali feldspars are found experimentally to concentrate O^{18} relative to the alkaline-earth feldspars concurs with the measurement and interpretation of natural samples (Taylor and Epstein, 1926b). The only

major differences between the alkali and alkaline-earth feldspars are the charge and size of the cation and the aluminum to silicon ratio. A smaller, more highly charged cation would be expected to exert a greater influence on the electronic environment surrounding the oxygen atoms, and thus affect the nature of their bonding and isotopic properties. However, the alkali-feldspar studies indicate that cation effects are only a minor perturbation on those resulting from the nature of the aluminosilicate framework. Thus it is concluded that the tendency to concentrate O^{18} is directly correlated with the relative numbers of Al-O and Si-O bonds (the O-O interactions being approximately the same for both feldspars). Isotopic fractionations between chemical species are known to be dependent upon the vibrational frequencies of the isotopically substituted molecules (Urey, 1947). In silicate minerals, the vibrational frequencies associated with Si-O bonds are higher than those associated with Al-O bonds, the tetrahedral Al-O bond length being greater than the Si-O bond length. The average (Si, Al)-O bond length changes progressively from quartz (1.607 Å) through the pure sodium and potassium feldspar polymorphs (1.642 to 1.645 Å) to anorthite (1.681 Å) (Smith and Bailey, 1963). On this basis it is possible to construct an empirical expression relating the oxygen isotope fractionations between aluminosilicate minerals to their Al/Si ratios. (See below.)

Theoretical arguments of Urey (1947) and Bigeleisen and Mayer (1947) have shown that for perfect gases the natural logarithm of the isotopic fractionation factor (α) varies linearly with T^{-2} in the high temperature limit. Thus equilibrium data for the alkali feldspar-water system are so presented graphically in Figure 2, and the resultant line is referred to as a fractionation curve. There is some suggestion of concave downward curvature in the data points which would be reasonable if some T^{-1} dependence (favored by high frequencies and/or "low" temperatures) is being manifest on this T^{-2} plot. However, these data fit a straight line within experimental error over the temperature range studied and the fractionation between alkali feldspar and water can be calculated at any temperature in this range from the following least-squares expression:

$$1000 \ln \alpha_{F-W} = 2.91 (10^6 T^{-2}) - 3.41.$$

A least-squares line for the anorthite-water system is given in Figure 3:

$$1000 \ln \alpha_{A-W} = 2.15 (10^6 T^{-2}) - 3.82.$$

The 420°C anorthite-water experimental fractionation is considerably smaller than expected with respect to the higher temperature data. Although the stability of anorthite in concentrated chloride solutions has

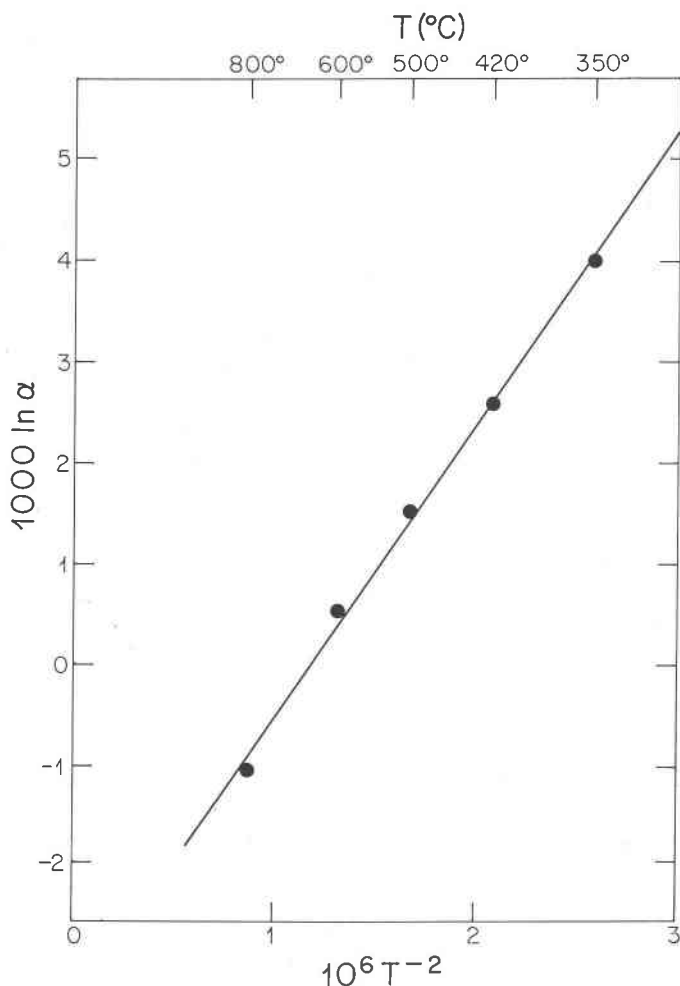


FIG. 2. Experimental alkali feldspar-water fractionations and least-squares fractionation curve.

not been investigated, it is possible that some zoisite, $Ca_2Al_3(OH)Si_3O_{12}$, may have formed at this temperature (Newton, 1965). Only anorthite was evident in the X-ray diffraction pattern, but a few percent zoisite might explain the isotopic result. Because of this uncertainty and the fact that it was a "partial-exchange" experiment, the result was not included in the least-squares analysis.

With sodium and calcium feldspars as end members, a fractionation curve for any plagioclase can be constructed by assuming the isotopic

properties of the feldspars to vary linearly from An_0 to An_{100} . With β equal to the fractional anorthite content, this expression is

$$1000 \ln \alpha_{P-W} = (2.91 - 0.76\beta)(10^6 T^{-2}) - 3.41 - 0.41\beta.$$

Fractionation curves for plagioclases of various anorthite contents are plotted in Figure 4.

In Figure 3 are shown the experimental anorthite-water fractionations (with the doubtful 420°C point in parenthesis) along with the least squares and predicted anorthite-water fractionation curves. The pre-

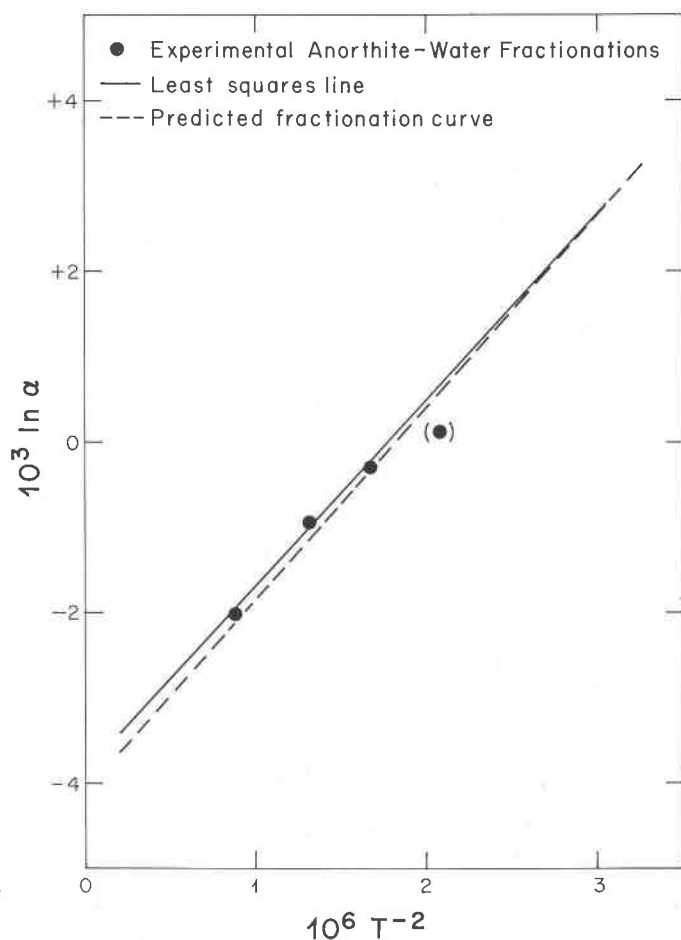


FIG. 3. Experimental anorthite-water fractionations and the least squares and predicted fractionation curves.

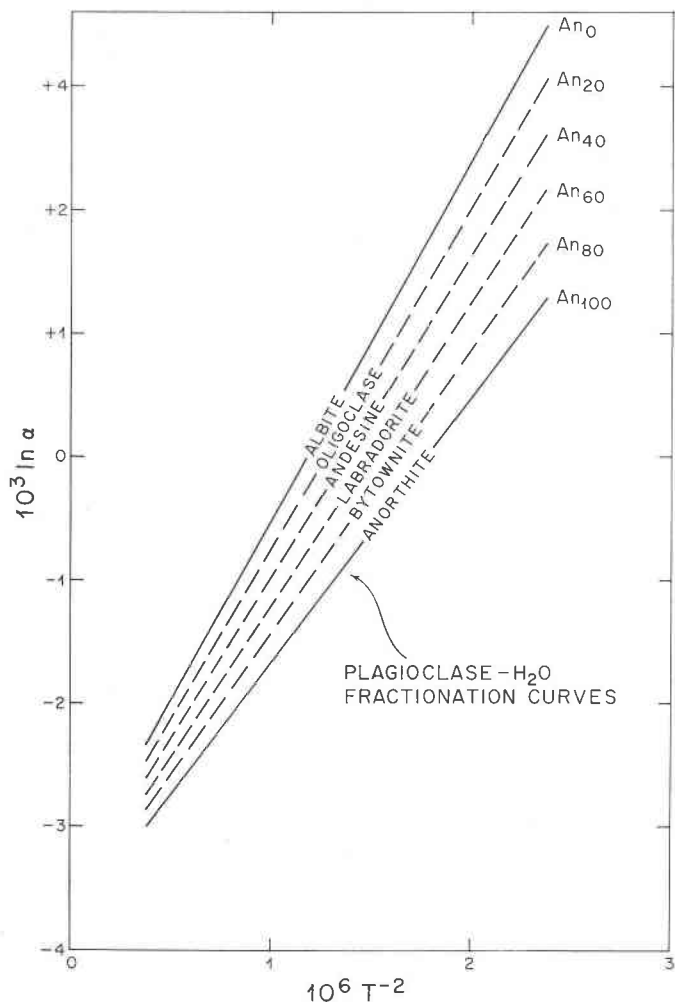


FIG. 4. Plagioclase-water fractionation curves for various anorthite contents.

dicted curve is derived by assuming a linear relationship between the isotopic properties and Al/Si ratios of framework silicates. This assumption is supported by the trends exhibited by the average Al-O and Si-O bond lengths discussed above. On combining the quartz-water data of Clayton, O'Neil, and Mayeda (in preparation)¹ in this manner with the

¹ At the time of this writing there is still some difficulty in the interpretation of the experimental data for this system. Thus, any quantitative statements made in this paper involving the quartz-water system may be subject to minor adjustments.

alkali feldspar-water data of the present paper, a general expression for an aluminosilicate-water fractionation is obtained:

$$1000 \ln \alpha = (2.64\gamma + 0.93)(10^6 T^{-2}) + 2.80\gamma - 5.51$$

where

$$\gamma = \frac{\text{Si}}{\text{Si} + \text{Al}}$$

An independent test of this expression is provided by the anorthite-water system. The close agreement between the experimental points and the predicted curve indicates that the hypothesis is essentially correct.

One of the most important aspects of the establishment of these equilibrium fractionation curves for the feldspars is their application to oxygen isotope geothermometry. These feldspar data are consistent with the results of the laboratory studies of quartz-water (Clayton, O'Neil, and Mayeda, in preparation), carbonate-water (Clayton, 1961; O'Neil and Clayton 1967), and muscovite-water (O'Neil and Taylor, 1966). Applied to the analyses of natural samples, these calibrations yield concordant "temperatures" of formation for many rocks which contain at least three of these minerals in isotopic equilibrium. These matters will be discussed in detail in a forthcoming paper.

In Table 3 are listed oxygen isotope analyses of coexisting quartz and feldspars from a variety of rock types. The SMOW (Standard Mean Ocean Water) standard used here is that against which a sample of Potsdam sandstone is +15.5 per mil and is essentially the same as that defined by Craig (Craig, 1961; O'Neil and Epstein, 1966; Clayton and Mayeda, 1963). Using the experimental fractionation curves, we have calculated "formation temperatures" and isotopic compositions of water present at the time the minerals crystallized. Even though the quartz-feldspar fractionations are not very temperature-sensitive (particularly at high temperatures), the mineral pairs in Table 3 are apparently close to oxygen isotope equilibrium at reasonable temperatures of formation. The effect of aluminum substitution is clearly shown in the isotopic compositions of the plagioclases. The calculated O^{18} contents of the waters indicate: (1) pegmatitic waters are highly variable in their oxygen isotopic compositions; (2) magmatic waters are fairly uniform in composition with values around 9 per mil; and (3) waters associated with the formation of metasediments are generally a few per mil heavier than magmatic waters.

From the laboratory calibrations it is now clear that any natural quartz-feldspar fractionations which are less than about +0.7 per mil at geologically reasonable temperatures (<1200°C) indicate nonequilibrium.

TABLE 3. TEMPERATURES AND ISOTOPIC COMPOSITIONS¹ OF FORMATION WATERS DERIVED FROM VARIOUS QUARTZ-FELDSPAR O¹⁸ FRACTIONATIONS

Sample	δ_{quartz}	$\delta_{\text{K-feldspar}}$	$\delta_{\text{plagioclase}}$	Temp. (°C)	$\delta_{\text{H}_2\text{O}}$
Rock Creek pegmatite border zone (Taylor and Epstein, 1962a)	11.9	10.5	10.3 (An ₁₀)	690, 640	10.4
Quartz-adularia vein, Hot Springs, Arkansas (Taylor, 1967)	18.3	15.3		265	8.7
Rose quartz pegmatite Pala, California, graphic granite (Taylor, 1967)	9.1	7.7		690	8.0
Bonsall tonalite (Taylor and Epstein, 1962a)	10.3		8.5 (An ₄₀)	750	9.6
San Jose tonalite (Taylor and Epstein, 1962a)	9.7		8.0 (An ₃₆)	755	9.0
Shake Flat quartz monzonite (Taylor and Epstein, 1962a)	10.3		9.0	760	9.7
Chloritoid-kyanite schist, Mt. Grant, Vermont (Taylor, Albee and Epstein, 1963)	16.0		13.9 (An ₅)	435	11.6
Staurolite schist, Dutchess County, New York (Garlick and Epstein, 1967)	15.6		13.3 (An ₅₅)	615	13.8

$$^1 \delta_x = \left[\frac{(\text{O}^{18}/\text{O}^{16})_x - (\text{O}^{18}/\text{O}^{16})_{\text{SMOW}}}{(\text{O}^{18}/\text{O}^{16})_{\text{SMOW}}} \right] 10^3 \text{ where SMOW is Standard Mean Ocean Water.}$$

rium pairs. Such "isotopic reversals" (with negative quartz-feldspar fractionations of as much as 2 per mil) occur in some pegmatites and red-rock granophyres (Taylor, unpublished) and also in the alteration zone adjoining the hydrothermal veins at Butte, Montana (Garlick and Epstein, 1966).

MECHANISM OF THE EXCHANGE REACTIONS

In their studies of the mechanism of the thermal and compositional transformations in silicates and the nature of the silicate-water interaction, Wyart and Sabatier (1958, 1959), Wyart *et al.*, (1959), Donnay *et al.*, (1959), Wyart *et al.*, (1961), Fructus-Ricquebourg *et al.*, (1963) have performed various cation exchange experiments and also tracer experiments using O¹⁸-enriched materials. They found that a large proportion of the oxygen in silicates exchange with the water when a granite is melted in the presence of water or when powdered microcline is heated with water at high temperatures. These results, in conjunction with their

pioneering studies of cation exchange between feldspars and alkali chloride solutions led them to the conclusion that both the presence of water and the substitution of cations were necessary for the motion of silicon and aluminum ions in the crystal structure. They proposed a solid state diffusion mechanism in which the aluminosilicate tetrahedra are pried open and closed by diffusing protons and hydroxyl ions.

TABLE 4. INCOMPLETE EXCHANGE RUNS FOR MECHANISM STUDIES

Group	Sam- ple	Description	Temp. (°C)	Time (hrs.)	% Ex- change
A	3	PE-2 perthite (−100, +200) and 3 m NaCl solution	585	64	87
	9	PE-2 perthite (−100, +200) and pure water	585	69	10
	25	PE-2 perthite (−100, +200) and pure water	585	260	15
	13	PE-2 perthite (−100, +200) and 3 m KCl solution	585	65	19
	17	PE-2 perthite (−100, +200) and 0.3 m NaCl solution	585	94	27
B	32A	Nat. Amelia alb. (−50, +100) and 3 m KCl solution	650	1	86
	32B	Nat. Amelia alb. (−50, +100) and 3 m KCl solution	650	1	78
	32C	Nat. Amelia alb. (−50, +100) and 3 m KCl solution	650	1	26
C	21	Nat. Amelia alb. (−200) and 3 m NaCl solution	650	62	9
	24	Nat. Amelia alb. (−200) and pure water	650	62	15
	31	Nat. Amelia alb. (−200) and 3 m KCl solution	650	2	92
D	36	Syn. san. (−200) and pure water	585	62	29
	37	Nat. Amelia alb. (−200) and pure water	585	62	5
	53	Nat. san. (−200) and pure water	585	62	8
E	40	Nat. Amelia alb. (−200) and 3 m KCl solution	650	8	>95
	46	Nat. san. (−200) and 3 m NaCl solution	650	22	>95
	78	Nat. san. (−200) and 3 m NaCl solution	585	7	72
	79	Nat. Amelia alb. (−200) and 3 m KCl solution	585	7	>95
F	100	Nat. Amelia alb. (−100, +200) and pure water	500	208	0
	101	Nat. Amelia alb. (−100, +200) and 3 m NaCl solution	500	208	0
	102-104	Nat. Amelia alb. (−100, +200) and 3 m (Na/K = 30, 5, 3) solution	500	208	0
	105	Nat. Amelia alb. (−100, +200) and 3 m KCl solution	500	208	87

Abbreviations same as in Table 1.

Listed in Table 4 are six groups of exchange experiments designed to elucidate the mechanism by which these reactions take place.

Group A. Used in this series was a perthitic microcline from a pegmatite located 2 miles southwest of Glenarm, Maryland (sample PE-2 of Wasserburg *et al.*, 1957). The sample contains 11.25 percent potassium with somewhat greater than 20 percent of the feldspar being exsolved albite lamellae. In no case was it possible to exchange completely the oxygen isotopes between the perthite and solution. Only 87 percent O^{18} exchange occurred with NaCl solution in times greater than is necessary to exchange albite completely with KCl solution at the same tempera-

ture. That the albite lamellae in the perthite did not exchange appreciably in this case is borne out by experiments 3 and 13; these latter complement each other in that some O^{18} exchange takes place even in pure water (samples 9 and 25). Therefore, as would be expected, the percent exchange of oxygen isotopes between PE-2 perthite and KCl solution is slightly greater than the percent albite phase in the perthite. It is clear from these experiments that cation exchange is necessary for rapid O^{18} exchange and there is an apparent 1:1 correlation between the two. Experiment 17 shows that with 0.3 molal NaCl solution exchange was more extensive than with 3 molal KCl solution or pure water. After exchanging to the extent of 27 percent, the Na/K ratio in the solution of experiment 17 was less than 3, where normally it was greater than 10.

Group B. In this experiment relatively large grains (pass 50 and retain 100 mesh) of Amelia albite were reacted with 3 molal KCl solution for only one hour at 650°C. Previous experiments had shown that under these conditions neither the cations nor oxygen isotopes would be completely exchanged. These partially exchanged crystals were then reacted with approximately one-third the stoichiometric amount of fluorine and the liberated oxygen was labeled 32A. The remaining crystals were then treated with an amount of fluorine which liberated about half the remaining oxygen of these crystals, and this sample was labeled 32B. The rest of the crystals were completely fluorinated and this resultant oxygen was called 32C. The fluorination reaction is believed to take place by the fluorine successively "stripping" off outer layers of the mineral. That is, the oxygen of the mineral is "stripped" off from the outside of the remaining crystal during the course of the reaction. The isotopic data reveal that extensive exchange occurred in the outer parts of the crystals, but that negligible exchange took place in the cores. When the PE-2 perthite was subjected to an identical hydrothermal treatment and then examined under the microscope the characteristic gridiron twinning of the unreacted feldspar was evident in every core. These observations lead to the conclusion that a reaction front is sweeping through the crystal grain and again that there is essentially a 1:1 correlation between cation and oxygen isotope exchange.

Group C. Amelia albite (pass 200 mesh) was reacted at 650°C for 62 hours with 3 molal NaCl solution and with pure water, and for only 2 hours with 3 molal KCl solution. Exchange was nearly complete in the short-term run in KCl solution and the rate of exchange in pure water was almost double that in the NaCl solution. It is concluded that a common cation in solution (sodium ion in this case) inhibits the exchange process. The question of dissolution of albite arises immediately from these

observations. Any substance will have a finite solubility in pure water. The establishment and maintenance of an equilibrium solubility is a dynamic process involving dissolution and reprecipitation at the surfaces of the crystals. Such a mechanism in conjunction with solid-state diffusion of some oxygen-containing species must be important in the O^{18} -exchange process between solids and pure water. One of the dissolution products of albite will be sodium ion, and simply by the law of mass action, the presence of sodium ion in solution will put restraints on the feldspar solubility and affect the rate of O^{18} exchange by a mechanism involving solution and redeposition. Now, albite in the presence of a concentrated KCl solution is far removed from chemical equilibrium—the stable solid phase under these conditions being a potassium feldspar. Considering the K/Na ratio in the solution to be infinite, the very unstable sodium feldspar will go into solution readily (no common cation) and on the precipitation necessary to establish the feldspar equilibrium solubility the stable potassium feldspar will form. A proposal as to how this occurs is explained in a later section; it incorporates all physical and chemical observations made during the present study.

Group D. This series of experiments demonstrates that these synthetic materials undergo reactions at rates which are markedly enhanced over those of natural materials. This phenomenon probably reflects the increased surface area and more reactive sites arising from crystal imperfections in the synthetic materials. In this case the synthetic sanidine exchanged at a rate almost six times as fast as the natural albite from which it was made. The synthetic sanidine also exchanged at a much faster rate than a natural sanidine. Nothing can be concluded about the importance to rate of the silicon-aluminum disorder in the natural sanidine relative to the natural albite (ordered) because the surface areas of the two are not the same. Nonetheless the exchange rates of these natural materials are roughly comparable. Of importance here is the fact that the physical properties of the synthetic feldspar grains are so markedly different from those of the natural feldspars from which they are made by cation exchange in alkali chloride solution. A simple atom-for-atom exchange by solid-state diffusion would not be expected to produce such changes.

Group E. In no case was it possible to exchange the PE-2 perthite as much as 90 percent, reflecting the exchange-inhibiting effect of the common sodium ion in solution on the albite phase of the perthite. However, experiment 46 demonstrates that a natural sanidine ($K_{80}Na_{20}$) is capable of complete exchange with an alkali chloride solution, although at a slower rate than Amelia albite (experiments 78 and 79). Inasmuch as the

sodium and potassium ions are randomized in sanidine, both alkalis go into solution if exchange takes place during a stage that involves solution and reprecipitation. However, the sodium in the sanidine would make the feldspar less soluble in NaCl solution, which may be related to its exchange rate being less than that of pure K-feldspar in NaCl solution.

Group F. Natural Amelia albite (pass 100 and retain 200 mesh) was reacted at 500°C for 208 hours with a series of solutions: pure water; 3 molal NaCl; 3 molal chloride solutions with Na/K ratios of 30, 5, and 3; and 3 molal KCl solution. Even though the feldspar was well-crystallized albite it exchanged 87 percent with the KCl solution but failed to exchange either O¹⁸ or cations with the other solutions. According to the findings of Orville (1963), the equilibrium feldspar in the solution where the Na/K ratio was 3 should have been K₈₆Na₁₄, and yet the albite did not change at all in this time, presumably due to the presence of the sodium ion in solution. (This result is not in conflict with Orville's because his experiments were carried out with synthetic feldspar with the concomitant increase in reaction rate.)

In addition to the information gleaned from these rate and partial exchange experiments, further insight into the nature of the exchange process was obtained by microscopic, X-ray, and electron microprobe examinations:

(1) In general, the gross morphology of the crystals remain the same throughout the transformation.

(2) The exchanged crystal is always in aluminum-silicon disorder, even at 350°C. This phenomenon is always found to occur when water is present.¹

(3) Occasional new euhedral crystals were formed in the high temperature runs demonstrating that gross solution and reprecipitation is possible in these systems.

(4) The exchanged feldspar is poorly crystallized and replete with imperfections. It is also very friable with little mechanical strength. Griggs and Balci (1965) have made detailed observations concerning the effect of water on the mechanical strength of synthetic quartz crystals. They saw evidence from an infrared measurement that their synthetic quartz crystals contained approximately 0.1 percent water by weight. Infrared measurements at the same level of detection were made in the present work on the exchanged feldspars and they failed to show the presence of water.

(5) By use of the electron microprobe, chloride ion was found in some of the cleavage cracks which developed in the exchanged crystal. This indicates that the alkali chloride solution has access to the interiors of the crystals along cleavage cracks and the newly formed minute surfaces of physical discontinuity.

(6) The reaction or phase boundary between exchanged and unexchanged feldspar is quite sharp although rough and imperfect in appearance (see Fig. 6). Figure 5 illustrates the results of an electron microprobe analysis of a sample of Amelia albite partially exchanged

¹ If cation exchange occurs between a low feldspar and an anhydrous alkali chloride melt or alkali feldspar glass, the original silicon-aluminum order is maintained (Wyart and Sabatier, 1961; Laves, 1951).

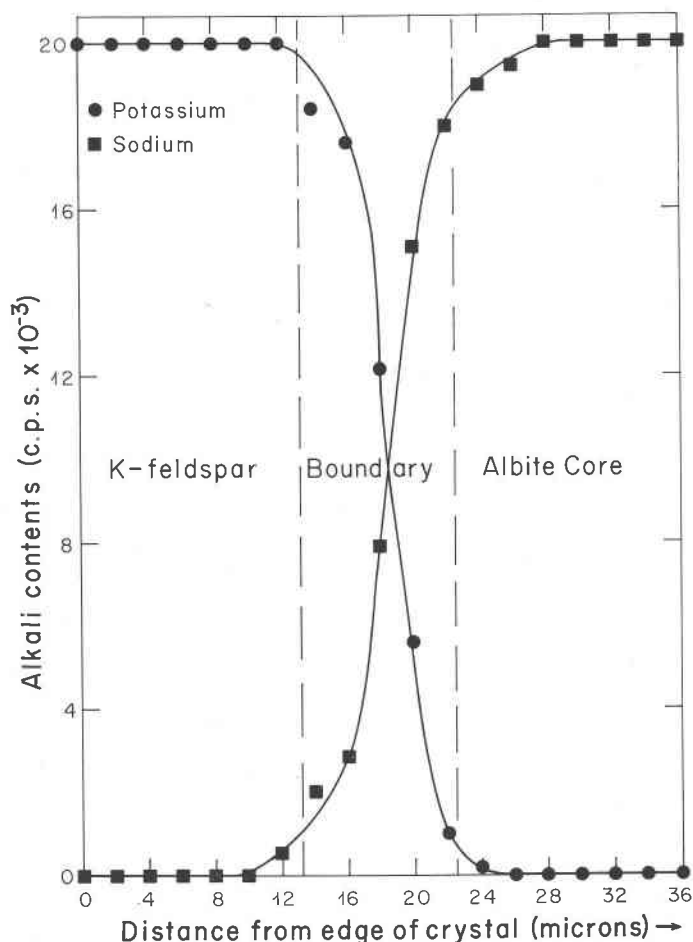


FIG. 5. Electron microprobe traverse from albite core through exchanged portion of crystal. Beam approximately 1 micron in diameter (20 Kv; 0.08 μ a). Readings taken at 2 μ intervals. Sodium values normalized by multiplying actual c.p.s. by 18.

at 700°C with KCl solution. No sodium was detectable in the exchanged potassium feldspar portion of the crystal. This is particularly significant considering that this experiment was carried out above the solvus temperature. There is apparently no appreciable solid-state diffusion of alkali ions across the boundary. Consequently the rate of communication of alkali ions at the boundary with the exteriors of the grains (or solution) is extremely rapid. In conjunction with the stripping experiment described above, it can be stated that there is an abrupt discontinuity in cation and O^{18} concentrations at the boundary.

(7) Figure 6 shows a series of photomicrographs of a partially exchanged crystal of Amelia albite, with the field focused either on the upper part of the grain (Figs. 6-1 and 6-2) or on the middle portion (Figs. 6-3 and 6-4). The bottom portion of the crystal (not

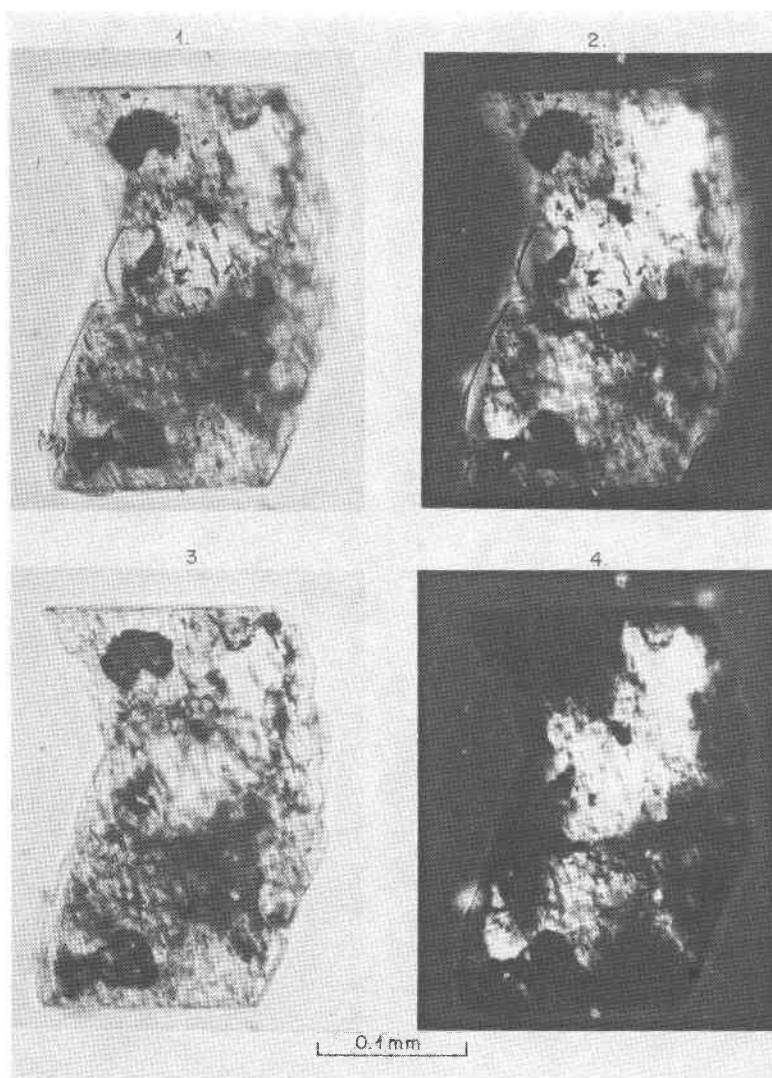


FIG. 6. Crystal of Amelia albite (0.27 mm in length) partially exchanged with KCl solution at 700°C. The crystal is lying on its (010) cleavage; in the photographs the top and bottom parallel edges correspond to the trace of the (001) basal cleavage. Note the large fluid inclusions in upper left- and lower left-hand corners of the crystal, tabular parallel to (010); the numerous small inclusions aligned along the (100) cleavage direction; separation of core remnants along (001) cleavage; the irregular but sharp boundary between core and rim; and the turbid, semiopaque appearance of the exchanged outer zone, particularly at the boundary between core and rim.

- (1) Focus on highest portion of crystal, the K feldspar envelope (plane light)
- (2) Focus on highest portion of crystal, the K feldspar envelope ($\times$ nicols)
- (3) Focus on middle portion of crystal, the albite core (plane light)
- (4) Focus on middle portion of crystal, the albite core ($\times$ nicols with rim at extinction)

shown) exhibits features essentially identical to the upper portion. The following were observed on microscopic examination of this and other exchanged crystals:

(a) In the exchanged outer zone there occur two large (0.03 mm), planar fluid inclusions, which are tabular parallel to (010), and are best seen in Figure 6-3 and 6-1.

(b) There are myriads of tiny inclusions oriented approximately along the (100) crystallographic direction in the exchanged outer zone. They can be seen above the unexchanged albite core in Figures 6-1 and 6-2.

(c) The boundary between albite core and exchanged outer zone is irregular, but sharp, semiopaque, and filled with inclusions.

(d) The remnant core is free of inclusions (Figs. 6-3 and 6-4).

(e) The core is optically continuous, as is the outer zone. In addition, the measured extinction angle difference between core and rim (15°) is that expected for albite and sanidine lying on (010) (Winchell and Winchell, 1959, p. 286).

(f) Replacement takes place preferentially along crystallographic directions. Note the bifurcation of the albite core by material which has entered along a (001) cleavage crack (Fig. 6-4).

Some of the features observed in these exchanged feldspars are similar to those noted by others in their studies of naturally occurring "clouded" or "turbid" feldspars. Poldervaart and Gilkey (1954) showed that deposition and replacement by other minerals occur along cleavage planes in natural feldspars and consequently proved that solutions do penetrate crystals along these passages. In addition to cleavage cracks these authors refer to "sub-boundaries" and "minute division surfaces" (a few unit-cell surfaces in size) as possible solution pathways. The fluid inclusions observed in the feldspars of this work are remarkably similar to features in turbid feldspars noted by Folk (1955). He observed fluid inclusions in feldspars strung out along cleavages, fractures, or certain crystallographic directions. The calcic cores of zoned plagioclase grains in igneous rocks are commonly sericitized or saussuritized, while the more sodic rims may be practically unaltered; this also suggests that aqueous solutions can penetrate feldspar grains along crystal imperfections.

With reference to the problem of "fitting-together" unexchanged albite and the pseudomorphing sanidine it is well to consider the significance of the particular orientation (100) of the fluid inclusions in the exchanged feldspar (Fig. 6). Although present in the Amelia albite used in this work, the (100) cleavage is not a major cleavage in albite. Of possible importance is the fact that this plane is perpendicular to the *a*-axis, which is the crystallographic direction of maximum expansion (or contraction) of the unit cell accompanying transformations from one alkali feldspar to another.

CONCLUSION

It is fairly clear from the isotopic data of the stripping experiment and other experiments and observations cited that there is a direct correlation between cation and O^{18} exchange. Exchange appears complete up to the phase boundary. This demands rapid communication between the boundary and the bulk solution. Alternatively stated, the rate of attainment of isotopic and cation exchange equilibrium is equal to or greater than the rate at which the reaction front sweeps through the crystal. On the basis of the results of this work, it is difficult to envision the isotopic exchange in these systems as resulting from simple solid-state diffusion of water molecules or hydroxyl groups in and out of the crystals (necessarily linked in some manner with the cations) and somehow causing

rupture and the reforming of Si-O and Al-O bonds (*e.g.*, Donnay *et al.*, 1959). This is to say nothing of the problems of size and charge of the diffusing species. It is well known that diffusion along grain boundaries or along surface films is much more rapid than solid-state diffusion through a crystal lattice, and this is the probable explanation of why synthetic crystals react so much faster than their well-crystallized natural equivalents.

The simplest proposal which accounts for all the observations would be one which involved a solution and redeposition step¹ (or at least extremely rapid oxygen exchange) at the boundary between exchanged and unexchanged feldspar. Certainly such phenomena are easily initiated at the surface of a crystal and can occur within the crystal itself at the reaction boundary if a fluid film is present. For that minute amount of material in solution at any one time the most convenient sites for feldspar "redeposition" are located in the immediate vicinity—the exchanged surface of the boundary. Once formed, the potassium feldspar is in chemical equilibrium with the KCl solution and the solution would further its attack on the remaining sodium feldspar by cation and H₂O diffusion along crystal imperfections in the exchanged feldspar. By growing in this manner the original morphology of the crystal could be retained. The new portion of the crystal, being rather quickly formed, (1) would not have time to establish aluminum-silicon order,² (2) would be poorly crystallized with resultant imperfections that allow the bulk solution access to inner portions of the crystal, (3) would have a tendency to incorporate fluid inclusions into the structure, and (4) having been in solution would have readily exchanged oxygen isotopes with the solution, equilibrating either during crystallization or by rapid surface exchange at active sites. With this explanation there must exist a fluid film at the boundary which is in direct communication and in isotopic and chemical equilibrium with the bulk solution. This fluid-filled boundary completely sweeps through the crystal. Using a homely analogy, every part of the crystal must have had to "swim" across this "river" in solution in order to reach the other side. It is not unreasonable that a single, optically continuous feldspar crystal could pseudomorphously replace another in this manner.

The natural extension of this postulated reaction mechanism is to the

¹ Goldsmith and Laves (1954) also discussed the possibility of dissolution of microcline and reprecipitation of sanidine in the presence of water and pointed out the difficulty of using such inversion information for establishing transformation temperatures in the alkali feldspar system.

² It is possible, however, that monoclinic sanidine may be the stable feldspar over the entire temperature range of these experiments.

problem of the importance of solid-state diffusion during alkali metasomatism in nature. The problem essentially involves whether or not large scale ionic replacements can take place without reconstruction of the aluminosilicate framework. In Battey's discussion of alkali metasomatism of feldspars in some keratophyres (1955), mention is made of the encroachment of K-feldspar around the borders of albite crystals and its advance along cleavages and other cracks. He states further that this progresses until tiny islands of albite remain enveloped in K-feldspar, and finally, until replacement is complete. It is conceivable that replacements in these feldspars took place by the mechanism suggested above and that the solution may not have interacted appreciably with the other minerals in the process. Such a phenomenon has already been observed in the case of the feldspars in certain red-rock granophyres mentioned above, where K-feldspar has apparently been deuterically exchanged, but coexisting quartz has not (Taylor, unpublished).

In addition to the application of the equilibrium oxygen isotope data presented in this paper to problems of geothermometry, oxygen isotope analyses of feldspars should prove to be a powerful tool in resolving such problems as discussed above for the case of alkali metasomatism. It has been demonstrated here that during reaction in the presence of a hydrothermal fluid, it is impossible to have cation exchange without accompanying oxygen isotope exchange. Cation exchange may well be the "driving force" which promotes oxygen isotope exchange between feldspars and aqueous fluids during deuteritic, hydrothermal, or metamorphic processes in nature.

ACKNOWLEDGMENTS

We thank Paul Yanagisawa for carefully performing most of the fluorine extractions of the oxygen in the feldspars, Fritz Laves, Leon T. Silver, W. Barclay Kamb, Samuel Epstein, P. M. Orville, and S. M. Sheppard for stimulating discussions, Arthur Chodos for the electron microprobe analyses, Elizabeth Bingham for various analytical services, and G. J. Wasserburg for supplying a sample of PE-2 perthite. Financial support for this research was provided by the National Science Foundation (Grants No. G23992, GP2254), by the Atomic Energy Commission Contract #AT (04-3)-427, CALT-427-15, and by the Alfred P. Sloan Foundation.

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Manuscript received, December 2, 1966; accepted for publication, April 19, 1967.