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The anomalous ion-exchange behavior of "ordered" orthoclase

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Abstract

In contrast to many successful previous ion-exchange studies of dry alkali feldspars, in which the aluminosilicate framework remained intact, "ordered" orthoclase from the Himalaya pegmatite–aplite dike system, San Diego County, California, invariably breaks down to sodalite spontaneously, very soon after Na-for-K exchange in a chloride medium. Our efforts to prepare a structurally-equivalent sodic feldspar in other exchange media, taking all precautions to eliminate water, also failed. Substitution of Rb for K appears very limited, and may also lead to breakdown and nucleation of other silicates. These anomalies are attributed to the mismatch between the coordination polyhedron about the alkali atom and an Al,Si framework unable to shrink or deform because of intimately balanced, very small triclinic domains set in a structure that is monoclinic to X-rays and neutrons. Our results support a proposal that this type of orthoclase is distinct, the first documented example of the "theoretical" maximum low sanidine or "theoretical" orthoclase structure type.

Introduction

Low microcline is the expected polymorph of K-feldspar in granitic pegmatites, and is the one found in the pegmatites of the Pala, Ramona, and Mesa Grande districts, southern California. Its prominent well-developed cross-hatch pattern of twinned crystalline domains interrelated by the albite and pericline twin laws results from the efficient Si–Al ordering of a higher-temperature, disordered, monoclinic parent single crystal. During this event, catalyzed by the aqueous fluid phase that characterizes pegmatitic systems, Al has preferentially ordered into the T_1O, T_1m, T_1Oc, or T_1mc site in different regions of the original crystal (Ribbe, 1975, p. R23), presumably at temperatures high enough for the coarsening of twinned individuals to proceed efficiently through solution and redeposition.

Orthoclase is not expected in microcline-bearing pegmatites, but its occurrence in gem-bearing central pockets (Jahns and Wright, 1951; Prince *et al.*, 1973, Fig. 1) in a number of pegmatitic bodies in southern California first aroused curiosity; the water-rich environment of a pegmatite pocket should have assured the transformation of any monoclinic precursor to low microcline. No hint of such a transformation can be found in the orthoclase. The cell dimensions of these orthoclases differ appreciably from the type of orthoclase commonly found in mesozonal to epizonal granitic rocks. A neutron diffraction structure refinement (Prince *et al.*, 1973), performed on a single-phase, gem-quality pocket orthoclase from the Himalaya Mine, Mesa Grande district, California, showed that the feldspar is monoclinic to neutrons and to X-rays, since a statistical analysis of diffracted intensities showed the reciprocal lattice to have point group symmetry $2/m$. The degree of Si–Al order is essentially complete for a monoclinic feldspar, as illustrated by the structural formula $(K,Na)(Al_{0.5}Si_{0.5})_2Si_2O_8$. Information bearing on the Si–Al distribution came from a direct site refinement using neutron-diffraction data. These data and a bond-valence summation showed no evidence of OH-for-O substitution.

It is incumbent upon those who propose a new polymorphic form of K-feldspar intermediate in degree of Si–Al order between high sanidine, $(K,Na)(Al_{0.25}Si_{0.75})_4O_8$, and low microcline, $(K,Na)AlSi_3O_8$, to demonstrate convincingly that the new form differs significantly in physical properties from known polymorphs. Ion-exchange experiments designed to prepare a series of isostructural alkali feldspars provide one sensitive test of the redundancy between the "ordered orthoclase" structure (Prince *et al.*, 1973) and previously-defined structure types. The anomalies we observed reinforce previous con-

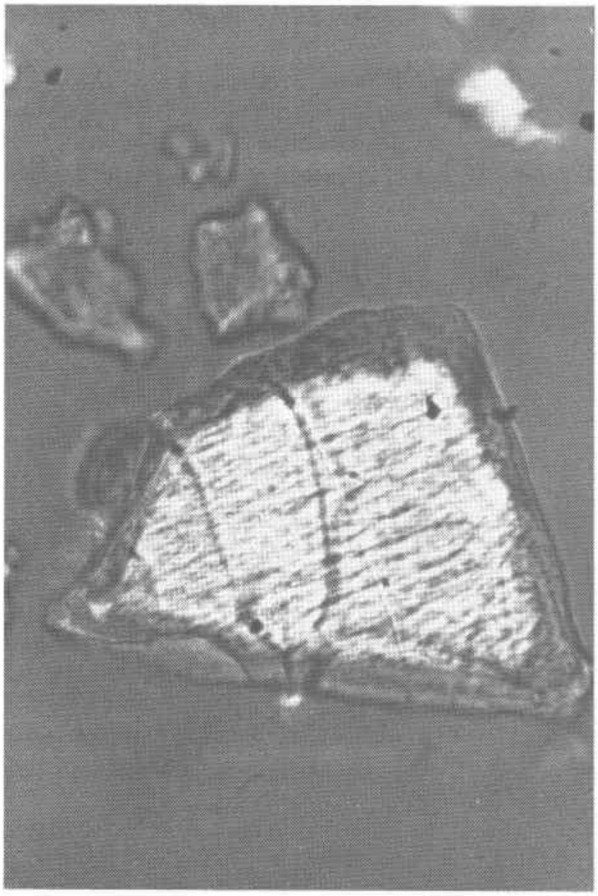

Fig. 1 Na-equivalent of Himalaya orthoclase after 48 hours ion exchange in NaCl at 775°C. Most of the grain is still Na-feldspar, but a continuous isotropic rim of sodalite has developed in this short time. Note that the feldspar looks "perthitic," due to the development of channels containing sodalite; the channels presumably reflect shrinkage during exchange. Grain mount photographed with crossed nicols, 700×, R.I. of oil 1.620.

clusions that this monoclinic feldspar is well-ordered and structurally distinct from previously-studied K-rich alkali feldspars.

Ion-exchange experiments: the influence of H_2O

Exchange of the alkali ion between feldspar and an exchange medium proceeds very differently, depending upon the presence or absence of water. Wyart and Sabatier (1956) found that the aluminosilicate framework could be preserved intact during alkali exchange in the absence of water. With molten alkali chlorides, for example, they obtained low albite from low microcline, even at 900°C. With aqueous solutions of alkali halides, even at much lower temperatures, the disordered polymorph, high sanidine or analbite, invariably appeared as a result of solution and redeposition steps. The direct involvement of water in the dissolution steps and in the precipitation of structurally-different products is clearly documented by concomitant oxygen exchange with the fluid, as monitored by $^{18}O/^{16}O$ ratios (O'Neil and Taylor, 1967; Mérigoux, 1968). Clearly, the preparation of isostructural feldspars from this unusual orthoclase requires the elimination of water from the reacting assemblage.

A number of investigators have substantiated the findings of Wyart and Sabatier (1956) that in dry ion-exchange experiments the framework remains intact, and that sodic analogues of ordered and disordered K-feldspars can be prepared. Orville (1967) reacted sanidine and microcline with 30 times their weight in NaCl at 900°C for 48 hours in a tightly-covered Pt dish. The resulting albites were back-exchanged in molten KCl to yield sanidine or microcline of the same structural state as the starting material. Wright and Stewart (1968) successfully prepared sodic equivalents of many structurally-intermediate K-feldspars, though with certain orthoclases, Na-for-K exchange was not complete even after 2 or 3 consecutive exchanges, each in fresh NaCl melt at 850°C for 24 hours. Manecki (1970) successfully prepared ordered albite from microcline (and vice versa) in experiments at 740°C for 50 hours, *i.e.,* at a temperature well below the melting point of the chloride exchange medium. He observed partial Na-for-K exchange in orthoclase and monoclinic adularia after 50 hours at 720° and 740°C, respectively; in all cases, the starting mixture was first dried at 105°C. Bachinski and Müller (1971) used "thoroughly dried" alkali iodide as exchange medium in sealed Pt capsules in their study of the miscibility gap between low albite and low microcline. The lower melting points of alkali iodides helped insure against structural changes in their study of ordered feldspars held beyond their field of stability. From alkali feldspars hydrothermally synthesized at 1 kbar and 600°C, Delbove (1971) obtained structurally-equivalent disordered feldspars. His exchange experiments in various halide melts at 800°C lasted from 10 to 15 days. Waldbaum and Robie (1971) prepared ordered and disordered varieties of pure Na- and K-feldspars from natural or heated Amelia albite. They found no detectable change in Si–Al distribution as a result of their 910°C, 24-hour exchange experiments in chloride melts. In his investigation of mechanism of ion-exchange, Petrović (1973) dried the NaCl and KCl at temperatures up to 400°C for at least 24 hours before mixing with feldspar in a 100 to 1 ratio by weight. Albite wedges developed in monoclinic adularia crystals exposed to molten NaCl in runs of 840° for 20 hours, at 940° for 22 hours, and at 960°C for 11 hours. Although no information is provided on the degree of Si–Al order in the albitic wedges, there is no reason to suspect structural reorganization of the framework (R. Petrović, private communication, 1976). Finally, Hovis (1974) exchanged Na for K in a number of monoclinic K-feldspars to obtain starting materials closer to $KAlSi_3O_8$ composition for his solution-calorimetry study of monoclinic feldspars. His feldspars were ground to −325 mesh, dried, placed in Pt crucibles with a large excess of KCl and exchanged at 820°C for 28 to 38 hours. Again, no structural changes were detected as a result of the exchange.

In the experiments reported here, the following efforts were made to remove water from the reacting assemblage. The exchange medium was pulverized, heated above 600°C for 24 hours, then stored in a dessicator until used in the experiment. Special precautions were also taken with the feldspar specimen itself; as with most minerals formed in pegmatitic systems, the feldspar contains numerous small fluid inclusions, many with a gas bubble. These inclusions, measuring up to 10 microns across, presumably account for most of the H_2O+ reported in the chemical analysis of the orthoclase (0.44 weight percent H_2O liberated above 117°C; Table 1), as no evidence could be found for structurally-bound OH (Prince *et al.*, 1973). Differential thermal analysis shows that the water starts to be given off almost as soon as the sample is heated and continues escaping until 450°; the curve from 450 to 1000°C is flat and featureless. The DTA pattern rather resembles that of opal, in which fluid inclusions occupy voids between closely-packed spheres of amorphous silica (Darragh *et al.*, 1976). The broad range of temperatures necessary to expel the water reflects the relatively strong adsorptive forces binding water to the walls of capillaries and cavities; the smaller the cavity, the stronger the forces.

Another indication that water is not structurally bound is provided by thermogravimetric analysis, unfortunately limited to 400°C in the apparatus available to us. The 0.44 weight percent lost by heating to 400° agrees well with the 0.46 weight percent loss during the Penfield test, in which the pulverized feldspar is heated above 1000°C, and with the 0.48 weight percent lost on ignition to 1000°C during chemical analysis. In view of these results, the pulverized feldspar was also heated to 1000° for one hour, then to approximately 600°C for 24 hours before the ion-exchange experiments.

Table 1. Chemical analysis and structural formula of an overgrowth orthoclase, Himalaya pegmatite–aplite dike system, Mesa Grande district, San Diego County, California

	% by weight	Atomic proportions		
SiO_2*	65.32	Si	3.005	T = 4.000
Al_2O_3	18.25	Al	0.990	
B_2O_3	0.06	B	0.005	
Fe_2O_3	0.001			
MnO	0.00			
MgO	0.00			
CaO	0.05	Ca	0.002	M = 0.959
SrO	0.006			
BaO	0.25	Ba	0.005	
Na_2O	1.12	Na	0.100	
K_2O	14.25	K	0.838	
Rb_2O	0.47	Rb	0.014	
H_2O^+	0.44			
H_2O^-	0.02			
	100.24			

* Wet chemical analysis by S.J. Horsky; details of analytical technique given in Horsky (1974). Slight deficiency in positive charges probably reflects analytical error.

The stringent measures taken before the experiments began helped eliminate water from the reacting assemblage in the tightly-covered Pt crucible. As Petrović (1973) points out, $P(H_2O)$ values in air above the chloride + feldspar assemblage in the crucible must have been of the order of 10^{-2} bar at the most. Many experiments were run a few degrees below the melting temperature of the exchange medium; in this way, the mixture chloride+feldspar could remain intimate, favoring efficient exchange. Some runs were repeated at higher temperatures, so that the layer of melt overlying the feldspar grains sedimented on the bottom of the crucible further minimized the negligible interaction with atmospheric moisture. End products of such duplicate runs were always identical. In all cases, the exchange medium was dissolved after 24 hours, the sample dried, and the experiment repeated for another 24 hours in a fresh batch of exchange medium. After washing the NaCl away, the experiment was prolonged for 52 hours, the product washed, dried, put in for another 100 hours, washed and dried again, and finally held for an additional 200 hours. Structural and mineralogical changes were monitored by powder X-ray diffractometry using a

Table 2. Cell parameters, Himalaya Mine orthoclase and derivative monoclinic feldspars

	a(Å)	b(Å)	c(Å)	β	V(Å^3)	standard error 2Θ	# of lines used
1*	8.5632	12.9633	7.2099	116.073°	718.90	0.010	27
	.0011	.0014	.0011	.009	.11		
2	8.5657	12.9682	7.2095	116.049°	719.49	0.008	32
	.0007	.0012	.0005	.006	.07		
3	8.6021	12.9729	7.2141	116.008°	723.53	0.013	40
	.0011	.0016	.0009	.010	.10		
4	8.6028	12.9700	7.2141	116.006°	723.43	0.006	34
	.0006	.0009	.0005	.005	.06		
5	8.6018	12.9727	7.2066	115.992°	722.84	0.017	28
	.0017	.0024	.0016	.015	.17		
6	8.5982	12.9685	7.2167	116.064°	722.87	0.009	36
	.0008	.0009	.0005	.006	.07		

1*: gem quality orthoclase, Himalaya pegmatite, Mesa Grande district, San Diego County, California. As used in neutron diffraction structure refinement of Prince *et al.*, (1973).

2: orthoclase heated to 1000°C for 1 hour; milky appearance.

3: K-exchanged orthoclase; held in KCl for 48 hours at 740°C.

4: K-exchanged orthoclase; held in KCl for 100 hours at 740°C.

5: Rb-exchanged orthoclase; held in RbCl for 400 hours at 650°C.

6: Rb-exchanged orthoclase; held in RbCl for 600 hours at 800°C.

Guinier-Hägg camera (Cu$K\alpha_1$ radiation, $\lambda = 1.54056$ A) and a synthetic spinel internal standard ($a = 8.0833$ A at room temperature).

Composition and structural state of starting material

Cell dimensions of the Himalaya orthoclase, calculated with the program of Appleman and Evans (1973) using indexed, corrected 2θ values, are presented in Table 2. The two estimates of composition, 88.9 and 88.6 mol percent Or, agree with the measured composition (Tables 1, 3). The orthoclase is definitely unusual in its high degree of Si–Al ordering, as indicated by its position in the b–c quadrilateral close to the microcline corner and in the b^*–c^* diagram (Smith, 1974, Fig. 9–11) in the field of high microcline, and its calculated Al occupancy in the T_1 site, 0.92 (Table 3). The direct refinement of site occupancy from neutron-diffraction data obtained on the same feldspar specimen (Prince *et al.*, 1973) indicates that Si–Al order is apparently even more perfect, and essentially complete for a monoclinic feldspar.

Chips of the transparent feldspar heated to 1000°C for one hour become milky. This startling change in appearance is attributed to decrepitation of the myriad fluid inclusions and propagation of the fluid along cracks and clevages in the chip. Cell dimensions recorded after this heat treatment (entry 2, Table 2) show that no structural changes have occurred.

Results of ion-exchange experiments

(1) Exchange with KCl

The sodium in the Himalaya Mine orthoclase (Table 1) can readily be exchanged by placing the feldspar in a large excess of KCl in two stages of 24 hours at 740 ± 20°C. The single-phase product has cell dimensions as given in Table 2 (entry 3). N_{Or} can be calculated using a and (t_1O + t_1m), or unit-cell volume (Martin, 1974a; Stewart and Wright, 1974). By the first method, the exchanged feldspar contains 97.1 mol percent Or, by the second 102.0 percent (Table 3); K-for-Na exchange must be essentially complete. Holding the feldspar in KCl for 100 hours at 740°C gives a feldspar virtually identical in cell dimensions (Table 2, entry 4). Interestingly, the estimate of composition based on *a* still is close to 97 percent Or (Table 3). Calculated occupancies of Al in the T_1 site, 0.927 after 48 hours, 0.933 after 100 hours, show that no significant structural changes involving Si–Al distribution have occurred during ion exchange.

(2) Exchange with NaCl

In view of our successful K-for-Na exchange and the success of others in preparing sodic equivalents of K-feldspars by dry ion exchange, we anticipated few problems in substituting sodium for potassium. Instead, we found unexpectedly that as soon as exchange with NaCl had been achieved at approximately 775°C, the structure broke down and sodalite appeared in place of the feldspar. After 48 hours of exchange only five relatively broad and diffuse X-ray diffraction lines could be unambiguously attributed to feldspar, too few for a cell refinement. The $(\bar{2}01)$ peak has a corrected value of 21.963 2θ, equivalent to 3.8 mol percent Or, using an equation relating 2θ (201) and N_{Or} for the orthoclase-equivalent series of Wright and Stewart (1968). The powder-diffraction pattern also contains five sharp lines attributed to the newly-formed sodalite. A grain mount shows that most grains are still Na-feldspar, but that many have an isotropic rim (Fig. 1). We note that the feldspar looks lamellar, and that sodalite is making inroads along boundaries between "lamellae." This "perthitic" aspect is attributed to shrinkage resulting from Na-for-K exchange. As only the strongest lines of albite are recorded on a Guinier film, it appears that much of the feldspar seen in Figure 1 is actually a feldspar+sodalite mixture, with sodalite distributed as films along shrinkage cracks.

After 100 hours of exchange, the X-ray pattern featured sharp, easily-measurable lines; fifteen of these now matched peaks of a well-characterized sodalite (Löns and Schulz, 1967). Only four belonged to Na-feldspar; the $(\bar{2}01)$ reflection had not shifted from its position in the 48-hour exchange product, indicating that ion exchange had not progressed. In view of these unexpected results, the experiment was repeated with a fresh portion of Himalaya Mine orthoclase. Results of this second experiment confirmed the rapid breakdown of Na-feldspar and growth of sodalite.

After 200 hours of exchange at 775°C, the total area of sodalite rims clearly exceeds that of Na-feldspar core (Fig. 2). Sodalite lines are now more numerous; the 2θ value of the weak feldspar $(\bar{2}01)$ reflection is 21.990°, equivalent to 1.42 mol percent Or, using an equation for Wright and Stewart's (1968) orthoclase-equivalent series. After 400 hours of exchange at 775°C, the grains were invariably isotropic, some of them having as inclusions minute domains of feldspar visible under the highest magnification. Domains of remnant feldspar were too small to produce measurable diffraction lines. Twenty-five indexed reflections of sodalite gave a cell edge of 8.8705(3) A, in agreement with the reference sodalite from Bolivia, 8.870 A (Löns and Schulz, 1967). The refractive index of our sodalite, 1.485, corresponds to the expected value.

Table 3. Composition and degree of Si–Al order, Himalaya Mine orthoclase and derivative monoclinic feldspars

	N_{Or}*		Al in T_1 site	Al in T_2 site
1	0.889,	0.886	0.921(1.0)	0.079(0)
2	0.894,	0.901	0.907	0.093
3	0.971,	1.020	0.027	0.073
4	0.973,	1.017	0.933	0.067
5	0.970,	0.998	0.878	0.122
6	0.964,	0.999	0.955	0.045

*N_{Or} calculated using *a* and $(t_1o + t_1m)$ parameters (Martin, 1974a) and the unit cell volume V (Stewart and Wright, 1974). N_{Or} = 1.0 for $KAlSi_3O_8$. Entry nomenclature as in Table 2.

Al in T_1, T_2 tetrahedral sites calculated by the expression of W.C. Luth (in Stewart and Wright, 1974). Value quoted in parenthesis in entry 1, the starting material, is the result of a site refinement of Al occupancies obtained in the final stages of structure refinement using neutron diffraction data (Prince *et al.*, 1973).

The NaCl exchange experiment was repeated at 850°C, well above the melting point of the exchange medium. After only 48 hours of exchange at this higher temperature, the breakdown of the feldspar structure to sodalite was complete.

The following simplified reaction could express the observed feldspar breakdown:

$$3Na(Al_{0.5}Si_{0.5})_2Si_2O_8 + NaCl = Na_4(AlSiO_4)_3Cl + 6SiO_2$$

Note that the coexistence of sodalite, a SiO_2-unsaturated mineral, and free silica is manifestly metastable. No crystalline form of SiO_2 was identified in grain mount nor detected by X-ray diffraction. However, light particles were observed on elutriation, as the NaCl was dissolved carefully after a long exchange experiment on chips of the heated orthoclase. SEM images of these chips show an irregular, cracked, corroded-looking surface consisting of sodalite covered by minute particles and spheres, presumably of

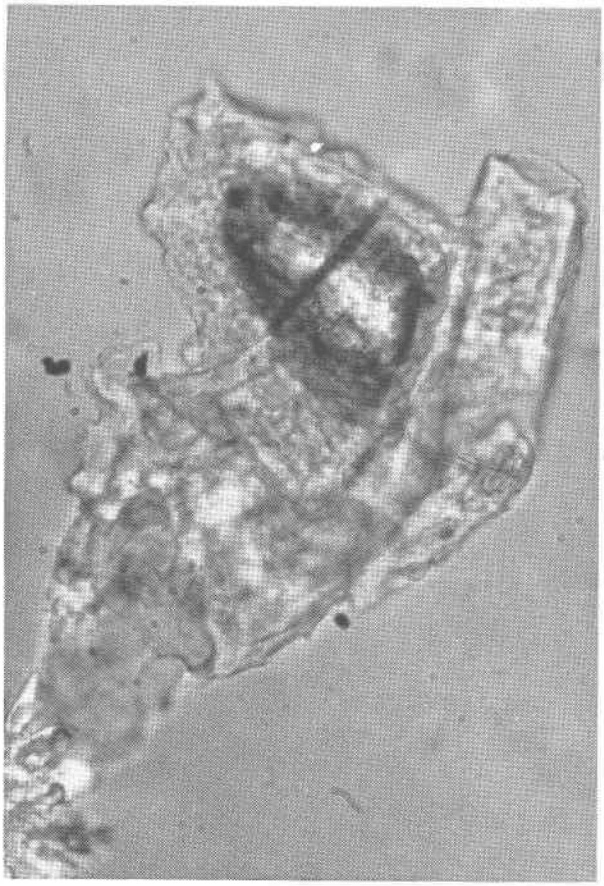

Fig. 2 Na-equivalent of Himalaya orthoclase after 200 hours ion exchange in NaCl at 775°C. The replacement of feldspar by sodalite is nearly complete. Only the core region consists of a Na-feldspar + sodalite assemblage. Grain mount photographed with crossed nicols, 700×, R.I. of oil 1.620.

amorphous silica. Most of the silica liberated was apparently washed away with NaCl, passing through the filter used to retain the feldspar.

(3) Exchange with Na_2SiO_3

Powdered and dried Himalaya Mine orthoclase was mixed with a large excess of anhydrous Na_2SiO_3, to see whether a sodic equivalent could be prepared more successfully in an exchange medium of higher silica activity. The feldspar was exchanged at approximately 775°C, and the products of ion exchange again examined after 48, 100, 200, and 400 hours. Microscopic observation confirmed that the feldspar framework was completely destroyed even after 48 hours of exchange; only isotropic material was observed microscopically. Powder patterns taken after each stage show consistent results: only lines for the spinel standard and a diffuse band typical of amorphous materials appeared.

(4) Exchange with NaI

Powdered orthoclase and a large excess of anhydrous NaI were held at 625 ± 20°C, *i.e.*, below the melting point of NaI, and examined after 48, 100, 200, and 400 hours. The feldspar framework broke down during the first stage of Na exchange; only after 400 hours of exchange, during which fresh NaI was added after 48, 100, and 200 hours, were sharp lines recorded on Guinier films. The forty lines recorded in the angular range 15–55° 2θ (Horsky, 1974, Appendix 7) do not match patterns of known compounds, including that of iodine sodalite (Taylor, 1975). The product appears to consist of a mixture of two phases.

Taking into account the difference of 150°C in the temperature of exchange, the results of the experiment with NaI agree with those runs made with NaCl and Na_2SiO_3 exchange media. All show that a sodium analogue of the Himalaya Mine orthoclase is most unstable; breakdown of the structure occurs rapidly even in the absence of water.

(5) Exchange with RbCl

In view of the instability of the structure when a small monovalent cation like sodium replaces potassium, we anticipated that a rubidium analogue could be prepared easily. The first series of experiments was run at 650 ± 20°C, well below the melting point of RbCl. After dissolving the exchange medium, fresh RbCl was added after 24, 48, 100, and 200 hours. The feldspar structure was not destroyed after the 400-hour treatment, but neither was $RbAlSi_3O_8$ formed. Cell dimensions of the product (entry 5, Table 2) resemble those of K-exchanged orthoclase (entry 3) rather than those expected for $RbAlSi_3O_8$ (Ghelis and Gasperin, 1970). Since the unit-cell volume has increased as a result of exchange, Rb has been added, but apparently not at the expense of Na. The proportion of Na to Rb must be close to unity, to give a ternary feldspar having a and V essentially those of $KAlSi_3O_8$. N_{Or}, calculated assuming the exchange product is an Na–K feldspar, approaches 1.0 (Table 3).

To test whether this restricted extent of Rb-for-K exchange could be attributed to the temperature of exchange, the sequence of experiments was repeated at 800°C, above the melting point of RbCl, and prolonged to 600 hours. The single-phase product recovered (entry 6, Tables 2, 3) is virtually identical to the product of the subsolidus experiment. Dilating the structure by increasing temperature has not led to greater exchange. Again, N_{Or} suggests an average cell size, as dictated by Na, K, and Rb population of the alkali site, very close to that of pure K-feldspar. Discrepancies in the estimate of Al in the T_1 site in the two feldspars obtained with RbCl (entries 5 and 6, Table 3) presumably reflect small differences in the ternary composition of the products rather than real structural differences.

(6) Exchange with Rb_2CO_3

In a final attempt to obtain a rubidium-bearing structural equivalent of the Himalaya Mine orthoclase, exchange experiments were run with Rb_2CO_3 at 800°C, the same temperature as in the last set of experiments with RbCl. Here, the final product is not a feldspar. Diffraction patterns and optical properties resemble, but do not match fully, those of cubic $RbAlSiO_4$. In contrast with RbCl at the same temperature, the presence of Rb_2CO_3 has caused complete breakdown of the feldspar structure and nucleation of a new phase. The difference in results may illustrate the greater tendency of an alkali carbonate to react with a silicate, a property applied routinely at temperatures above 1000°C during the chemical analysis of silicates by classical techniques.

Discussion

Results of previous ion-exchange studies of alkali feldspars, reviewed in the introduction, corroborate the findings of Wyart and Sabatier (1956): in the absence of water, the Si–Al distribution of the starting material is preserved despite complete exchange of the monovalent cation. None of the authors cited above observed structural breakdown of a feldspar framework during their anhydrous ion-exchange experiments, despite a wide variety of starting materials. Of course, when ion exchange is carried out in the presence of water, precautions must be taken to prevent desilication that reflects short-term incongruent dissolution phenomena (Currie, 1968). For example, R. F. Fudali (unpublished data) did observe partial conversion of alkali feldspars to a sodalite-type phase as a consequence of interaction with hot alkali chloride brines (discussion in Wyart and Sabatier, 1961). As we have taken extreme precautions to remove water from the reacting assemblage, the structural changes observed cannot be attributed to incongruent dissolution. The experiment with Na_2SiO_3 further demonstrates that in an environment where products of desilication (*e.g.*, sodalite or other silica-unsaturated minerals) are precluded, this feldspar structure is still effectively destroyed. Purely structural reasons must account for the unusual behavior exhibited by the Himalaya Mine orthoclase.

Prince *et al.* (1973) have identified the structural features that distinguish this alkali feldspar from others studied so far by X-ray or neutron diffraction. On the basis of a careful neutron diffraction study, fractional Al contents in the T_1 site of 0.516 ± 0.029, and in T_2 of −0.016 ± 0.029 were found. As fractional occupancies cannot be negative, the T_2 site is therefore populated by Si atoms, whereas the T_1 site is filled by Si and Al in the proportion 1 : 1. This pattern of Al distribution in a structure monoclinic to X-rays and to neutrons corresponds to Smith's *theoretical maximum low sanidine* (= *theoretical orthoclase;* Smith, 1974, p. 430). The word "theoretical" in Smith's system of nomenclature implies that this form of K-feldspar occurs in theory, not in nature; to most geologists, the term "sanidine" implies a volcanic environment. The name *ordered orthoclase* proposed by Prince *et al.* (1973) has no place in schemes of nomenclature currently in vogue, but does convey succinctly the essential features of this structure: (1) Al is completely ordered into the T_1 site; (2) this K-rich feldspar appears monoclinic to optical tests and to X-ray and neutron-diffraction techniques, and (3) it occurs in a mesozonal plutonic environment.

Although no violations of monoclinic symmetry have been found in precession and Weissenberg X-ray photographs, in statistical studies of intensities of selected diffraction peaks using an automated diffractometer system (Horsky, 1974), or in the neutron-diffraction study (Prince *et al.*, 1973), diffuse streaks passing through several strong reflections in Weissenberg *c*-axis zero-level photographs do occur (Horsky, 1974). These probably result from both normal thermal scattering and development of submicroscopic triclinic domains. These must be very small and regularly disposed so that the mirror plane is obeyed. More information on the scale of these domains must await electron diffraction and high-resolution electron imaging studies.

A slight coarsening of the triclinic domains from the scale initially present in the pegmatitic maximum low sanidine may well have occurred during the subsolidus evolution of the Himalaya pegmatite, as the feldspar crossed the field of stability of low microcline. The fact that ordered orthoclase (or maximum low sanidine) did form in a hydrous environment such as a pocket in a pegmatite suggests that it may be a thermodynamically stable phase at temperatures near the pegmatite solidus (Martin, 1974b), above the field of stability of low microcline. The equilibrium attainment of maximum low sanidine during the Si–Al ordering of a disordered feldspar in a pegmatitic system would agree with what Smith (1974, p. 72, 430) has considered the ideal two-step trend of ordering in K-rich feldspars, to be expected wherever true equilibrium has been reached in nature. Failure to follow the trend fully thus implies failure to attain equilibrium, evidently the case in most natural environments. In the pocket portion of the Himalaya pegmatitic system, the two-stage trend was arrested soon after the first stage was reached. This may reflect a sudden and explosive loss of the volatile phase from which growth occurred; equilibrium with such a fluid would be required to transform the ordered orthoclase into low microcline at a somewhat lower temperature. Foord and Jahns (1975) found clear evidence for episodes of violent rupture of the pegmatite pockets in the Himalaya system from detailed investigations of zonation in tourmalines. A fluid phase out of equilibrium with the ordered orthoclase may have been introduced after rupture. For purely kinetic reasons, reflecting in part the compositional influence of the fluid phase (Martin, 1974b), the transformation to low microcline locally has not proceeded to completion.

Why does this unusual structure react the way it does during ion-exchange experiments? An answer emerges from a discussion of the changes that accompany ion exchange in more ordered and more disordered feldspars. In high sanidine, the *M* cation has nine nearest neighbors disposed in an irregular polyhedron. When Na replaces K the nine oxygens cannot all approach the *M* cation and simultaneously respect the *T*–O distances of the disordered framework (Smith, 1974, p. 95). As a result, high albite has no plane of symmetry, though the topochemistry of the Al,Si distribution is still consistent with monoclinic symmetry. When Na replaces K in a fully-ordered structure, the additional distortion from collapse about the Na causes an even greater deviation from monoclinic symmetry, and the five closest oxygens now define a distorted trigonal bipyramid, as in the reedmergnerite structure (Smith, 1974, p. 38, 113). When Na replaces K in common orthoclase (usage of Smith, 1974, p. 419), exchange is notably incomplete, and cell parameters of the product are invariably those of a disordered feldspar (Wright and Stewart, 1968, p. 69). The Himalaya orthoclase differs from common orthoclase in containing no Al in the T_2 site, all the aluminum being distributed randomly among T_1O, T_1m, T_1Oc, and T_1mc (Ribbe, 1975, Fig. R-16). Such a pattern of random distribution means that the structure is "balanced" on a very fine scale, and effectively locked; it cannot collapse in response to introduction of Na in the place of K, which results in an attempt by the *M*–O polyhedron to contract. The coherency stresses due to mismatch may exceed 10 kbar, if an analogy can be made with the stresses between coherent sodic and potassic domains in a feldspar undergoing replacement (Petrović, 1973). We conclude that the coherent strain developed between the coordination polyhedron about the *M* cation and the unusual monoclinic (Al,Si)–O tetrahedral linkage described above is sufficiently great when Na occupies the monovalent cation site to lead to spontaneous breakdown of the structure. The efficiency of this breakdown in the absence of the hydrogen ion is especially surprising, in view of the catalytic role of H in the breaking of strong Si–O and Al–O bonds in other mineral reactions (Donnay *et al.,* 1959), including the ordering of a disordered feldspar (Martin, 1974b).

Presumably for the same reason of mismatch between *T*–O network and the *M*–O coordination polyhedron, rubidium fails to diffuse into the structure to any appreciable extent. At least at the temperatures of the ion-exchange experiments, the limiting mean atomic radius that can be accomodated in the *M* site to minimize mismatch would appear to approach that of the potassium atom. The same phenomenon may well explain the inability of certain common orthoclases to exchange Na for K completely, as suggested by Wright and Stewart (1968, p. 69).

Conclusion

The ordered structure of the Himilaya Mine orthoclase was apparently stable near the pegmatite solidus, and has survived metastably, perhaps because of sudden loss from the pegmatitic system of a suitable aqueous medium for Si–Al ordering to proceed. It has remained as a vestige of the end of the first step in the ideal two-step ordering scheme proposed for K-rich feldspars. Whereas a potassic analogue of the structure can be prepared with ease, sodic and rubidic analogues are clearly unstable; breakdown invariably occurs if sodium enters the *M* site. Very little rubidium can be accomodated by the structure, and breakdown occurs in an exchange medium more reactive than chloride. The anomalies described are consistent with the proposal that the Himalaya Mine orthoclase is structurally distinct, the first documented example of *theoretical maximum low sanidine* (= *theoretical orthoclase*), a structure type that should no longer be considered only in theoretical terms.

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