

Neutron Diffraction Refinement of an Ordered Orthoclase Structure

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Abstract

The crystal structure of a pegmatitic monoclinic potassium feldspar, $(K_{0.86}Na_{0.10}\square_{0.04})(Si_{1.00}Al_{1.00})[O_{7.96}(OH)_{0.04}]$, from the Himalaya mine in the Mesa Grande pegmatite district, California, has been refined with 3-dimensional neutron-diffraction data to an unweighted R value of 0.031 for 721 symmetry-independent observed reflections. Atomic coordinates differ by no more than 3 estimated standard deviations from those of Spencer B adularia, yet the specimen does not have the adularia morphology, and no diffuse reflections with $(h + k)$ odd have been observed. Direct refinement of the tetrahedral cation distribution shows that the Al content of the $T(2)$ sites is not significantly different from zero (actually -0.016 with an e.s.d. of 0.029); in other words the Al-Si ordering in the tetrahedral sites is essentially complete. The mean Si-O distance in the $T(2)$ sites is 1.616\AA , appreciably greater than the values predicted by various regression lines relating bond distance to aluminum content. This indicates that the observed mean $T_1(m)\text{-O}$, $T_2(O)\text{-O}$, and $T_2(m)\text{-O}$ bond lengths reported for low albite and maximum microcline are consistent with full Si occupancy. This ordered orthoclase occurs in gem pockets in a microcline-bearing pegmatite. The association suggests stable growth of ordered orthoclase above the field of stability of microcline and metastable persistence to lower temperatures. Perhaps because of more rapid crystal growth, the bulk of the pegmatitic K-feldspar ordered to common orthoclase, then transformed to maximum microcline.

Introduction

During a continuing study of the occurrence of hydroxyl ions and water molecules in minerals, a valence sum (Donnay and Allmann, 1970) was performed on orthoclase, using published atomic parameters (Jones and Taylor, 1960; Colville and Ribbe, 1968). This summation showed a low value of the sum for the oxygen atom in position O_c , and, therefore, a neutron diffraction study of a feldspar crystal was undertaken to investigate the possible substitution of small amounts of OH^- for the oxygen in this position. However, even before our own negative results were obtained, a neutron refinement of a sanidine structure (Brown, Hamilton, Prewitt, and Sueno, 1971) ruled out any measurable amount of H in this feldspar species. Infrared absorption spectra of clear hydrothermal feldspar have shown no evidence of hydroxyl-for-oxygen substitution (J. Zemann, private communication, August 10, 1971).

As the investigation progressed, however, another

interesting aspect became apparent: the refinement of the structure of this feldspar, which was classified as orthoclase on the basis of chemical composition, apparent symmetry from the powder pattern, angle between optic axes ($2V_\alpha = 63^\circ \pm 1^\circ$), and morphology, indicated essentially complete order of the aluminum and silicon cations between the $T(1)$ and $T(2)$ tetrahedral sites, although the mean $T\text{-O}$ distances for these sites would have indicated less than complete order according to the published regression lines (Jones, 1968; Ribbe and Gibbs, 1969). The purpose of this paper is to describe the refinement of the structure, to compare the results with those of studies on similar crystals, and to discuss the implications our findings may have on feldspar mineralogy.

Specimen Description

The neutron diffraction data were collected from a cleavage fragment taken from an overgrowth which occurs on perthite individuals from the Himalaya

tourmaline mine (Jahns, 1954, map 8, locality 20) in the Mesa Grande pegmatite district, San Diego County, California. As in other granite pegmatite dikes of San Diego County, long pendants of microcline perthite having quartz rods in graphic intergrowth grow from the hanging wall (Figure 1). Towards the core of the pegmatite, the quartz rods die out abruptly, presumably in response to slower crystal growth, and massive quartz aggregates form separate bodies next to microcline perthite (Jahns and Wright, 1951). Nearer the gem pockets, microcline perthite gives way to orthoclase perthite; these perthites are coated by a single-phase orthoclase overgrowth up to 1 cm thick where they project into the gem pockets. Simpson (1962) suggests a hydrothermal origin for the microcline perthite-quartz intergrowths from this area. Jahns and Burnham (1969, p. 856) propose growth of relatively few feldspar nuclei from an aqueous fluid, with the constituents transported through the fluid from an adjacent silicate melt. The presence of hydrothermal fluids is further suggested by corrosion features observed on distal portions of blocky perthites (*cf* Simpson, 1964, p. 23) and by fluid inclusions in the feldspars. The overgrowth postdates the main episode of corrosion; it occurs in pockets in association with gem tourmaline, beryl, quartz, and fine-grained muscovite, which also coats the etch features. Jahns and Wright (1951) note the occurrence of a clear variety of orthoclase ("dental spar") among pocket pegmatite minerals in the adjacent Pala district, and mention that microcline is subordinate in such pockets.

Table 1 is a summary of chemical and crystallographic data on this crystal, along with similar information, as given by Colville and Ribbe, for Spencer B adularia and Spencer C orthoclase. X-ray raster scan images of a portion of the neutron crystal, at a scale of $100 \mu = 3.5 \text{ cm}$, give no indication of Na and K inhomogeneity (S. Horska, private communication). No variations in Al to Si ratio were noted in additional electron-microprobe analyses; no correlation can be made with the very subtle variations in extinction angle, well within 1° , that are found in the untwinned overgrowth.

R. H. Jahns and A. A. Chodos (unpublished data) consistently find rubidium and cesium enriched in the pocket orthoclase crystals of the San Diego County pegmatites; one specimen of Himalaya orthoclase overgrowth contains 0.11 percent Rb_2O and 0.014 Cs_2O (R. H. Jahns, private com-

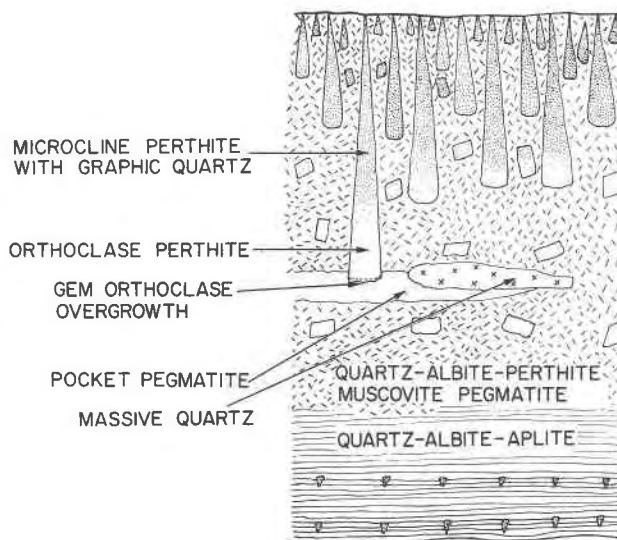


FIG. 1. Cross section of an asymmetrically-zoned pegmatite dike, modified after Figure 5B of Jahns and Burnham (1969). Thickness of dike is measured in meters. The clear, single-phase overgrowth (labeled "gem orthoclase overgrowth"), which coats orthoclase perthites which project into gem pocket, yielded the specimens used in this study. The country rock is gabbroic.

munication, 1972). A value of 0.47 percent Rb_2O has been found by wet chemical analysis of the specimen from which the neutron crystal was obtained (S. Horska, private communication, 1972), and this is confirmed by the value of 0.49 percent Rb_2O from the electron-probe analysis (Table 1).

Experimental Procedure

The cleavage fragment used in the neutron refinement weighs 48.356 mg so that on the basis of an observed density of 2.563 g/cm^3 , it has a volume of about 19 mm^3 . It was mounted with its b axis approximately but not exactly parallel to the ϕ axis of a computer-controlled, 4-circle, neutron diffractometer at the National Bureau of Standards Reactor (Alperin and Prince, 1970). All reflections with $\chi \geq -5^\circ$ and within a sphere defined by a limiting 2θ angle of 100° and a wavelength of 1.232 \AA were measured by a procedure which first measured the intensity at the peak position and at background positions on either side. If the peak intensity did not exceed the mean background by at least 2σ ($\sigma = (I_p + I_b)^{1/2}$), the reflection was considered to be "unobserved", and assigned an upper limit of intensity based on σ . If the peak intensity was greater than 2σ , the peak was measured by a θ - 2θ step scan. If the peak intensity exceeded 1000 counts, the counting time was reduced in order to avoid spending time on meaningless statistical precision.

For each observed reflection the integrated intensity was determined, and from it a value of the structure factor, F , and

TABLE 1. Compositions and Crystal Data of Potassium Feldspars

Chemical Analysis weight percent	Himalaya orthoclase [‡]	Himalaya orthoclase [‡]	Spencer B adularia [*]	Spencer C orthoclase [*]
SiO ₂	65.32	65.39	63.8	64.2
Al ₂ O ₃	18.25	18.45	18.5	18.3
K ₂ O	14.25	14.76	15.1	15.3
Na ₂ O	1.12	1.08	1.1	0.9
CaO	0.05	nil	0.01	0.1
SrO	nil	nil	0.5	0.1
BaO	0.25	0.02	0.7	0.1
Rb ₂ O	0.47	0.49	-	-
H ₂ O [†]	0.44	-	-	-
H ₂ O ⁻	0.02	-	-	-
TOTAL	100.17	100.19	99.26	99.0
Formula based on 4(Si, Al) per F.U. (Martin & Donnay, 1972); Z = 4	(K _{0.84} Na _{0.10} Rb _{0.01} □ _{0.05}) (Si _{3.01} Al _{0.99}) [0 _{7.96} OH _{0.04}]	(K _{0.86} Na _{0.10} □ _{0.04}) (Si _{3.00} Al _{1.00}) [0 _{7.96} OH _{0.04}]	(K _{0.90} Na _{0.10} Ba _{0.01}) (Si _{2.98} Al _{1.02}) [0 _{7.98} (OH) _{0.02}]	(K _{0.91} Na _{0.08} Ca _{0.01}) (Si _{2.99} Al _{1.01}) 0 _{8.00}
Formula weight:	275.80	275.27	276.72	277.05
Wavelength used (Å)	1.54051		not given	not given
a (Å)	8.5632(11)		8.554(2)	8.561(2)
b (Å)	12.963(14)		12.970(4)	12.996(4)
c (Å)	7.2099(11)		7.207(2)	7.192(2)
α	90°		90°	90°
β	116.073(9)		116.007(10)°	116.010(10)°
γ	90°		90°	90°
V (Å ³)	718.90(11)		718.7	718.9
D _{calc} (g/cm ³)	2.543		2.557	2.559
D _{obs} (g/cm ³)	2.563(1) at 23°C		2.566	2.563
2V _α	63°		68.4°	43.6°
Observed diffuse reflections	---		(h + k) odd	---

[‡]Wet chemical analysis by S. Horská, McGill University. H₂O[†] designates H₂O liberated between 117°C and 1000°C.

[†]Analytical data obtained by C. G. Hadjidacos on the electron microprobe of the Geophysical Laboratory, Carnegie Institution of Washington.

^{*}Data from Colville and Ribbe (1968, Table 1). The given formulae differ slightly; the conversion factor used by Colville and Ribbe is based on 8 oxygen atoms per cell. Optic axial angles (2 V_α) from Spencer (1937).

[#]All dimensions for Himalaya orthoclase determined by R. F. Martin.

its standard deviation, σ_p , based on counting statistics. At this stage a systematic comparison of pairs of reflections of the type hkl and $\bar{h}\bar{k}\bar{l}$ was made in order to determine whether a departure from monoclinic symmetry was observable. The overall agreement index, defined by $S = \sum |F(hkl) - F(\bar{h}\bar{k}\bar{l})| / \sum F(hkl)$, was about .02, and there was no discernible trend as a function of $\sin \theta$ or of reflection index k . Therefore in the subsequent stages of refinement we have assumed that the structure is monoclinic, belonging to space group $C2/m$, with the cell dimensions given in Table 1. There are 764 independent reflections within the limiting sphere, of which 721 were observed.

The observed reflections were used in a least-squares refinement, using the program *REFINE* (Finger, 1968a), starting with the position parameters of Jones and Taylor

(1961). The scattering factor for the tetrahedral sites was assumed initially to be that for Si, which is $0.42 \times 10^{-14}m$ (Bacon, 1972). The scattering factor for Al is $0.35 \times 10^{-14}m$, so that substitution of small amounts of Al in either point-position will reduce the scattering factor by a few percent. This will appear in the final parameters as a slightly larger temperature factor. The scattering factors for Na and K are both $0.35 \times 10^{-14}m$, so that the Na:K occupancy of the alkali sites is immaterial to the refinement. Substitution of other alkali metals, such as Rb, or vacancies in amounts up to a few percent also appears in the form of slightly different temperature factors, and has an entirely negligible effect on these calculations.

Repeated cycles of refinement with isotropic temperature

TABLE 2. Atomic Coordinates and Anisotropic Temperature Factors for Himalaya Orthoclase

Atom	x	y	z	B ₁₁ [*]	B ₂₂	B ₃₃	B ₁₂	B ₂₃	B ₃₁	B _{1eo}
K	.2840(3)	0	.1388(4)	1.5(1)	2.4(1)	2.0(1)	0	0	.52(7)	2.08(4)
T(1)	.0095(2)	.1842(1)	.2247(2)	1.38(5)	.99(5)	.94(5)	-.23(4)	-.15(4)	.59(4)	1.08(3)
T(2)	.7085(2)	.1176(1)	.3446(2)	1.38(5)	.95(5)	1.10(5)	.02(4)	.03(3)	.55(4)	1.14(3)
C _A (1)	0	.1451(1)	0	2.13(6)	1.54(5)	1.88(5)	0	0	.95(4)	1.82(3)
O _A (2)	.6365(2)	0	.2853(2)	1.94(6)	.97(5)	1.53(5)	0	0	.33(4)	1.64(3)
O _B	.8256(1)	.1459(1)	.2279(2)	2.18(4)	2.45(4)	2.23(4)	-.24(3)	.16(3)	1.47(3)	2.11(3)
O _C	.0353(1)	.3118(1)	.2599(2)	1.66(4)	1.40(4)	1.75(3)	-.30(3)	-.36(3)	.64(3)	1.65(2)
O _D	.1818(1)	.1252(1)	.4080(1)	1.91(4)	1.60(4)	1.00(4)	.14(3)	.13(3)	.23(3)	1.65(2)

* B's are expressed in Å² and are given as the coefficients of the expression $\exp\{-1/4(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hka^*b^*B_{12} + 2kb^*c^*B_{23} + 2hc^*a^*B_{31})\}$. Standard deviations in the last significant figure are shown in parentheses.

factors led to a weighted R value of 0.094 and a conventional R of 0.082. Four more refinement cycles with anisotropic temperature factors and an extinction parameter of the Zachariasen (1968) type led to a weighted residual R of 0.038, and a conventional R of 0.033.

At this point the chemical analysis shown in Table 1 became available, and two further stages of least-squares refinement, each with four cycles, were performed. In one, the alkali site was assumed to contain 4 atomic percent vacancies, and silicon and aluminum were distributed between the tetrahedral sites according to the regression formula of Jones (1968).¹ (See Table 4.) The weighted residual R after this stage was 0.03532. In the other refinement the above content of the alkali sites was kept fixed but the contents of the tetrahedral sites were allowed to vary under the constraint that the overall ratio of Si to Al must be 3.0 to 1.0. This refinement led to a weighted residual R of 0.03494. The ratio of residuals is 1.0110, compared with a ratio (Hamilton, 1965) of 1.0062 necessary for the result to be significant at the .005 level of confidence. In other words there is only one chance in 200 that this amount of improvement could be due to chance alone. This result is therefore highly significant. It should be noted that the constraint on the overall chemical composition removes much of the correlation between occupancy factors and temperature factors which would otherwise make simultaneous refinement of both a more uncertain procedure (Finger, 1968b). The final unweighted R was 0.031. The largest correlation between the occupancy factor and any other parameter was 0.434 with β_{33} of $T(1)$. The final parameters are shown in Table 2 and observed and calculated structure factors are given in Table 3.

The fractional Al content of the $T(1)$ sites is 0.516(29), with a corresponding value for the Al content of the $T(2)$ sites of $-0.016(29)$, where the number in parenthesis is the estimated standard deviation of the least significant figures. Because the actual fractional Al content of the $T(2)$ site cannot be negative, we assume the $T(2)$ site to be occupied only by silicon and the Si to Al ratio in the $T(1)$ site to be 1.0.

¹ Use of the linear relationship obtained by Ribbe and Gibbs (1969) does not change the present conclusions.

Discussion

Cation distribution

Figure 2 is a plot of the Al/(Al + Si) distributions, as determined directly by neutron diffraction, relative to the mean T -O distance for the two sites in this study (circles) and the two sites in sanidine (squares) as determined by Brown *et al.* (1971). The figure also shows the regression line proposed by Jones (1968) for evaluation of aluminum content when only the mean T -O distances are available. The points from this study are plotted at Al/(Al + Si) ratios of 0.0 and 0.5 because these are maximum likelihood points, due to the impossibility of an aluminum content being negative or greater than 0.5. The one-ended error bars on these points indicate the confidence interval determined by a 2σ range from the value determined in the refinement, and the shaded area is a 2σ confidence band as given by Jones.

Although the confidence limits on the direct refinement in this study and those on the regression line do overlap slightly, the agreement must be considered poor. There is a strong indication that a range of possible T -O distances exists for a given Al/Si ratio, and that at the pure silicon end this range lies mostly above the regression line. The mean $T_1(m)$ -O, $T_2(O)$ -O, and $T_2(m)$ -O bond lengths of 1.610, 1.615, and 1.612Å in low albite (Ribbe, Megaw, and Taylor, 1969) and 1.614, 1.611, and 1.612Å in maximum microcline (Brown and Bailey, 1964) are then consistent with full Si occupancy. These results indicate that, although the mean T -O distance can be used as an indication of the degree of order, the range of uncertainty in any given case is at least 5 percent in aluminum content. The fact that the orthoclase and sanidine points happen to lie on a straight line may well be fortuitous.

TABLE 3. Observed and Calculated Structure Factors of Himalaya Orthoclase*

H10-8	1 221 -209	2 377 -365	-3 921 -921	-2 754 789	H6+5	H7-2	1 179 -159	H10-1	6 517 -528
3 1572 1582	-3 309 -310	4 1103 -1101	-1 826 -824	0 1566E-1576	H6+5	H7-2	3 691 650	H10-1	6 517 -528
0 907 918	5 897 -903	6 665 -680	1 544 529	H5+8	-4 247 239	-7 869 847	5 1233 -1219	-6 678 -685	H12,0
2 1359 1366	7 428 417	8 111 41	3 1259 -1224	H5+8	-2 91* 26	-5 167 -157	7 553 553	-4 88* 51	-6 233 -217
4 206 187	9 625 634	10 96* 49	5 731 -756	H5+8	0 320 300	-3 355 354	H9+5	-2 1321 -1311	-2 502 -521
6 415 407	H1-5	H2+3	7 827 835	3 253 -260	2 556 560	-1 335 343	H9+5	2 882 885	-2 653 627
8 995 1018	H1-5	H2+3	9 261 -252	5 105 -80	1 169 176	H9+5	4 421 -423	-4 811 -506	H13-5
H9-7	-5 634 637	-6 376 -366	H3+1	H3+1	6 1111 1112	3 235 247	-3 590 -589	6 112 83	H13-5
-3 309 -310	-4 995 -995	-2 259 243	-7 769 -769	H5+7	8 163 120	5 414 394	-1 383 -356	6 112 83	H13-5
-2 432 427	-1 1016 1023	-2 259 243	-7 769 -769	H5+7	-1 1459 -1419	H6+6	9 986 975	3 1164 -1155	H10,0
0 159 135	1 870 908	0 164 158	-5 1031 -1029	-1 1459 -1419	-2 365 364	H7-1	5 62 69	H10,0	1 933 -939
2 94* 6	3 993 -1022	2 202 -218	-3 457 -465	1 445 -427	-4 552 544	H7-1	7 293 315	-6 333 -291	3 433 422
4 797 -797	5 1125 1103	4 506 513	-1 1005 -1005	3 195 189	-2 365 364	H9+4	-7 317 325	-4 293 294	H13-4
6 615 -611	7 201 187	6 896 903	1 328 321	5 743 -760	0 1523 1497	H9+4	1 507 549	-2 365 341	H13-4
8 328 -341	9 388 -407	8 567 580	3 901 -901	7 576 579	2 1221 1214	-5 809 -823	H9+4	0 685 649	H13-4
H9-6	H1-4	H2+2	5 159 153	H5+6	4 228 231	-3 525 532	-3 102 -74	H11-6	-1 101* -68
-2 99* -14	-5 373 412	H2+2	7 817 809	H5+6	6 939 939	-1 855 874	-1 609 620	H11-6	1 978 983
0 1102 -1114	-3 81* -42	-8 321 -314	H3+0	-3 911 -888	8 419 427	1 388 -400	1 1281 -1277	1 619 615	3 189 -200
2 708 -715	-1 855 863	-6 384 365	H3+0	-1 338 318	H6+3	5 915 899	5 362 369	3 447 -439	5 571 568
4 265 243	1 654 -668	-4 531 563	-9 129 -122	3 285 -263	-6 303 304	H6+3	9 321 341	H9+3	H11-5
6 587 -594	3 162 130	-2 968 972	-7 1015 -1016	5 481 633	-4 362 339	H7,0	4 492 507	H11-5	-3 588 585
8 88* 825	5 847 848	0 515 620	-5 1052 -1059	7 261 -253	-2 731 746	H7,0	1 149 -159	-5 293 315	-1 439 457
10 883 904	7 350 -372	2 553 554	-3 1173 1149	9 9* 55	2 303 305	-7 238 237	-3 304 285	1 232 -187	3 210 191
H9-5	H1-3	6 314 329	4 1057 1037	H5+5	4 961 -951	-5 844 850	1 266 249	3 453 463	5 284 288
-4 434 -428	-5 373 412	8 79 -48	10 241 -212	H5+5	6 280 -279	-3 96 -86	5 315 308	5 856 -862	H13-2
-2 105 -95	-7 576 -595	10 241 -212	2 524 -522	-3 559 550	8 93* 38	-1 762 759	7 154 105	7 154 105	H13-2
0 1119 1143	-5 435 448	H2+1	4 477 475	-1 1249 1232	H6+2	H8-7	H9+2	H11-4	-3 270 280
2 142 13	-3 436 464	-8 92* 51	6 589 -595	3 815 825	-6 682 -671	2 466 458	H9+2	-3 229 215	-1 138 -92
4 1542 1637	-1 1282 -1306	-8 92* 51	6 589 -595	3 815 825	-6 682 -671	2 466 458	H9+2	-3 229 215	-1 138 -92
6 1554 -1523	0 515 620	-8 92* 51	6 589 -595	3 815 825	-6 682 -671	2 466 458	H9+2	-3 229 215	-1 138 -92
8 401 413	3 652 685	-2 440 -446	0 583 573	H5+4	0 1434 -1411	-2 72* -36	6 1060 1065	-3 565 -565	1 617 -646
10 1460 1430	5 710 -727	2 126 -130	2 613 -611	H5+4	4 250 411	-2 72* -36	6 1060 1065	-3 565 -565	1 617 -646
H9-4	H1-3	0 99 14	4 578 -649	-5 274 270	2 601 -607	4 250 411	H8-6	3 1220 -1198	7 316 -305
-6 690 694	H1-2	8 1146 -1139	8 194 -166	-3 404 408	-1 668 -680	-3 404 408	8 9* -8	2 565 575	7 184 -172
-4 554 560	H1-2	8 1146 -1139	8 194 -166	-1 668 -680	-1 180 -119	3 743 -735	6 525 503	H9+1	-3 952 -984
-2 1399 1415	-7 404 409	H2+0	-2 174 -155	3 743 -735	-1 180 -119	3 743 -735	6 525 503	H9+1	-1 243 -243
0 1157 1177	-5 323 -315	H2+0	-2 174 -155	3 743 -735	-1 180 -119	3 743 -735	6 525 503	H9+1	3 183 -179
2 1895E 2021	-3 104 203	H2+0	-2 174 -155	3 743 -735	-1 180 -119	3 743 -735	6 525 503	H9+1	5 1179 1145
4 307 298	-1 361 369	-8 87* 68	0 306 300	7 292 299	-6 319 316	-4 575 -573	H8-5	-1 186 -188	7 1052 -1042
6 1345 1322	1 696 688	-6 553 -578	2 744 -751	9 496 -471	-4 575 -573	-2 98 -39	0 529 542	-2 152 -58	1 320 -331
8 596 814	3 141 -97	-4 907 -926	4 648 -638	6 665 676	6 648 -638	-2 98 -39	0 529 542	-2 152 -58	1 320 -331
10 96* 80	5 568 561	-2 1140 -1136	6 648 676	6 637 -650	-5 238 -249	-3 978 -986	6 204 166	4 279 -256	7 300 271
H9-3	9 418 432	H3+8	H3+5	-3 978 -986	-1 425 -437	1 425 -437	8 756 773	6 597 -607	8 1215 -1196
-6 166 132	H1-1	1 995 -983	-4 789 782	-1 425 -437	-2 25 -262	3 136 -103	H6+0	-8 358 376	H8-4
-4 1764 1755	-7 463 475	1 995 -983	-4 789 782	-1 425 -437	-2 25 -262	3 136 -103	H6+0	-8 358 376	H8-4
-2 450 -490	-5 269 -275	5 599 620	0 1568 -1566	5 999 953	2 1056 1055	7 941 -978	H8-4	-7 57* 28	3 736 -740
0 720 760	-3 812 749	7 647 -677	4 724 -733	9 817 824	4 621 -677	8 92* -11	10 174 -98	-5 482 -489	5 685 -676
2 582 560	-1 866 890	4 724 -733	9 817 824	4 621 -677	8 92* -11	10 174 -98	H5+2	-3 386 394	7 265 277
4 1640 -1618	-1 866 890	4 724 -733	9 817 824	4 621 -677	8 92* -11	10 174 -98	H5+2	-3 386 394	7 265 277
6 88 57	3 281 281	H3+7	4 621 -677	8 92* -11	10 174 -98	H5+2	-3 386 394	7 265 277	H14-3
8 88 57	3 281 281	H3+7	4 621 -677	8 92* -11	10 174 -98	H5+2	-3 386 394	7 265 277	H14-3
10 1233 -1239	5 308 321	-1 105 -87	1 198 252	3 278 267	5 225 -224	7 120 117	-6 210 169	-3 218 -198	1 802 -774
H9-2	H1,0	7 94* -56	3 278 267	5 225 -224	7 120 117	-6 210 169	-3 218 -198	1 802 -774	3 183 -186
-8 247 -242	-9 496 -523	7 214 -202	4 293 -268	1 802 778	5 191 202	H8-3	4 797 -798	5 247 -254	0 430 449
-6 256 268	-7 590 594	H3+6	0 169 142	5 873 -866	4 404 415	9 374 -381	H7-7	-6 749 -760	4 437 453
-4 1583 -1561	-5 546 574	-3 1155 -1145	2 310 -333	7 404 415	9 374 -381	H7-7	-6 749 -760	4 437 453	H10-6
-2 945 942	-7 590 594	-3 1155 -1145	2 310 -333	7 404 415	9 374 -381	H7-7	-6 749 -760	4 437 453	H10-6
0 1461E-1666	-5 546 574	-3 1155 -1145	2 310 -333	7 404 415	9 374 -381	H7-7	-6 749 -760	4 437 453	H10-6
2 1394E-1437	-3 388 -117	-1 377 -368	6 908 -676	6 92* 11	10 122 6	H4+3	-7 759 760	-5 161 -127	-3 754 765
4 1297 1276	-1 232 223	-1 377 -368	6 908 -676	6 92* 11	10 122 6	H4+3	-7 759 760	-5 161 -127	-3 754 765
6 1741 -1655	1 305 311	8 92* 11	10 122 6	H4+3	-7 759 760	-5 161 -127	-3 754 765	-1 94* -131	-6 1185 1155
8 414 419	H2+8	3 1455 -1460	5 284 -279	7 759 760	-5 161 -127	-3 754 765	-1 94* -131	-6 1185 1155	-2 394 -410
10 380 395	2 412 -412	9 484 -510	5 284 -279	7 759 760	-5 161 -127	-3 754 765	-1 94* -131	-6 1185 1155	0 690 -574
H9-1	4 171 -142	9 484 -510	5 284 -279	7 759 760	-5 161 -127	-3 754 765	-1 94* -131	-6 1185 1155	0 690 -574
-8 242 257	8 130 47	H3+5	-4 2010 -1925	1 184 160	1 458 -458	-6 1185 1155	-2 633 -410	0 676 -675	H14,0
-6 883 -906	-5 1220 -1203	-3 676 -686	-1 711 -717	4 558 568	9 945 -986	H7-5	2 540 546	4 2453E 2228	-4 62* -66
-2 334 333	-1 711 -717	-1 711 -717	4 558 568	9 945 -986	H7-5	2 540 546	4 2453E 2228	-4 62* -66	-2 711 -722
0 418 -535	-2 230 -226	-1 1199 -1202	6 451 -461	8 305 -312	10 214 -161	H6+2	-7 795 785	-1 829 830	8 489 489
2 1386E 1410	0 547 527	3 385 392	8 305 -312	10 214 -161	H6+2	-7 795 785	-1 829 830	8 489 489	8 489 489
4 1183 1139	3 281 281	5 1357 -1355	7 383 385	9 420 421	H2+5	-7 181 -177	1 432 437	-5 71* 50	3 916 -930
6 802 814	4 266 254	5 1357 -1355	7 383 385	9 420 421	H2+5	-7 181 -177	1 432 437	-5 71* 50	3 916 -930
8 1203 1209	6 750 751	7 383 385	9 420 421	H2+5	-7 181 -177	1 432 437	-5 71* 50	3 916 -930	5 1333 1303
10 971 992	8 542 552	7 383 385	9 420 421	H2+5	-7 181 -177	1 432 437	-5 71* 50	3 916 -930	7 296 297
H9,0	H2+6	H3+4	-6 804 -818	-4 1022 1042	-1 797 -804	H6+8	9 201 -134	-2 510 501	0 674 -692
-8 423 -437	-2 429 410	-5 643 -642	-2 1156 -1177	-3 341 343	2 158 129	H6+8	9 201 -134	-2 510 501	0 674 -692
-6 2051 1926	0 669 675	-3 341 343	2 158 129	2 886 871	-5 285 277	2 865 868	H7-4	-4 578 -586	2 367 -372
-4 1085 1089	2 252 224	-1 429 -446	4 1133 -1133	2 886 871	-5 285 277	2 865 868	H7-4	-4 578 -586	2 367 -372
-2 149 -124	4 118 400	1 342 -359	5 735 754	4 165 139	-3 90* 90	6 985 -972	H7-3	-2 328 331	4 167 173
H1-8	8 315 -325	5 90 12	6 682 -698	4 446 431	-1 946 958	8 354 -357	H7-3	-2 2064E-2023	-1 280 272
10 184 -170	7 520 -515	10 429 -449	9 563 -576	H4+1	0 269 273	2 191 -152	7 129 2	-8 696 -706	-6 425 413
1 886 866	H2+5	H3+3	-8 1390 -1347	2 191 -152	7 129 2	-8 696 -706	-6 425 413	-4 915 -914	-2 2064E-2023
3 685 -685	-2 162 -84	-7 512 526	-6 949 943	4 557 -551	9 99* 72	-4 915 -914	-2 2064E-2023	-2 2064E-2023	0 1165 1134
5 136 -136	0 682 -676	-5 544 546	-4 354 -338	6 664 -659	8 139 27	H7+3	-5 1126 1131	-3 1054 1064	-1 941 -945
7 981 964	2 124 70	-3 254 -236	-2 1341 -1342	2 866 -862	0 633 626	H7+3	-5 1126 1131	-3 1054 1064	-1 941 -945
H1-7	4 662 -671	-1 816 834	2 866 -862	0 633 626	2 678 -682	3 751 866	H8,0	6 505 -510	H12-2
-1 168 169	4 662 -671	-1 816 834	2 866 -862	0 633 626	2 678 -682	3 751 866	H8,0	6 505 -510	H12-2
1 580 -582	6 910 -930	1 760 -755	2 866 -862	0 633 626	2 678 -682	3 751 866	H8,0	6 505 -510	H12-2
3 425 -415	8 809 -819	3 966 -485	4 213 175	6 883 -892	8 131 -18	H4+0	-2 674 265	-1 941 -945	1 467 -464
5 358 375	10 518 -526	5 723 725	6 883 -892	8 131 -18	H4+0	-2 674 265	-1 941 -945	1 467 -464	

TABLE 4. Bond Lengths, Site Occupancies, and Inter-bond Angles of Orthoclase (Himalaya and Spencer C) and Adularia (Spencer B). Data for Spencer Samples from Colville and Ribbe, 1968.

	Himalaya Orthoclase	Spencer B adularia	Spencer C Orthoclase
Bond lengths and site occupancies			
T(1)-O _A (1)	1.664 (1)Å	1.667 (2)Å	1.654 (4)Å
-O _B	1.661 (2)	1.646 (6)	1.641 (6)
-O _C	1.673 (2)	1.670 (3)	1.661 (7)
-O _D	1.672 (2)	1.671 (4)	1.666 (5)
T(1)-O	1.667 ± .001	1.663 ₅	1.655 ₅
T(1) occupancy*	S _{10.59} Al _{0.41}	S _{10.61} Al _{0.39}	S _{10.66} Al _{0.34}
T(1) occupancy**	S _{10.50} Al _{0.50}		
T(2)-O _A (2)	1.627 (1)	1.632 (2)	1.641 (3)
-O _B	1.609 (2)	1.623 (6)	1.620 (6)
-O _C	1.617 (2)	1.615 (5)	1.631 (6)
-O _D	1.612 (1)	1.618 (3)	1.621 (5)
T(2)-O	1.616 ± .001	1.622 ₀	1.628 ₂₅
T(2) occupancy*	S _{10.91} Al _{0.09}	S _{10.88} Al _{0.12}	S _{10.84} Al _{0.16}
T(2) occupancy**	S _{11.00}		
Alk.-O _A (1)	2x 2.884 (2)	2x 2.878 (4)	2x 2.893 (7)
-O _A (2)	2x 2.724 (3)	2x 2.717 (8)	2x 2.711 (9)
-O _B	2x 3.044 (3)	2x 3.025 (4)	2x 3.045 (6)
*-O _B	2x 3.113 (2)	2x 3.117 (4)	2x 3.129 (6)
-O _D	2x 2.942 (3)	2x 2.949 (4)	2x 2.945 (7)
Alk.-O	2.966	2.962 ₀	3.005 ₀
Alk. occupancy	K _{0.86} Na _{0.14} O _{0.04}	K _{0.9} Na _{0.1}	K _{0.91} Na _{0.09} Ca _{0.01}
Inter-bond angles			
O _A (1)-T(1)-O _B	106.3(1)*	105.9(2)*	106.6(3)*
O _A (1)-O _C	113.3(1)	113.3(2)	113.6(4)
O _A (1)-O _D	106.2(1)	106.0(2)	106.2(3)
O _B -O _C	110.9(1)	111.7(2)	110.4(4)
O _B -O _D	111.4(1)	111.1(2)	111.5(3)
O _C -O _D	108.7(1)	108.8(2)	108.5(3)
O _A (2)-T(2)-O _B	109.1(1)	108.5(2)	110.2(5)
O _A (2)-O _C	104.6(1)	104.6(3)	104.4(4)
O _A (2)-O _D	108.5(1)	108.8(2)	108.5(4)
O _B -O _C	110.6(1)	111.0(2)	110.8(4)
O _B -O _D	111.8(1)	111.3(3)	111.4(3)
O _C -O _D	112.0(1)	112.2(2)	111.3(3)

* Tetrahedral occupancy is calculated with the equation of Jones (1968):
Al/(Al + Si) = 6.3481 $\bar{E}(T-O) - 10.178$, given for feldspar use.

** Tetrahedral occupancy from neutron refinement.

In no way do we wish to imply that a straight line function can be extended beyond 50 percent Al occupancy (Fig. 2).

Hydrogen content

The valence summation (Donnay and Allmann, 1970) based on the experimental interatomic distances (Table 4) and an ordered occupancy does not show a significantly low value for O_C (Table 5). Experience has shown (Donnay and Allmann, 1972) that deviations from ideal values of less than 10 percent are of dubious significance, and we are therefore not surprised that a difference Fourier map computed with the final set of calculated F^2 s contained no negative peaks with depressions greater than -168 on a scale on which a hydrogen atom would show up with amplitude -6000. Moreover the -168 peak, which lay on a mirror plane between the T(2) sites, was in quite an inappropriate place for the hydrogen atom of a hydroxyl group. We may thus conclude that systematic substitution of (OH)-

for O cannot exceed 3 atomic percent on any one site.

Comparison with other feldspars

A comparison of interatomic distances and angles between the present Himalaya orthoclase and the Spencer B and C data of Colville and Ribbe (1968) shows agreement within experimental limits, namely 3 sigma or better, between Spencer B adularia and our crystal. Indeed, if the detailed crystal structure is considered the criterion of all feldspar classifications, the present orthoclase is indistinguishable from Spencer B adularia (Table 4). This fact serves to emphasize the confusion that exists in feldspar nomenclature.

The stability of orthoclase

Growth of the Himalaya orthoclase from hydrothermal fluids in a pegmatite gem pocket was presumably very slow, as was regional cooling in this mesozonal plutonic environment; conditions in the pockets would therefore seem ideal for attaining maximum microcline. Yet, perthitic maximum microcline crystals give way to orthoclase perthite away from the hanging wall, and to ordered orthoclase as overgrowths when the perthites project into the

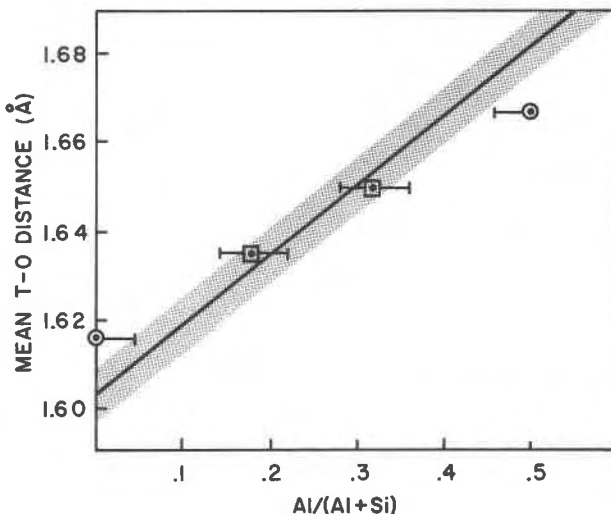


FIG. 2. Plot of the mean T-O distance as a function of the atom fraction Al/(Al + Si) as determined by neutron diffraction. The circles are points from the present work and the squares are the sanidine results of Brown *et al.* (1971). The indicated errors in the present work represent 2σ from the physically impossible values resulting from the refinement. The line is the regression line of Jones (1968) and the shaded area is a 2σ confidence band on either side of it.

TABLE 5. Valence Summation for Himalaya Orthoclase, with Tetrahedral Occupancies Based on Least-Squares Refinement of Neutron Data

Cations Anions	$\sum x_{\text{Alkali}}$ K _{0.86} Na _{0.10} □ _{0.04}	$\sum v_{T(1)}$ Si _{0.50} Al _{0.50}	$\sum v_{T(2)}$ Si _{1.00}	$\sum v(\text{v.u.})$ C
$\bar{l}i\bar{l}O_A(1)$	(0.138) 0.125*	#0.878		1.881
$\bar{l}i\bar{l}O_A(2)$	(0.204) 0.185		#0.982	2.149
$\bar{l}i\bar{l}O_B$	(0.094) 0.085*	0.883	1.018	1.986
$\bar{l}i\bar{l}O_C$	(0.076) 0.069*	0.863	1.002	1.934
$\bar{l}i\bar{l}O_D$	(0.120) 0.109*	0.865	1.012	1.986
$\bar{L}(\text{\AA})$	2.977	1.666	1.618	
$L_{\text{max}}(\text{\AA})$	3.412 [†]	2.195	2.130	
P	6.844	3.149	3.160	
$v_i(\text{v.u.})$	0.96/9	3.50/4	4.00/4	
$\sum_A v(\text{v.u.})$	(1.060) 0.961	3.489	3.999	

* Two bonds from cation.

Two bonds to anion.

[†]The 4% vacancies in the alkali position increase \bar{L}_{obs} and this effect must be taken into account when deriving the L_{max} value. The effective ionic radii of nine-coordinated alkali ions, properly weighted on the assumption of full occupancy, are added to that of three-coordinated oxygen ion to give an \bar{L}_{pred} of 2.887 \AA . The ratio $\bar{L}_{\text{obs}}/\bar{L}_{\text{pred}}$ is used to multiply L_{max} , 3.309 \AA , determined on the basis of full occupancy, to give the vacancy-corrected value of L_{max} of 3.412 \AA .

gem pockets. The apparent anomaly of the persistence of the monoclinic phase may be due to the presence of small amounts of the large Rb and Cs ions that would act as stabilizers of the monoclinic structure. Indeed, Gordiyenko and Kamentsev (1967) have found pegmatitic K-feldspars to be monoclinic if they contain more than 2.5 percent Rb₂O, but this is a value much higher than that recorded in this case.

Rate of crystal growth is one factor which might explain the association of maximum microcline and ordered orthoclase in the same dike. Where growth was faster, perhaps in response to more rapid cooling, the monoclinic K-feldspar began ordering but only got as far as a "normal" orthoclase. As the rate of growth decreased, with the temperature still above the orthoclase-microcline transition, perfect, gem-quality crystals of ordered orthoclase, quartz, beryl, and tourmaline formed in pockets. When the temperature fell below the orthoclase-microcline transition, the "normal" orthoclase near the hanging wall transformed to maximum microcline. In contrast, the ordered orthoclase, which had presumably attained a stable balanced Al distribution in the T_1 sites, persisted metastably to lower temperatures.

This occurrence strongly suggests that ordered orthoclase does have a field of thermodynamic stability, close to the pegmatite solidus; the usual rates of regional cooling may be too rapid for ordinary orthoclase to attain the ordered configuration reached in the pegmatite gem pockets discussed here.

Although the intensity agreement between hkl and $\bar{h}\bar{k}\bar{l}$ reflections indicates that the bulk crystal is monoclinic, on the average, the temperature factors suggest that there is appreciable structural disorder. For example, the equivalent isotropic temperature factors of the $T(1)$ and $T(2)$ sites are 1.08(3) \AA^2 and 1.14(3) \AA^2 respectively, as compared with values ranging from 0.29(3) \AA^2 to 0.38(2) \AA^2 in maximum microcline (Brown and Bailey, 1964). Some of the disorder may be due to non-homogeneous alkali distributions. In addition, the $T(1)$ sites occur in pairs, and aluminum atoms can substitute for silicon atoms at either site of any given pair. Therefore aluminum can be assigned exclusively to the $T(1)$ sites and still give only short-range order, leaving the possibility of considerable long-range disorder. The incipient long-range ordering indicated by diffuse reflections with $h+k$ odd, which was reported for adularia (Colville and Ribbe, 1968), was not

observed for the Himalaya orthoclase, nor could we detect any evidence of twinning. We looked for both phenomena using chips from the neutron crystal and exposing them to $\text{CuK}\alpha$ radiation for periods of up to 100 hours on precession and Weissenberg cameras.

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