

Neutron Diffraction Refinement of an Ordered Orthoclase Structure

EDWARD PRINCE

*Institute for Materials Research, National Bureau of Standards,
Washington, D. C. 20234*

GABRIELLE DONNAY AND R. F. MARTIN

Department of Geological Sciences, McGill University, Montreal, Canada

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 $T_1(m)$ -O, $T_2(O)$ -O, and $T_2(m)$ -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 -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-

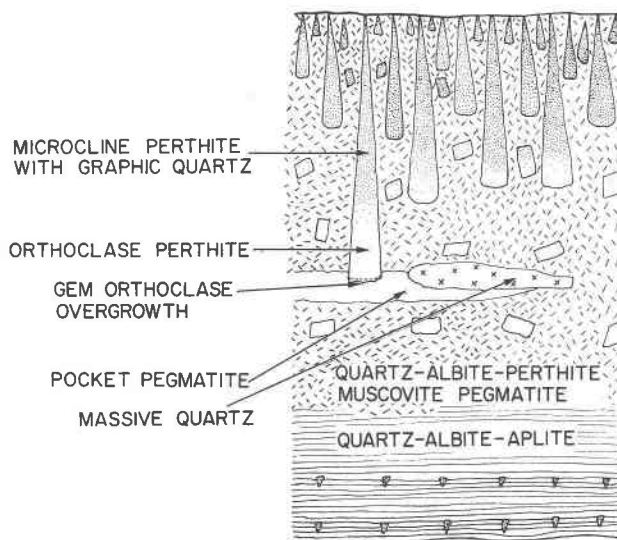


FIG. 1. Cross section of an asymmetrically-zoned pegmatite dike, modified after Figure 5B of Jahns and Burnham (1969). Thickness of dike is measured in meters. The clear, single-phase overgrowth (labeled "gem orthoclase overgrowth"), which coats orthoclase perthites which project into gem pocket, yielded 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. Hadidiacos 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 $\bar{h}k\bar{l}$ was made in order to determine whether a departure from monoclinic symmetry was observable. The overall agreement index, defined by $S = \sum |F(hkl) - F(\bar{h}k\bar{l})| / \sum F(hkl)$, 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 0.42×10^{-14} m (Bacon, 1972). The scattering factor for Al is 0.35×10^{-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 0.35×10^{-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	1 179 -159	H10-1	6 517 -528
0 907 918	3 1572 1582	4 1103 -1101	-1 826 -824	0 156E-1576	H7-2	3 691 650	H12-0	-4 88*
2 130 1366	5 897 -903	6 665 -680	1 544 529	H5+8	-4 247 239	-7 869 847	5 1233 -1219	-6 678 -685
4 206 187	7 428 417	8 111 41	3 1259 -1224	H5+8	-2 91* 26	-5 167 -157	7 553 553	-2 1321 -1311
6 415 407	9 625 634	10 96* 49	5 731 -756	H5+8	0 320 300	-3 355 354	H9+5	-2 502 -521
8 995 1018	H1+5	H2+3	9 261 -252	3 253 -260	2 556 560	-1 335 343	H9+5	2 882 885
H0-7	-5 634 637	-6 376 -366	H3+1	5 105 -80	6 1111 1112	3 235 247	-3 590 -589	4 421 -423
-2 432 427	-3 309 -310	-4 995 -995	H3+1	7 662 -619	8 163 120	5 414 394	-1 383 -356	6 112 83
0 159 135	-1 1016 1023	-2 259 243	H3+1	H5+7	H6+6	9 986 975	3 1164 -1155	H10-0
2 94* 6	3 993 -1022	2 202 -218	-3 457 -465	-1 1459 -1419	H6+6	5 62 69	H10-0	1 933 -939
4 797 -797	5 1125 1103	4 506 513	-1 1005 -1005	3 195 189	-2 365 364	H7-1	7 293 315	-6 333 -291
6 615 -611	7 201 187	6 896 903	1 328 321	5 743 -760	0 1523 1497	-7 317 325	H9+4	-4 293 294
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
H0+6	H1+4	H2+2	9 717 809	H5+6	4 228 231	-3 525 532	H11-6	-1 101* -68
-2 90* -14	-5 373 412	-6 321 -314	7 819 809	H5+6	6 939 939	-1 855 874	H11-6	1 978 983
0 1102 -1114	-3 81* -42	-4 995 -995	H3+0	-3 911 -888	8 419 427	1 388 -400	H11-6	3 189 -200
2 708 -715	-1 855 863	-2 384 365	H3+0	-1 338 318	H6+3	-1 855 874	H11-6	5 571 568
4 265 243	5 165 -668	-6 531 563	-9 129 -122	3 285 -263	-6 303 304	H7-0	H9+3	-3 588 585
6 587 -594	3 142 130	-2 968 972	-7 1015 -1016	5 641 633	-4 362 339	H7-0	H9+3	1 600 621
8 88* 825	5 847 848	4 515 620	-5 1052 -1059	7 261 -253	-2 731 746	H7-0	H9+3	3 210 198
10 883 904	7 350 -372	2 553 554	-3 1173 1149	9 9* 55	0 149 -159	-5 293 315	H9+3	5 284 288
H0+5	H1+3	H2+1	4 1057 1037	H5+5	2 303 305	-7 238 237	H9+3	1 232 -187
-4 434 -428	-5 373 412	-6 321 -314	6 314 329	H5+5	4 961 -951	-5 844 850	H9+3	3 453 463
-2 105 -95	-7 576 -598	-8 384 365	8 79 -48	H5+5	6 280 -279	-3 96 -86	H9+3	5 856 -862
0 1119 1143	-5 435 448	-6 384 365	10 241 -212	H5+5	8 93* 38	-1 762 759	H9+3	7 150 122
2 142 -123	-3 436 464	-4 995 -995	H2+1	2 524 -522	H6+2	H8-7	H9+2	-3 270 280
4 1542 1037	-1 1282 -1306	-2 968 972	H2+1	4 477 475	H6+2	H8-7	H9+2	-1 138 -92
6 155* 154	3 1023 1018	-4 995 -995	H4+7	6 589 -595	H6+2	H8-7	H9+2	-1 93* -37
8 401 413	3 652 685	-4 731 743	H4+7	3 815 825	H6+2	H8-7	H9+2	5 690 -700
10 1460 1430	5 710 -727	-2 440 -446	0 126 -130	5 583 573	H6+2	H8-7	H9+2	H13-1
H0+4	H1+2	H2+0	2 90 5	2 613 -611	H5+4	4 230 -617	H9+2	H13-1
-6 690 694	-7 401 -383	-8 1146 -1139	4 678 -659	4 251 -254	H5+4	2 747 -743	H9+2	H13-1
-4 554 560	-5 409 409	-6 365 -373	8 316 -314	8 91 -77	H5+4	8 9* -8	H9+2	H13-1
-2 1399 1415	-7 404 409	-8 1146 -1139	10 241 -212	0 180 -119	H6+1	4 1098 1089	H9+2	-5 1007 -996
0 1157 1177	-5 323 -315	-6 384 365	H2+0	3 743 -735	H6+1	6 525 503	H9+2	-3 912 931
2 1895E 2021	-3 104 203	-4 995 -995	H2+0	5 122 87	H6+1	8 173 70	H9+2	-1 412 430
4 307 298	-1 361 369	-2 174 -155	H2+0	7 292 299	H6+1	8 173 70	H9+2	-3 952 -984
6 1345 1322	1 696 688	-2 744 -751	H2+0	9 496 -471	H6+1	8 173 70	H9+2	-1 243 -173
8 596 614	3 141 -97	-4 907 -926	H2+0	6 648 -638	H6+1	8 173 70	H9+2	3 183 -169
10 96* 810	5 588 561	-2 1140 -1136	H2+0	4 665 676	H6+1	8 173 70	H9+2	5 1179 1145
H0+3	H1+1	H2+1	7 401 -383	8 637 -650	H5+3	0 529 542	H9+2	H13-0
-6 166 132	-7 463 475	-8 1146 -1139	H3+8	-5 238 -249	H5+3	2 269 192	H9+2	H13-0
-4 1764 1755	-5 463 475	-6 384 365	H3+8	-1 425 -437	H5+3	6 204 166	H9+2	H13-0
-2 450 -490	-7 463 475	-8 1146 -1139	H3+8	1 833 -837	H5+3	8 756 773	H9+2	H13-0
0 720 760	-5 269 -275	-6 384 365	H3+8	-2 251 -262	H5+3	3 136 -103	H9+2	H13-0
2 582 560	-3 812 795	-4 995 -995	H3+8	0 1568 -1566	H5+3	5 999 953	H9+2	H13-0
4 1640 -1618	-1 866 894	-2 1056 1055	H3+7	7 981 -978	H5+3	9 817 824	H9+2	H13-0
6 88 57	1 800 491	4 724 -733	H3+7	4 621 -677	H5+3	6 597 -607	H9+2	H13-0
8 291 -268	3 281 291	5 122 87	H3+7	8 92* -11	H5+3	8 1215 -1196	H9+2	H13-0
10 1233 -1239	5 308 321	10 174 -98	H3+7	10 174 -98	H5+3	8 1215 -1196	H9+2	H13-0
H0+2	H1+0	H2+0	-1 105 -87	-7 299 -305	H6+0	-8 358 376	H9+2	H13-0
-8 247 -242	-5 225 -224	-6 210 169	1 198 -176	-5 218 -234	H6+0	-4 887 -879	H9+2	H13-0
-6 256 268	7 120 117	8 292 -298	3 183 -186	3 217 -198	H6+0	-2 354 -324	H9+2	H13-0
-4 1583 -1561	-9 496 -523	-10 102 102	5 191 202	1 002 778	H6+0	0 1359 -1342	H9+2	H13-0
-2 945 942	-7 590 592	-8 1146 -1139	7 292 299	3 190 196	H6+0	2 93 -20	H9+2	H13-0
0 1461E -1666	-5 546 574	-6 384 365	9 496 -471	5 873 -866	H6+0	-6 749 -760	H9+2	H13-0
2 1394E -1437	-3 388 -17	-4 995 -995	6 648 -638	7 404 415	H6+0	-4 437 453	H9+2	H13-0
4 1297 1276	-1 232 223	-2 1155 -1145	8 92* -11	9 374 -381	H6+0	-2 833 -837	H9+2	H13-0
6 1741 -1655	1 305 311	-3 377 -368	10 122 6	10 174 -98	H6+0	0 833 851	H9+2	H13-0
8 414 419	3 1455 -1460	-4 907 -926	H4+3	-7 759 760	H6+0	4 149 76	H9+2	H13-0
10 380 395	5 284 -279	-6 384 365	H4+3	-5 161 -127	H6+0	6 1691 1597	H9+2	H13-0
H0+1	H1+1	H2+1	H4+3	-3 754 765	H6+0	8 1114 1101	H9+2	H13-0
-8 242 257	4 171 -142	-5 284 -279	H4+3	-1 278 288	H6+0	6 597 -607	H9+2	H13-0
-6 883 -906	8 130 47	-6 337 344	H4+3	1 184 160	H6+0	8 1215 -1196	H9+2	H13-0
-4 115 -94	-5 1220 -1203	-2 1553 1547	H4+3	3 1083 -1069	H6+0	6 597 -607	H9+2	H13-0
-2 334 333	-3 676 -686	-4 995 -995	H4+3	5 689 -692	H6+0	8 1215 -1196	H9+2	H13-0
0 418 -555	-2 230 -226	-3 711 -717	H4+3	7 944 -59	H6+0	6 597 -607	H9+2	H13-0
2 1386E 1410	0 547 527	-1 1199 -1202	H4+3	9 985 -986	H6+0	8 1215 -1196	H9+2	H13-0
4 1183 1139	2 56* 30	-2 305 -312	H4+3	10 122 6	H6+0	6 597 -607	H9+2	H13-0
6 802 814	4 266 254	-3 1214 -1216	H4+3	-7 759 760	H6+0	8 1215 -1196	H9+2	H13-0
8 1203 1209	6 750 751	-4 907 -926	H4+3	-5 218 -234	H6+0	6 597 -607	H9+2	H13-0
10 971 992	8 542 552	-6 384 365	H4+3	3 217 -198	H6+0	8 1215 -1196	H9+2	H13-0
H0+0	H2+5	H3+4	H4+3	1 002 778	H6+0	6 597 -607	H9+2	H13-0
-8 423 -437	-2 429 410	-3 643 -642	H4+3	3 190 196	H6+0	8 1215 -1196	H9+2	H13-0
-6 2051 1926	0 669 675	-1 341 343	H4+3	5 873 -866	H6+0	6 597 -607	H9+2	H13-0
-4 1085 1089	2 252 224	-2 158 129	H4+3	7 404 415	H6+0	8 1215 -1196	H9+2	H13-0
-2 149 -124	4 118 400	-4 1133 -1133	H4+3	9 374 -381	H6+0	6 597 -607	H9+2	H13-0
H1+8	4 662 671	-5 735 754	H4+3	10 122 6	H6+0	8 1215 -1196	H9+2	H13-0
1 886 866	3 185 -325	5 90 12	H4+3	10 122 6	H6+0	6 597 -607	H9+2	H13-0
3 685 -685	8 314 -170	7 520 -515	H4+3	10 122 6	H6+0	8 1215 -1196	H9+2	H13-0
5 136 -136	9 563 -576	-6 384 365	H4+3	-7 759 760	H6+0	6 597 -607	H9+2	H13-0
7 981 964	-4 557 570	-5 711 -717	H4+3	-5 218 -234	H6+0	8 1215 -1196	H9+2	H13-0
H1+7	-2 162 -84	-3 544 546	H4+3	3 217 -198	H6+0	6 597 -607	H9+2	H13-0
0 682 -676	-5 544 546	-6 384 365	H4+3	5 873 -866	H6+0	8 1215 -1196	H9+2	H13-0
2 124 70	-3 254 -236	-2 1341 -1342	H4+3	7 404 415	H6+0	6 597 -607	H9+2	H13-0
-1 168 169	4 662 -671	-1 816 834	H4+3	9 374 -381	H6+0	8 1215 -1196	H9+2	H13-0
1 580 -582	6 910 -930	1 760 -755	H4+3	10 122 6	H6+0	6 597 -607	H9+2	H13-0
3 425 -415	8 809 -819	3 466 -485	H4+3	10 122 6	H6+0	8 1215 -1196	H9+2	H13-0
5 358 375	10 518 -526	5 723 725	H4+3	10 122 6	H6+0	6 597 -607	H9+2	H13-0
7 432 -430	7 1970 -1876	8 131 -18	H4+3	10 122 6	H6+0	8 1215 -1196	H9+2	H13-0
9 566 568	9 312 332	-6 384 365	H4+3	10 122 6	H6+0	6 597 -607	H9+2	H13-0
H1+6	-6 204 -136	-7 727 -723	H4+3	10 122 6	H6+0	8 1215 -1196	H9+2	H13-0
-3 563 575	-4 727 -723	-5 745 -767	H4+3	10 122 6	H6+0	6 597 -607	H9+2	H13-0
-1 84 5	0 1031 -1034	-1 382 390	H4+3	10 122 6	H6+0	8 1215 -1196	H9+2	H13-0

* The column headings are h , $200F_0$ and $200F_c$; k and l are listed at the head of each group of reflections. Unobserved reflections are indicated by asterisks and strongly extinguished reflections by Es.

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*'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

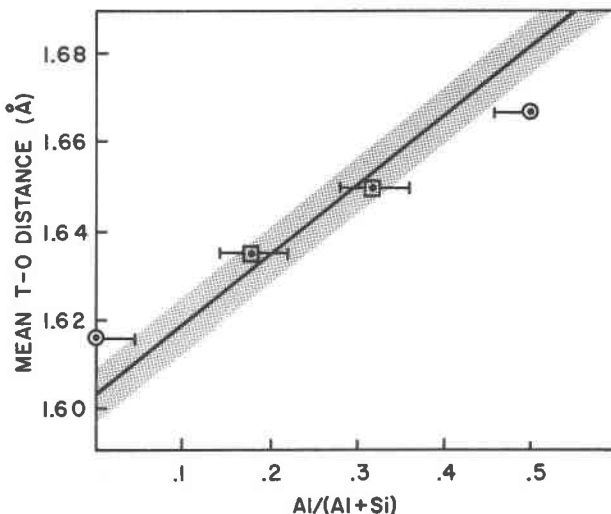


FIG. 2. Plot of the mean T-O distance as a function of the atom fraction Al/(Al + Si) as determined by neutron diffraction. The circles are points from the present work and the squares are the sanidine results of Brown *et al.* (1971). The indicated errors in the present work represent 2σ from the physically 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
$ii^i_{O_A(1)}$	(0.138) 0.125*	#0.878		1.881
$ii^i_{O_A(2)}$	(0.204) 0.185		#0.982	2.149
iii_{O_B}	(0.094) 0.085*	0.883	1.018	1.986
iii_{O_C}	(0.076) 0.069*	0.863	1.002	1.934
iii_{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 $\bar{h}k\bar{l}$ 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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