Canadian Mineralogist
Vol. 29, pp. 543-552

STRUCTURE REFINEMENT OF AN ADULARIAN END-MEMBER HIGH SANIDINE FROM THE BUCK CLAIM PEGMATITE, BERNIC LAKE, MANITOBA

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ABSTRACT

The structures of an adularian end-member high sanidine and of three closely related specimens from a granitic pegmatite at the Buck Claim, Bernic Lake, Manitoba, have been refined in space group *C*2/*m*. The end-member high sanidine ("Buck-18-I") has the following respective unit-cell parameters, $<T\text{-}O>$ distances, and Al contents t_i in the tetrahedra (1σ errors in brackets): a 8.603(2), b 13.036(4) c7.174(2) Å, β 116.03(2)°, V 722.9(3) Å^3, $<T_1\text{-O}>$ 1.640(1) Å, $< T_2\text{-O}>$ 1.642(1) Å, t_1 0.25(1) Al, t_2 0.25(1) Al. Electron-microprobe analyses of six crystals, including the four that were structurally analyzed, gave the mean composition $K_{0.991}Al_{1.008}Si_{2.996}O_8$ (*i.e.*, Or_{100}). The results indicate that Buck-18-I is completely disordered with respect to (Si,Al), and that it is the first structural and chemical end-member high sanidine yet to be described. The structural results for the other three crystals indicate that they consist of high sanidine of variable but largely slight degree of incipient order. The structure and composition of these four samples of adularia and the unit-cell parameters of one other are in agreement with the suggestion of Černý & Chapman (1984) that such metastable high sanidine originated by rapid nucleation and crystal growth on fissure walls after a sudden drop in P_{fluid}; the high sanidine was preserved because of minimal subsequent exposure to order-promoting agents.

Keywords: high sanidine, end-member, adularia, pegmatite, Si,Al disorder-order, structure refinement, Bernic Lake, Manitoba.

SOMMAIRE

La structure d'un échantillon de sanidine désordonnée, de variété dite adulaire, et de trois autres échantillons semblables, tous en provenance de la pegmatite granitique de Buck Claim, au lac Bernic (Manitoba), a été affinée dans le groupe spatial *C*2/*m*. L'échantillon le plus près du pôle désordonné (Buck-18-I) possède les paramètres réticulaires, distances $<T\text{-O}>$, et teneurs en Al des sites tétraédriques t_i suivants (avec erreurs 1σ entre parenthèses): a 8.603(2), b 13.036(4), c 7,174(2) Å, β 116.03(2)°, V 722.9(3) Å^3, $<T_1\text{-O}>$ 1.640(1), $<T_2\text{-O}>$ 1.642(1) Å, t_1 = 0.25(1) Al, t_2 = 0.25(1) Al. Une analyse de six cristaux à la microsonde électronique, y inclus les quatre dont la structure a été déterminée, a donné, comme composition moyenne, $K_{0.991}Al_{1.008}Si_{2.996}O_8$, c'est-à-dire Or_{100}. Les résultats montrent que Buck-18-I est complètement désordonné par rapport à Al et Si, et qu'il s'agit du premier exemple du pôle désordonné ainsi décrit structuralement and chimiquement. Les résultats obtenus pour les trois autres cristaux montrent qu'il s'agit également de sanidine désordonnée; ils possèdent un degré variable de mise en ordre. La structure et la composition de ces quatre échantillons à habitus d'adulaire, et les paramètres réticulaires d'un cinquième, confirment l'hypothèse de Černý et Chapman (1984), à savoir que de tels exemples de sanidine désordonnée se sont formés hors de son champ de stabilité par nucléation et croissance rapides sur les parois de fissures, suite à une décompression rapide impliquant P_{fluide}. De tels exemples de métastabilité ont été préservés à cause du peu d'influence des agents promoteurs de la mise en ordre.

(Traduit par la Rédaction)

Mots-clés: sanidine désordonnée, pôle, adulaire, pegmatite, degré d'ordre (Al,Si), affinement de la structure, lac Bernic, Manitoba.

INTRODUCTION

A monoclinic K-rich feldspar in which Si and Al are completely disordered is generally regarded as the structural end-member of the maximum (low) microcline (triclinic) - high sanidine (monoclinic) series. If such a disordered sanidine is also chemically pure $KAlSi_3O_8$, it would be logical to consider it as "end-member" high sanidine. The b and c unit-cell parameters are sensitive to the degree of Si,Al order in monoclinic K-rich feldspar. Values of b of about 13.03–13.04 Å and of c of about 7.17 Å have been proposed for completely disordered end-member high sanidine (Ferguson 1980, Kroll & Ribbe 1983, 1987, Smith & Brown 1988).

To date, structure refinements of natural sanidine have been performed mainly on Na-rich, high-temperature feldspar of igneous origin, and only rarely on feldspar from metamorphic rocks (see summaries by, *e.g.*, Smith 1974, Ferguson 1980, Scambos *et al.* 1987, Smith & Brown 1988). It is only recently that Na-poor, highly disordered potassium feldspar has been found in hydrothermal environments, outside the P–T range of their stability (Foord & Martin 1979, Lenton 1979). Černý & Chapman (1984, 1986) identified such material in a number of specimens of adularia, the low-temperature variety of Or-rich feldspar with characteristic habit, from diverse hydrothermal veins and low-grade metamorphic or metasomatic rocks (for definition and characteristics see Nissen 1967, Černý & Chapman 1984, 1986, Smith & Brown 1988).

Černý & Chapman (1984, 1986) found that certain samples of adularia from granitic pegmatites and hydrothermal vein deposits have three distinctive characteristics: (1) *b* and *c* values derived from powder-diffraction data closely approach the values proposed for end-member high sanidine, (2) characteristic bands of the infrared absorption spectrum are shifted beyond the values that, until then, had been observed on other samples of sanidine, and (3) chemical compositions closely approach $KAlSi_3O_8$. In the present paper we describe single-crystal structure refinements of four crystals, and electron-microprobe data for six crystals, from one of the adularia specimens of pegmatitic provenance (Černý & Chapman 1984) that closely approaches end-member high sanidine.

Prior to the present investigation, the structurally refined sanidine that most closely approximates end-member high sanidine has a composition $Or_{97.6}$, *b* 13.028(5), *c* 7.175(2) Å, and an origin in the upper mantle (Scambos *et al.* 1987). Structurally, this crystal has, respectively, mean $<T_1\text{-O}>$ and $<T_2\text{-O}>$ distances of 1.644(1) and 1.639(1) Å, and Al contents t_1 and t_2 of 0.266 and 0.234 Al, whereas a completely Si,Al-disordered high sanidine would be expected to have $<T_1\text{-O}> = <T_2\text{-O}>$ of about 1.642 Å, and $t_1 = t_2 = 0.25$ Al. Available unit-cell and chemical data for the adularia samples studied by Černý & Chapman (1984, 1986) suggest that they are even closer to the disordered end-member.

Specimen Buck-18, selected for structure analysis, comes from the Buck Claim pegmatite in southeastern Manitoba (Lenton 1979, Černý & Chapman 1984). These authors had found, from results of electron-microprobe analyses, that a closely related sample of adularia habit consists of Or_{100} and, from X-ray powder diffractometry, that Buck-18 has a *b* of 13.046(4) and a *c* of 7.172(2) Å. To assess the closeness of the structures of some of the Buck-18 crystals to end-member high sanidine and to each other, four were refined using a single-crystal four-circle diffractometer. Several others were examined on that instrument for crystal quality and to obtain precise unit-cell parameters. Six of the crystals were chemically analyzed by electron microprobe.

TABLE 1. CELL PARAMETER AND STRUCTURE ANALYSIS DATA FOR THE FOUR REFINED CRYSTALS

Crystal designation					
full		Buck-18-I	Buck-18-II	Buck-18-III	Buck-18-IV
brief		I	II	III	IV
Feldspar name		End-Member High Sanidine	High Sanidine	High Sanidine	High Sanidine
Crystal size, mm		0.24x0.18x0.16	0.28x0.16x0.14	0.22x0.16x0.14	0.18x0.14x0.12
μ, cm^{-1}		13.5	13.3	13.5	13.5
Rad/Mono			-- MoKα/graphite --		
Limiting 2θ angles,°		3 - 100	3 - 60	3 - 100	3 - 100
Asymmetric units collected		1	2	1	1
Total unique Fo		3929	1106	3911	3924
Merging *R*, %		1.7	1.5	1.7	1.5
Total Fo used		($I>5\sigma$) 1799	($I>4\sigma$) 978	($I>5\sigma$) 2201	($I>5\sigma$) 1724
Final R, wR[1], %		5.8, 6.1	4.2, 4.4	5.8, 6.1	5.6, 5.9
Space group			-- C2/m --		
Unit cell parameters	powder[2]				
a, Å	8.602(2)	8.603(2)	8.608(3)	8.611(2)	8.606(2)
b, Å	13.046(4)	13.036(4)	13.041(5)	13.046(5)	13.017(4)
c, Å	7.172(2)	7.174(2)	7.180(1)	7.175(3)	7.185(2)
β, °	116.01(2)	116.03(2)	115.98(2)	116.01(2)	115.97(2)
V, Å^3	723.4(2)	722.9(3)	724.5(4)	724.4(4)	723.6(3)
Unit cell content			$4[K_{0.99}Al_{1.01}Si_{3.00}O_8]$ (Table 2)		

[1] $R = \Sigma(||Fo|-|Fc||)/\Sigma|Fo|$, $wR = \{\Sigma w[(|Fo|-|Fc|)]^2/\Sigma w[|Fo|]^2\}^{½}$, $w = 1$.
[2] from Černý & Chapman (1984); bulk sample of crystals separated from a random collection of specimens.

DESCRIPTION OF THE MATERIAL STUDIED, AND RESULTS OF THE ELECTRON-MICROPROBE ANALYSES

Specimen Buck-18 (Černý & Chapman 1984) is from the quartz core of an Archean granitic pegmatite at the Buck Claim, Bernic Lake in southeastern Manitoba (Lenton 1979). The pegmatite is of the complex (Li, Rb, Cs)-enriched type, petalite subtype (Černý 1989). The adularia occurs in open fractures on drusy surfaces in the massive quartz as iron-oxide-stained but otherwise colorless crystals of the Felsöbanya–Maderaner type (Černý & Chapman 1986). (In some crystals the staining appears to be in very thin, morphologically compatible zones.) The crystals are up to about 0.25 mm across, and are closely associated with more abundant milky white carbonate-rich apatite crystals of equidimensional doubly terminated quartz-like habit, and up to about 0.5 mm across. All of the dozen or so crystals we examined optically have marked wavy extinction. All crystals that form part of this investigation come from three different fist-sized hand specimens that had been collected from material excavated during trenching. The spatial relationship of the specimens to each other within the quartz core exposed along 25 m is thus not known.

The first crystal whose structure we refined (subsequently designated crystal II) proved, as we describe below, to be slightly Si,Al-ordered, and thus not, strictly speaking, end-member high sanidine. We therefore refined three more crystals (Table 1) to see if any of these is, within the limit of error, completely disordered, and to determine the structural relationship among the four crystals. After the four had been analyzed, they were given the full designations Buck-18-I, -II, -III, -IV (in brief, simply I, II, III, IV) in the sequence of increasing Si,Al order. Only crystal I proved to be completely disordered, and hence to be end-member high sanidine. The other three crystals differ slightly but measurably in Si,Al order from I and from one to the other, and they were thus, in the first instance, considered to be simply examples of high sanidine. (However, see below under DISCUSSION.)

The electron-microprobe analyses were carried out on structurally analyzed crystals I and IV and on four other undesignated crystals. The analyses were done on a CAMECA SX-50 instrument using the wavelength-dispersion mode and a beam diameter of 5 μm. Operating conditions were, for Na, K, Al and Si, 15 kV, 20 nA, and 20 s (peak) and 10 s (background) counting times; for Rb, Cs, Fe, Mg, Ca, Sr, Ba, Ti, P, 15 kV, 40 nA, and 50 s for both peak and background. The following standards were used: albite (Na), orthoclase (K, Fe, Al, Si), sanidine (Ba), anorthite (Ca), microcline (Rb), pollucite (Cs), hornblende (Mg, Ti), VP_2O_7 (P), $SrTiO_3$ (Sr). The detection limits (Table 2) were deduced using the formula $3/m(R_b/T_b)^{1/2}$, where m = (peak count rate – background count rate)/% conc., R_b = background count rate (c/s) and T_b = background time (s).

TABLE 2. CHEMICAL COMPOSITION OF THE CRYSTALS[1]

CRYSTAL[2]	Mean of 4 crystals[3] [17]	I [12]	IV [12]	Mean of 6 crystals [41]	atomic content[4]
K_2O	16.81(16)	16.71(28)	16.86(17)	16.79(12)	K 0.991(7)
Al_2O_3	18.47(22)	18.50(26)	18.53(21)	18.50(13)	Al 1.008(7)
SiO_2	64.92(56)	64.90(63)	64.55(25)	64.79(29)	Si 2.996(13)
Σ	100.24	100.11	99.94	100.08	-

Molecular formula $K_{0.991}Al_{1.008}Si_{2.996}O_8$ = Or_{100}[5]

[1] Obtained by electron microprobe analysis; results in wt.%; standard deviations in parentheses. In addition to the elements shown in the table, the various means for the following elements were determined as below the detection limits (given in wt.%): Na_2O 0.03; Rb_2O,0.016; Cs_2O 0.030; Fe_2O_3 0.02; MgO 0.008; CaO 0.011; SrO 0.063; BaO 0.023; TiO_2 0.031; P_2O_5 0.018. [2] For full designations and feldspar names of I and IV, see Table 1; numbers of points analyzed in square brackets. [3] Crystals undesignated. [4] Normalized on the basis of 8 oxygen atoms. [5] See text.

The results of the electron microprobe analyses are given in Table 2. As noted in footnote 1 of the table, the means for all elements except major K, Al and Si are less than the detection limits (given in the footnote). Furthermore, the atomic contents of the three major cation sites K, Al and Si are within, or very close to, 1σ of 1, 1 and 3 respectively, as expected. From these results, one may draw two important conclusions, (1) that the six crystals analyzed have the same composition within the limits of error, and (2) that their composition is, within the limits of error, that of ideal $KAlSi_3O_8$ *(i.e.,* Or_{100}).

STRUCTURE AND UNIT-CELL PARAMETER REFINEMENTS

The structure refinements of the four crystals were carried out in the order II, IV, I, and III, this order being significant only because the initial parameters used for some refinements were the final parameters of the preceding one. All four refinements were done in the same way, but with some differences in operating conditions as shown in Table 1. Each crystal was mounted on a Nicolet *R*3*m* automated four-circle diffractometer, centered optically, and then automatically centered more precisely using the *x, y* coordinates for 25 low-angle X-ray reflections recorded on a rotation photograph. These reflections gave a set of moderately accurate unit-cell parameters, which provided the orientation matrix that was used for the data collection. This followed the procedure of Ercit *et al.* (1986). Empirical absorption (ψ-scan), L–p and background corrections were made, and equivalent reflections merged. Details of the numbers of asymmetric units over which intensities were collected, and the numbers of reflections involved, are given in Table 1. Following collection of each data-set, a "high-angle" refinement of the unit-cell parameters was carried out by a repeat of the initial automatic centering step but using as input, in place of photographic reflection-coordinates, the *hkl* values for 25 reflections chosen arbitrarily for (1) the absence of zeros in *h, k, l* (except for the first crystal II), (2) a good variety of *hkl* values, and (3) intensities that are medium to strong (taken from the data collection). The unit-cell parameters in Table 1 were derived in this way.

During this investigation, we found it desirable to use the four-circle diffractometer to determine, for a given crystal, refined unit-cell parameters from a "high-angle" refinement *before* necessarily embarking on collection of a full data-set. This was done simply by bypassing the data collection described in the above procedure, and proceeding directly to a high-angle refinement for which the input was a set of 25 *hkl* values arbitrarily chosen according to the three criteria given immediately above. One such unit-cell refinement required, in our case, about five hours of instrument plus operator's time, and we applied the procedure, in the first instance, to several of the crystals whose structures or unit-cell parameters are given in the paper.

The SHELXTL package of programs was used for the structure refinements. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The form of the R indices is given in Table 1.

The following conditions held for the analysis of crystals II and III. The starting positional parameters were taken from Table 2 of Scambos *et al.* (1987) for their high sanidine [their parameter *y* for T_2 should read 0.11813(4)]. The starting (isotropic) $U_{equiv.}$ values for the cations were taken from the same authors' Table 4; for the oxygen atoms, the widely assigned starting value of 0.015 Å was used. The two T sites were given the scattering factor for Si. This isotropic refinement gave R = 5.27 and 7.7%, respectively. In the second and final refinements, the temperature factors were set to be anisotropic, and the two *T* sites were given scattering factors corresponding to $Si_{0.75}Al_{0.25}$. These refinements gave the *R* and *wR* values shown in Table 1.

For the second and third crystals refined, IV and I, the starting positional parameters and the isotropic temperature-factors were chosen close to the final values for the preceding crystal analyzed, and the site occupancies of the two *T* sites were fixed at $Si_{0.75}Al_{0.25}$. The final anisotropic refinements gave the *R* and *wR* values shown in Table 1. These refinements excluded reflections with $I < 5\sigma(I)$ (Table 1); refinements of the same data that excluded reflections with $I < 4\sigma$ (as was done in the case of II) gave corresponding *R* and *wR* values about 1% higher, although all corresponding positional parameters were found to be within 1σ of each other, and most anisotropic temperature-factor coefficients, within 2σ. We attribute the

TABLE 3. POSITIONAL PARAMETERS AND $U_{EQUIVALENT}$ VALUES FOR THE FOUR STRUCTURALLY ANALYZED CRYSTALS

Site	X	Y	Z	$U_{equiv.}$[1]
		I^2: End-Member High Sanidine		
K	0.2869(2)	0	0.1383(2)	3.01(4)
T_1	0.0100(1)	0.18584(7)	0.2239(1)	1.21(1)
T_2	0.7108(1)	0.11828(7)	0.3442(1)	1.19(1)
O_{A1}	0	0.1476(3)	0	2.19(11)
O_{A2}	0.6396(5)	0	0.2839(6)	2.16(10)
O_B	0.8301(3)	0.1486(2)	0.2264(4)	2.59(8)
O_C	0.0361(3)	0.3103(2)	0.2572(4)	2.02(7)
O_D	0.1782(3)	0.1272(2)	0.4026(4)	2.19(7)
		II: High Sanidine		
K	0.2868(2)	0	0.1383(2)	3.00(4)
T_1	0.0100(1)	0.18569(7)	0.2237(1)	1.27(1)
T_2	0.7108(1)	0.11824(7)	0.3442(1)	1.22(1)
O_{A1}	0	0.1475(3)	0	2.26(13)
O_{A2}	0.6393(4)	0	0.2841(6)	2.18(12)
O_B	0.8301(3)	0.1482(2)	0.2268(4)	2.58(9)
O_C	0.0363(3)	0.3107(2)	0.2579(4)	2.00(8)
O_D	0.1785(3)	0.1272(2)	0.4036(4)	2.14(8)
		III: High Sanidine		
K	0.2865(1)	0	0.1382(2)	3.04(3)
T_1	0.0100(1)	0.18572(6)	0.2238(1)	1.29(1)
T_2	0.7107(1)	0.11825(6)	0.3442(1)	1.27(1)
O_{A1}	0	0.1474(3)	0	2.29(9)
O_{A2}	0.6398(4)	0	0.2850(5)	2.19(9)
O_B	0.8299(3)	0.1482(2)	0.2265(4)	2.64(7)
O_C	0.0362(3)	0.3109(2)	0.2576(3)	2.05(6)
O_D	0.1788(3)	0.1268(2)	0.4035(3)	2.24(6)
		IV: High Sanidine		
K	0.2864(2)	0	0.1384(2)	2.85(4)
T_1	0.0098(1)	0.18558(7)	0.2239(1)	1.18(1)
T_2	0.7106(1)	0.11816(7)	0.3444(1)	1.10(1)
O_{A1}	0	0.1470(3)	0	2.12(11)
O_{A2}	0.6392(5)	0	0.2844(6)	2.10(10)
O_B	0.8293(3)	0.1479(2)	0.2267(4)	2.46(8)
O_C	0.0362(3)	0.3112(2)	0.2581(4)	1.91(7)
O_D	0.1788(3)	0.1268(2)	0.4046(3)	2.04(7)

[1] $U_{equiv.} = U_{equiv.} \times 10^2$ (Å^2). [2] For full crystal designation see Table 1.

lower *R* and *wR* values (4.2 and 4.4%) for the first crystal refined, II, even with the exclusion of reflections with $I<4\sigma$, to the presumed better quality of that crystal relative to the other three because, as we describe below, the quality of different crystals of this specimen of adularia appears to vary widely. We also attribute the relatively high *R* indices (4–6%), in general, to the presumed poor quality of these metastable crystals implied by the wavy extinction noted earlier.

STRUCTURE RESULTS

The positional parameters and $U_{equiv.}$ values, and the anisotropic temperature-factor coefficients for the four structures, are given in Tables 3 and 4, respectively. Observed and calculated structure-factors for them are given in Table 5, which is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected bond-lengths and bond angles for the four are given in Table 6. This table also gives the Al contents of the tetrahedra, t_j, which can be deduced from the $<T$–O$>$ distances using any one of several equations proposed to interrelate t_j and $<T$–O$>$ in alkali feldspar (see, *e.g.*, the discussion in Kroll & Ribbe 1983). We arrived at the values of t_j given in Table 6 by applying, for example for crystal II, the departure in size of the tetrahedra from ideal disorder, *i.e.*, 1.644–1.642 = 1.642–1.640 = 0.002 Å, to the "modified Jones–Ribbe–Gibbs" relationship in Ferguson (1980) to give differences in Al content δt_j of 0.02 Al. In this way, we have arrived at Al contents t_1 of 0.27 and t_2 of 0.23 Al for crystal II; the other t_j values in the table have been arrived at in the same way. In the case of crystal III, the t_j values were calculated using the actual $\ll T$–O$\gg$ value of 1.6425 Å rather than the rounded value of 1.643 Å given in Table 6. The t_j values for crystals II, III and IV can be taken as a measure

TABLE 4. ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS FOR THE FOUR STRUCTURALLY ANALYZED CRYSTALS

Site	U_{11}[1]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			I[2]: End-Member High Sanidine			
K	203(4)	393(7)	296(5)	0	100(4)	0
T_1	121(1)	121(1)	121(1)	0	53(1)	0
T_2	119(1)	119(1)	119(1)	0	52(1)	0
O_{A1}	316(17)	211(14)	163(12)	0	136(12)	0
O_{A2}	189(13)	180(14)	232(15)	0	49(11)	0
O_B	225(10)	332(13)	263(11)	3(10)	147(9)	-58(10)
O_C	192(9)	203(10)	214(10)	-18(8)	93(8)	-25(8)
O_D	227(10)	236(11)	160(8)	13(8)	53(7)	27(9)
			II: High Sanidine			
K	231(5)	351(6)	305(6)	0	106(5)	0
T_1	127(2)	127(2)	127(2)	0	56(1)	0
T_2	122(2)	122(2)	122(2)	0	54(1)	0
O_{A1}	352(20)	185(16)	173(15)	0	146(14)	0
O_{A2}	196(17)	148(15)	245(17)	0	37(14)	0
O_B	257(13)	291(14)	261(12)	0(11)	147(10)	-38(11)
O_C	229(12)	143(11)	236(12)	-23(9)	109(10)	-21(9)
O_D	257(12)	192(12)	173(11)	11(9)	78(9)	19(10)
			III: High Sanidine			
K	207(4)	388(5)	298(5)	0	93(3)	0
T_1	129(1)	129(1)	129(1)	0	57(1)	0
T_2	127(1)	127(1)	127(1)	0	56(1)	0
O_{A1}	298(14)	228(13)	171(10)	0	114(10)	0
O_{A2}	192(11)	176(11)	235(12)	0	44(10)	0
O_B	218(9)	351(12)	259(9)	1(9)	135(8)	-43(8)
O_C	193(7)	199(8)	219(8)	-29(7)	86(6)	-28(7)
O_D	233(8)	231(9)	168(7)	12(7)	51(6)	23(7)
			IV: High Sanidine			
K	201(4)	351(6)	288(5)	0	93(4)	0
T_1	118(1)	118(1)	118(1)	0	52(1)	0
T_2	110(1)	110(1)	110(1)	0	48(1)	0
O_{A1}	300(17)	181(14)	183(13)	0	132(12)	0
O_{A2}	184(13)	149(13)	241(15)	0	42(12)	0
O_B	224(11)	318(13)	236(11)	11(10)	138(9)	-32(10)
O_C	198(9)	168(9)	212(10)	-26(8)	93(8)	-28(8)
O_D	224(10)	213(11)	136(8)	14(8)	44(7)	22(9)

[1] U_{ij} = U_{ij} x 10^4. [2] For full crystal designation, see Table 1.

TABLE 6. SELECTED T-O AND K-O BOND LENGTHS, T-O-T BOND ANGLES AND TETRAHEDRAL Al-CONTENTS t_j FOR THE FOUR STRUCTURALLY ANALYZED CRYSTALS

Bond lengths (Å) and Al-contents t_j (Al) in the tetrahedra

	I[1]:EMHS[2]	II:HS[2]	III:HS	IV:HS
T_1-O_{A1}	1.648(1)	1.648(2)	1.648(1)	1.652(1)
-O_B	1.630(3)	1.633(3)	1.634(3)	1.637(3)
-O_C	1.641(3)	1.649(3)	1.652(2)	1.655(3)
-O_D	1.641(2)	1.647(2)	1.650(2)	1.653(2)
$<T_1$-O$>$	1.640(1)	1.644(1)	1.646(1)	1.649(1)
T_2-O_{A2}	1.645(1)	1.646(1)	1.645(1)	1.642(1)
-O_B	1.639(4)	1.636(4)	1.637(3)	1.632(4)
-O_C	1.641(3)	1.638(3)	1.636(2)	1.632(3)
-O_D	1.644(2)	1.640(2)	1.638(2)	1.633(2)
$<T_2$-O$>$	1.642(1)	1.640(1)	1.639(1)	1.635(1)
$<<$T-O$>>$	1.641(1)	1.642(1)	1.643(1)	1.642(1)
t_1	0.25(1)	0.27(1)	0.27(1)	0.30(1)
t_2	0.25(1)	0.23(1)	0.23(1)	0.20(1)

T-O-T angles (°)

	I:EMHS	II:HS	III:HS	IV:HS
T_1-O_{A1}-T_1	144.8(3)	144.8(2)	144.7(2)	144.6(3)
T_2-O_{A2}-T_2	139.2(2)	139.0(2)	139.4(2)	139.0(2)
T_1-O_B-T_2	152.9(2)	153.1(2)	152.9(1)	152.8(2)
T_1-O_C-T_2	131.3(2)	131.2(2)	131.1(1)	131.0(2)
T_1-O_D-T_2	141.4(2)	141.7(2)	141.3(2)	141.8(2)

K-O bond lengths (Å)

	I:EMHS	II:HS	III:HS	IV:HS
K-O_{A2} (x1)	2.742(4)	2.742(4)	2.748(3)	2.744(4)
-O_{A1} (x2)	2.937(3)	2.938(3)	2.937(2)	2.928(3)
-O_D (x2)	2.962(3)	2.967(3)	2.961(3)	2.965(3)
K-O_B (x2)	3.050(3)	3.051(3)	3.048(3)	3.048(3)
-O_C (x2)	3.136(3)	3.135(3)	3.135(2)	3.127(3)
-O_{A2} (x1)	3.355(5)	3.361(5)	3.363(4)	3.367(5)

[1] For full crystal designation, see Table 1. [2] Symbols EMHS and HS denote respectively End-Member High Sanidine and High Sanidine.

of the departure of these structures from complete Si,Al-disorder ($t_1 = t_2 = 0.25$ Al).

Discussion

Comparison of unit-cell parameters determined on powder and single crystal

Because the crystals ground and used to obtain the powder diffractogram of Černý & Chapman (1984) had been taken from a random collection of specimens, including the Buck-18 samples, one can only compare their unit-cell parameters with those for the near-end-member crystal(s) with which they agree most closely. Such a comparison can be made from cell parameters in Table 1 and in Figure 1 which is an adapted portion of the *b*-*c* diagram for K-rich alkali feldspars of Černý & Chapman (1984, Fig. 3). This comparison shows that the powder-derived cell parameters are very close to those for our three most disordered crystals, I, II and III. In particular, the *b* parameter determined on powder is very nearly within 1σ of the values for those three single crystals and the *c* parameter determined on powder, mostly within 2σ of the three single-crystal values. One may thus reasonably conclude (1) that the powder sample of Černý & Chapman must have consisted predominantly, or almost completely, of crystals of disordered high sanidine, and (2) that unit-cell parameters derived for the "same" specimen by the powder and the single-crystal methods using the standard procedures practiced in our laboratory are, as one might expect, closely comparable.

Closeness of Buck-18 crystal I to end-member high sanidine, and comparison with similar samples

With respect to structure, it has long been established for the feldspars and other aluminosilicate minerals that the mean bond-length, <*T*-O> is within a given chemical structure-type such as the K-feldspars, a function of the (statistical) Si,Al content. It is generally assumed that, for an

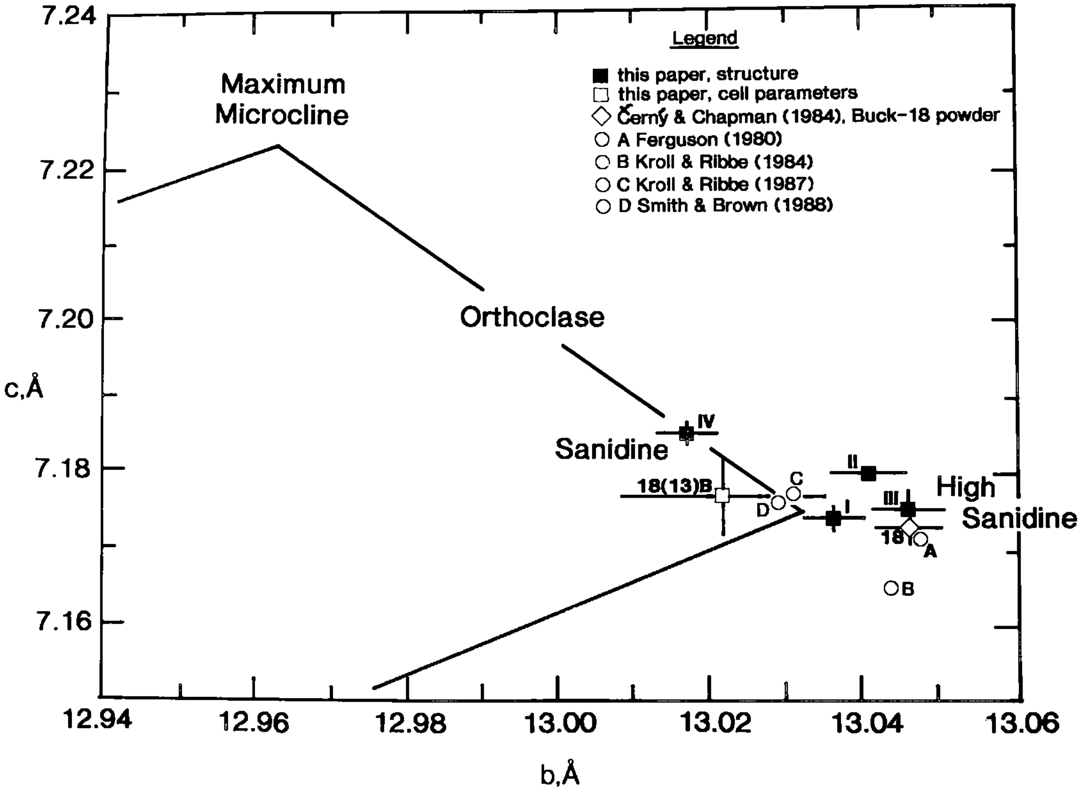

FIG. 1. Plot of unit-cell parameters *c versus b* for the samples of high sanidine described in this paper. Crystal 18(13)B was not given a Roman designation because its structure was not refined. Diagram modified from Figure 3 in Černý & Chapman (1984); solid lines are from Figure 1 in Stewart & Wright (1974). The value plotted as "Kroll & Ribbe (1984)" is taken from Černý & Chapman (1984) (priv. comm. to Černý).

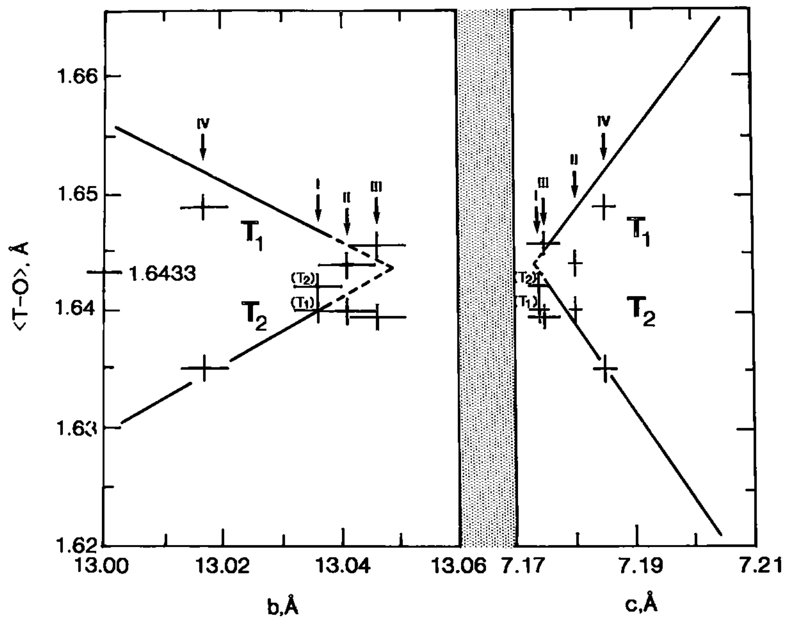

FIG. 2. Plots of $<T_1\text{-O}>$ and $<T_2\text{-O}>$ *versus* b and c for the samples of high sanidine described in this paper. Diagram modified from Figure 4 in Ferguson (1980); solid lines result from linear regressions for the 10 samples of monoclinic K-feldspar whose structures had been refined at that time. The $<T\text{-O}>$ value of 1.6433 Å is that for the (1980) convergence points. Note the inversion of the pairs of points for crystal I with respect to the regression lines for T_1 and T_2; see text.

$AlSi_3$-type feldspar, all tetrahedra within which the Si and Al atoms are completely disordered will be of the same size, and that the size will be close to the mean value of all tetrahedra in alkali feldspar structures, namely about 1.642 Å.

If we assess our structurally analyzed crystal designated I with respect to these two criteria, we can see first (from Table 2) that it has the composition Or_{100} within the errors of the microprobe analysis. This crystal thus fulfills the chemical requirement for end-member high sanidine. Secondly, from a structural point of view, (1) Table 1 and Figure 1 show that its b and c unit-cell parameters are among the most extreme yet observed, (2) Table 6 shows that with $<T_1\text{-O}>$ and $<T_2\text{-O}>$ values of 1.640(1) and 1.642(1) Å, respectively, the sizes of the two tetrahedra are equal within an error of 1σ (Fig. 2, modified from Fig. 4 in Ferguson 1980), and (3) Table 6 also shows that the overall mean $\ll T\text{-O} \gg$ is 1.641(1) Å, in agreement within 1σ with the earlier given value of 1.642 Å expected for complete disorder. We attach no significance to the fact that in (2), $<T_1\text{-O}>$ is, contrary to the usual situation, smaller than $<T_2\text{-O}>$, because both are equal within 1σ. The two $<T_j\text{-O}>$ values indicate that the structure is completely disordered with respect to Si and Al, *i.e.*, that the Al contents of the two tetrahedra obey the relationship $t_1 = t_2 = 0.25$. One may thus conclude that the crystal designated Buck-18-I can reasonably be described as "end-member high sanidine".

Chemical, unit-cell and structural data for previously published refinements of high sanidine are compared with corresponding data for our four refined structures in Table 7. The sanidine that, until now, has most closely approached end-member high sanidine is the one from the upper mantle described by Scambos *et al.* (1987). It has a composition $Or_{97.6}Ab_{1.8}Cn_{0.4}$, and $<T_1\text{-O}>$ and $<T_2\text{-O}>$ values of 1.644(1) and 1.639(1) Å, respectively. A comparison with the properties of our crystal I shows that, with respect to both chemistry and structure, our crystal is virtually identical with end-member high sanidine, and definitely much closer to such an end member than the upper-mantle sanidine.

Because $<T_1\text{-O}>$ had been found to be larger than $<T_2\text{-O}>$ by small but significant amounts in the high sanidine of Scambos *et al.* (1987) as well as in all the other previously refined unheated and heated crystals of high sanidine (Table 7), those

TABLE 7. COMPARISON OF CHEMICAL AND STRUCTURAL DATA FOR STRUCTURALLY REFINED END-MEMBER AND NEAR-END-MEMBER HIGH SANIDINE CRYSTALS

Ref.[1]	Sample no. or source	Comp. mol.% Or Ab	An Cn	Heating: T/t	Refinement/no. of refls.	Unit cell parameters[2] a, Å b, Å	c, Å β, °	<T-O>, Å[2] T_1 T_2
1[3]	getempert Sanidin	87 13	- -	750°C ?	X-ray 2000	8.546(5) 13.037(5)	7.178(5) 115.97(5)	1.645(2) 1.641(2)
2a[4]	SANI	85 14	- 1	950°C 20h	X-ray 6378	8.546(1) 13.033(2)	7.176(2) 115.97(2)	1.6443(9) 1.6402(10)
2b[4]	SANN			1050°C 500h	X-ray 9319			1.6445(8) 1.6400(8)
2c[4]	SAGT			as preced.	Neutron 3450			1.6454(5) 1.6401(6)
3	upper mantle	97.6 1.8	0.2 0.4	none	X-ray 2150	8.595(3) 13.028(5)	7.175(2) 115.94(2)	1.644(1) 1.639(1)
4	heated LM	90.7[5] 8.8	0.1 0.2	1050°C 200d	X-ray 817	8.5646(2) 13.0334(3)	7.1747(2) 115.984(2)	1.643(2)[6] 1.640(2)[6]
5a	Buck-I[7]	100[8] 0	0 0	none	X-ray 1799	8.603(2) 13.036(4)	7.174(2) 116.03(2)	1.640(1) 1.642(1)
5b	Buck-II				X-ray 978	8.608(3) 13.041(5)	7.180(1) 115.98(2)	1.644(1) 1.640(1)
5c	Buck-III				X-ray 2201	8.611(2) 13.046(5)	7.175(3) 116.01(2)	1.646(1) 1.639(1)
5d	Buck-IV				X-ray 1724	8.606(2) 13.017(4)	7.185(2) 115.97(2)	1.649(1) 1.635(1)
5e	Buck-18(13)B[9]				X-ray 25[9]	8.604(7) 13.020(10)	7.177(5) 116.03(5)	- -

[1] References: 1 Weitz (1972); 2 Gering (1985); 3 Scambos *et al.* (1987); 4 Blasi *et al.* (1987); 5 present paper, Buck-18 adularia crystals. [2] 1σ error in brackets ( ). [3] Unheated specimen gave (X-rays) $<T_1\text{-O}>$, $<T_2\text{-O}>$ 1.653(2), 1.635(2) Å. [4] Unheated specimen (SVG1) gave (neutrons) $<T_1\text{-O}>$, $<T_2\text{-O}>$ 1.6505(7), 1.6353(7) Å. [5] Composition given (incl. Rbf 0.2, Srf 0.1) is for the sample in Blasi *et al.* (1984) from which this analyzed crystal was taken. [6] Error assumed by the present authors. [7] For full crystal designation, see Table 1. [8] See authors' Table 2. [9] Refinement of unit cell parameters only.

authors considered the matter of apparent residual preference of Al for site T_1, and the limit of Si,Al-disorder observable in alkali feldspar. They offered two possible explanations, (a) that the thermal energy of the cation available for randomizing position within the structure is limited by the melting temperature, and (b) that the assumption of equal size of tetrahedral sites at full disorder may be invalid. The present results for our crystal I, in which the two tetrahedra are, within the limit of error, of identical size, appear to invalidate their suggestion that a shallower potential well for T_1 as calculated from Madelung electrostatic site-energies might account for its slightly larger size, even where $t_1 = t_2 = 0.25$ Al. Our results for crystal I suggest, furthermore, that the assumption that $<T_1\text{-O}>$ equals $<T_2\text{-O}>$ in cases where $t_1 = t_2 = 0.25$ Al is indeed a valid one.

The naming of slightly ordered crystals II, III and IV

The small departures from complete Si,Al-disorder of these three crystals is shown by their t_i values in Table 6. It seems reasonable that at least II and III should, from the smallness of their departures, be termed *high sanidine* in contrast to *end-member high sanidine* for completely disordered crystal I. Crystal IV, however, shows the greatest degree of order, with $t_1 = 0.30$ Al. Is its position within the high sanidine – low sanidine series such that it should still be called high sanidine? The only definite demarkation in name within this series appears to be the one based on optics: high sanidine changes to low sanidine with the change of the optic axial plane from ∥ (010) to ⊥(010) (Smith & Brown 1988, p. 189). Because we have no optical measurements on this or any other of our crystals, we attempt to place crystal IV in the context of the high sanidine – low sanidine series by plotting its distinguishing structural characteristics on Figure 3, which consists of plots against $2V_X$ of b, c, $<T_1\text{-O}>$ and $<T_2\text{-O}>$ for crystals for which these are known. Figure 3 shows that, for crystal IV, all parameters except $(T_2\text{-O})$ intersect the curves at low values of $2V_X$, $<12°$, *i.e.*, within the high sanidine range but close to the demarkation value with low sanidine. Such being the case, we feel it appropriate to designate crystal IV, like II and III, as high sanidine.

Possible origin of the different subsamples of high sanidine identified among the Buck-18 adularia

The paragenesis and origin of adularian K-feldspar, including the Buck-18 sample, from granitic pegmatites were described by Černý & Chapman (1984). They accept as the likely origin of such adularia the one proposed by Foord & Martin (1979) and Martin (1982) for late K-feldspar overgrowths in miarolitic vugs in the Pikes Peak pegmatites. Open fissures produced by deformation or, in other cases, miarolitic cavities or vugs due to leaching, were subjected to sudden drastic reductions in P_{fluid}, with the consequent rapid nucleation and growth of precipitates on cavity surfaces. Such a mode of precipitation generated disordered K-feldspar identical with, or very close to, end-member high sanidine. This metastable structural state was preserved in those cases where a low temperature of crystallization (≪250°C; Černý & Chapman 1984) was followed by cooling, draining of the parent fluids and the absence of any subsequent (hydro)thermal events that would surpass the energy barrier critical for the ordering process.

The above interpretation was based on structural states derived from X-ray powder diffraction, which unavoidably averages the characteristics of the multitude of crystals utilized for the preparation of powder mounts. The present study based on the examination of single crystals shows that the structural state of individual crystals of adularia habit is distinctly variable ($0.25 < t_1 < 0.30$ Al), although their unit-cell dimensions are largely identical within ±2σ (Fig. 1), and the X-ray powder

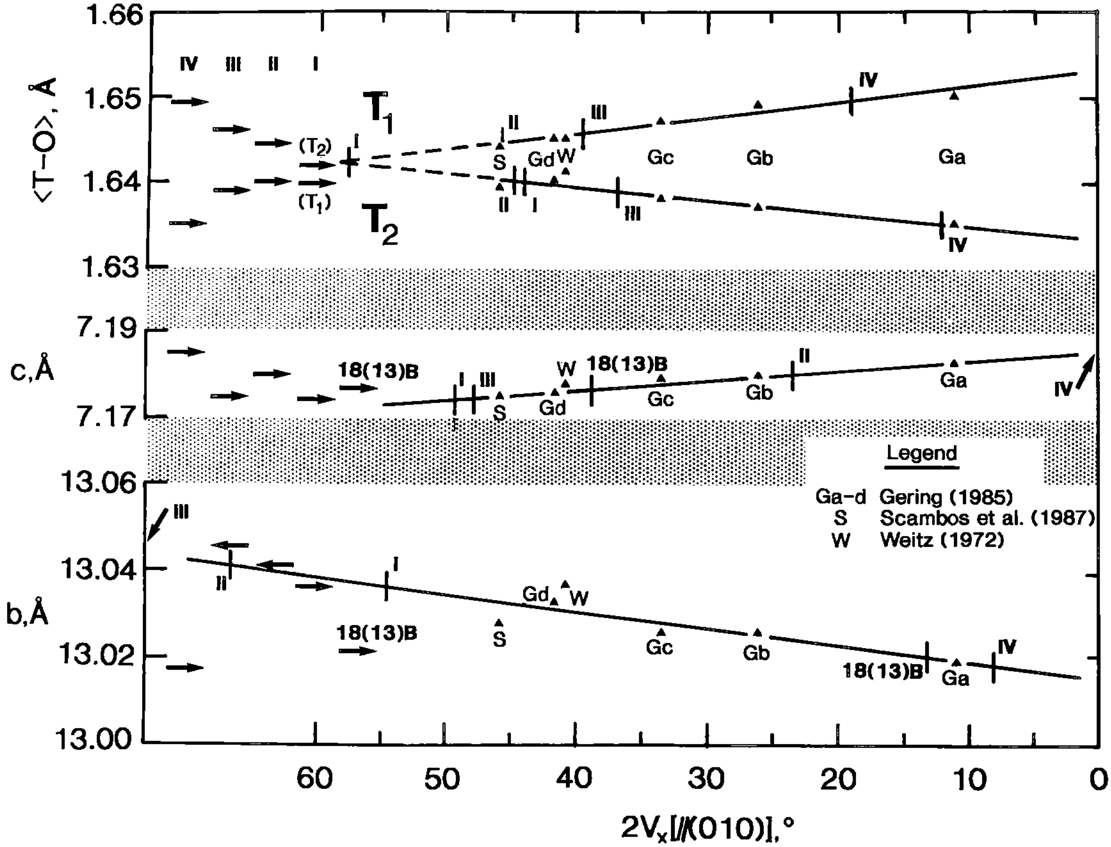

FIG. 3. Linear regression lines through plots of b, c and $<T_j\text{–O}>$ *versus* $2V_X[\,||\,(010)]$ for the samples of high sanidine for which these data are known, and application to the curves of b, c and $<T_j\text{–O}>$ for the four refined examples of adularian high sanidine, particularly crystal IV, and b and c for 18(13)B, as described in this paper. See text. The four columns of arrows on the left side of the diagram indicate the respective ordinate values of the four analyzed crystals I, II, III, IV shown at the top of each column. Regarding crystal 18(13)B, see note in the description of Figure 1. As in Figure 2, the T_1 and T_2 points for crystal I are inverted with respect to the regression lines.

diffractograms do not suggest heterogeneous mixtures (Černý & Chapman 1984, p.376).

Despite this evidence for structural states variable within crystal populations covering just a few cm^2 of fissure walls, we consider the genetic interpretation outlined above to be essentially correct. The range of structural states covered by the crystals examined is rather narrow within the monoclinic K-feldspar family (26–33% of the full range; Fig. 4 in Ferguson 1980), and several factors operating within the proposed model may be responsible for such a limited variation: (i) primary random differences in Si,Al disorder among individual nuclei could have been propagated during the subsequent growth; (ii) different crystals could have been exposed to the order-promoting action of fluids at the relatively high temperatures of crystallization for different periods of time, depending on the timing of their nucleation and growth, consequently developing different degrees of secondary ordering; and (iii) such a differential exposure to order-promoting agents also could have been generated by repeated releases of pressure in a cooling environment, with the last generation of sanidine being least affected and consequently remaining most disordered. The style of precipitation in the second and third models may be supported by variable size of the crystals, suggestive of different generations or protracted nucleation within a single precipitation event. However, statistically meaningful data would be required to test these models in their entirety, with documentation of frequencies of crystal sizes and their correlation with structural states.

ACKNOWLEDGEMENTS

The authors thank Ronald Chapman for the electron-microprobe data, Frank C. Hawthorne and Peter Burns for advice about, and assistance with, the structure refinements, Robert E. Meintzer for computational advice, and Dr. Horst Pentinghaus of Karlsruhe for a copy of Dr. E. Gering's Dissertation. The authors also thank the two referees, Achille Blasi and Tamsin McCormick, for constructive critiques, and Robert F. Martin for invaluable improvements to the manuscript. Two of us, R.B.F. and P.Č., thank the Natural Sciences and Engineering Research Council of Canada for operating and equipment grants that made this research possible.

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Received September 14, 1990, revised manuscript accepted March 27, 1991.