

REFINEMENT OF AN INTERMEDIATE MICROCLINE STRUCTURE

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ABSTRACT

The structure of Spencer *U* microcline has been refined again by modern computing methods. The $T-O$ bond lengths differ only slightly from those of the previous study, but in a consistent direction to indicate a smaller degree of Si, Al order.

INTRODUCTION

The crystal structure of an intermediate microcline, specimen *U* of Spencer (1937), was originally determined by Bailey and Taylor (1955). Although the large total of 2,652 nonequivalent reflections was recorded in that study, the refinement techniques available would be considered primitive by today's standards. Two and three dimensional electron density maps were constructed with the aid of a desk calculator, Beever-Lipson strips, and an IBM Card Programmed Calculator. An artificial temperature factor of $B=4.0 \text{ \AA}^2$ was employed to reduce diffraction effects due to finite termination of series, and final correction for diffraction effects and overlap of electron density peaks was made by the back synthesis method.

Because of the great interest among mineralogists in the degree of Si,Al ordering in feldspars and the critical position of Spencer *U* in the sanidine-microcline series, the structure has been refined again with more modern techniques.

REFINEMENT

Examination of the original film data revealed systematic errors in the hand-calculated $\sin^2\theta$ values and resultant L_p corrections and scaling factors for over 500 high-angle reflections. These reflections were deleted to leave a total of 2,124 unique reflections.¹ Refinement was accomplished with a full matrix least-squares program ORFLS-A on a CDC 3600 electronic computer and further calculations with program ORFFE run on a Univac 1108.

Scattering factors, modified for 50 percent ionization, were taken from Vol. III of *International Tables for X-ray Crystallography*. Tetrahedral cations were assumed to have scattering factors appropriate to the Si,Al contents determined in the original study. Unit weights were used throughout.

¹ Available upon request to the author.

TABLE 1. FINAL POSITIONAL PARAMETERS OF SPENCER U^a

Atom	x	y	z
K	0.2837(2) ^b	-0.0032(1)	0.1378(2)
$T_1(0)$	0.0095(2)	0.1856(1)	0.2214(2)
$T_1(m)$	0.0095(2)	0.8173(1)	0.2280(2)
$T_2(0)$	0.7098(2)	0.1189(1)	0.3421(2)
$T_2(m)$	0.7076(2)	0.8833(1)	0.3466(2)
$O_A(1)$	0.0005(5)	0.1447(4)	-0.0072(6)
$O_A(2)$	0.6369(5)	0.0020(3)	0.2857(6)
$O_B(0)$	0.8238(5)	0.1468(4)	0.2239(6)
$O_B(m)$	0.8279(5)	0.8545(4)	0.2331(6)
$O_C(0)$	0.0350(5)	0.3153(3)	0.2549(6)
$O_C(m)$	0.0366(5)	0.6914(3)	0.2635(6)
$O_D(0)$	0.1842(5)	0.1245(3)	0.4065(6)
$O_D(m)$	0.1777(5)	0.8741(3)	0.4095(6)

^a Transformed to Laves' (1951) orientation of axes by $y_{\text{Laves}} = -y_{\text{B\&T}}$. This also interchanges the atoms designated (0) and (m) by Bailey and Taylor (1955). The cell dimensions are transformed to $a=8.5784$, $b=12.9600$, $c=7.2112$ Å, $\alpha=90^\circ 18'$, $\beta=116^\circ 02'$, and $\gamma=89^\circ 07\frac{1}{2}'$. The β value is corrected from that of the original study.

^b For all tables numbers in parentheses are errors in last decimal place.

In the first set of least-squares cycles the atomic coordinates and scale were varied, and arbitrary isotropic temperature factors of $B=1.5$ for potassium, 1.0 for oxygen, and 0.4 for tetrahedral cations were held constant. Moderate correlation coefficients of 0.42 were found between the x and z coordinates of each atom during the first cycle. Thereafter these parameters were never varied at the same time. No other correlations were larger than 0.06.

The discrepancy factor R_1 decreased only slightly as a result of varying the positional parameters for several least squares cycles. R_1 decreased from an initial value of 9.7 percent, based on the positional parameters of Bailey and Taylor, to a final value of 9.3 percent. The R_1 value decreased to 9.2 percent with variation of isotropic B values and to 8.0 percent with variation of anisotropic B values. The final positional parameters are listed in Table 1, temperature factors in Table 2, and interatomic bond lengths and angles in Table 3.

DISCUSSION

Less changes were found in the atomic parameters than anticipated in view of the different refinement techniques involved. Most changes were less than 0.01 Å. One parameter for each of five atoms [$T_2(0)$, $O_A(2)$, $O_B(0)$, $O_B(m)$, and $O_D(0)$] changed by amounts between 0.012 Å and

TABLE 2. TEMPERATURE FACTORS OF SPENCER U^a

Atom	Isotropic B	Anisotropic thermal ellipsoids				
		axis	r.m.s.	Angles to crystal axes ($^\circ$)		
				X	Y	Z
K	1.48(2)	1	0.120(2)	45(4)	88(3)	71(4)
		2	0.143(3)	133(6)	72(19)	27(14)
		3	0.149(2)	102(14)	162(19)	72(18)
$T_1(0)$	0.41(2)	1	0.035(9)	113(5)	88(7)	4(7)
		2	0.070(5)	122(5)	146(5)	86(7)
		3	0.097(3)	41(5)	124(5)	91(3)
$T_1(m)$	0.43(2)	1	0.038(8)	109(4)	100(5)	12(6)
		2	0.075(4)	128(6)	40(6)	78(6)
		3	0.095(3)	135(7)	128(7)	91(4)
$T_2(0)$	0.40(2)	1	0.035(9)	106(3)	133(7)	43(7)
		2	0.067(4)	89(5)	135(7)	130(6)
		3	0.095(3)	16(3)	99(5)	104(4)
$T_2(m)$	0.41(2)	1	0.055(5)	106(5)	100(20)	13(14)
		2	0.066(4)	93(7)	169(20)	99(19)
		3	0.088(3)	17(5)	95(8)	100(5)
$O_A(1)$	1.15(7)	1	0.098(11)	115(7)	100(19)	10(19)
		2	0.120(8)	86(11)	170(18)	100(19)
		3	0.144(6)	25(7)	89(12)	91(7)
$O_A(2)$	0.90(6)	1	0.067(9)	81(5)	76(9)	38(5)
		2	0.106(8)	88(10)	166(10)	78(8)
		3	0.144(9)	9(5)	89(10)	125(5)
$O_B(0)$	1.36(7)	1	0.079(17)	38(5)	71(6)	145(5)
		2	0.149(4)	53(21)	103(75)	65(58)
		3	0.151(5)	83(83)	157(75)	113(62)
$O_B(m)$	1.30(7)	1	0.084(15)	31(5)	93(8)	146(5)
		2	0.139(7)	73(11)	29(18)	77(12)
		3	0.151(5)	65(8)	118(18)	59(7)
$O_C(0)$	0.86(6)	1	0.076(8)	109(10)	118(7)	127(11)
		2	0.112(11)	36(29)	70(26)	143(11)
		3	0.124(7)	60(29)	144(18)	88(26)
$O_C(m)$	1.01(7)	1	0.075(11)	50(7)	129(6)	85(8)
		2	0.119(7)	92(21)	58(20)	39(27)
		3	0.131(9)	140(70)	125(19)	52(27)
$O_D(0)$	1.03(7)	1	0.067(12)	93(5)	124(7)	40(60)
		2	0.115(7)	100(10)	145(8)	115(7)
		3	0.148(8)	10(10)	99(9)	119(6)
$O_D(m)$	1.01(7)	1	0.084(8)	89(6)	102(33)	29(12)
		2	0.096(9)	93(7)	168(34)	100(29)
		3	0.149(8)	3(7)	92(7)	117(5)

^a Assuming 50% ionization and Si, Al-occupancies of tetrahedra as determined by Bailey and Taylor (1955).

TABLE 3. FINAL INTERATOMIC DISTANCES AND ANGLES FOR SPENCER U

Interatomic Distances (Å)							
$T_1(0)$ —0		$T_1(m)$ —0		$T_2(0)$ —0		$T_2(m)$ —0	
$O_A(1)$	1.696(5)	$O_A(1)$	1.637(5)	$O_A(2)$	1.629(5)	$O_A(2)$	1.634(5)
$O_B(0)$	1.685(5)	$O_B(m)$	1.640(5)	$O_B(0)$	1.600(5)	$O_B(m)$	1.613(5)
$O_C(0)$	1.701(5)	$O_C(m)$	1.650(5)	$O_C(0)$	1.623(5)	$O_C(0)$	1.607(5)
$O_D(0)$	1.695(5)	$O_D(m)$	1.643(5)	$O_D(m)$	1.622(5)	$O_D(0)$	1.610(5)
Mean	1.694		1.642 ₆		1.618 ₅		1.616
	in $T_1(0)$	in $T_1(m)$	in $T_2(0)$	in $T_2(m)$	K —0		
O_A — O_B	2.694(7)	2.638(7)	2.649(7)	2.631(7)	$O_A(1)$	2.874(5),	2.890(5)
O_A — O_C	2.833(6)	2.746(6)	2.572(6)	2.560(6)	$O_A(2)$	2.738(5),	3.408(5)
O_A — O_D	2.706(7)	2.630(7)	2.629(6)	2.634(6)	$O_B(0)$	3.001(5)	
O_B — O_C	2.804(6)	2.696(7)	2.656(7)	2.643(6)	$O_B(m)$	3.087(5)	
O_B — O_D	2.789(7)	2.712(7)	2.665(7)	2.659(7)	$O_C(0)$	3.026(5)	
O_C — O_D	2.767(6)	2.668(6)	2.678(6)	2.693(6)	$O_C(m)$	3.212(5)	
Mean	2.765	2.682	2.641 ₅	2.637	$O_D(0)$	2.932(5)	
					$O_D(m)$	2.972(5)	
Interatomic Angles (°)							
	in $T_1(0)$	in $T_1(m)$	in $T_2(0)$	in $T_2(m)$	$T_1(0)$ — $O_A(1)$ — $T_1(m)$	144.31	
O_A — T — O_B	105.64	107.24	110.31	108.24	$T_2(0)$ — $O_A(2)$ — $T_2(m)$	138.80	
O_A — T — O_C	113.03	113.29	104.52	104.38	$T_1(0)$ — $O_B(0)$ — $T_2(0)$	151.84	
O_A — T — O_D	105.91	106.58	107.96	108.60	$T_1(m)$ — $O_B(m)$ — $T_2(m)$	153.94	
O_B — T — O_C	111.79	110.09	111.00	110.35	$T_1(0)$ — $O_C(0)$ — $T_2(m)$	130.62	
O_B — T — O_D	111.20	111.39	111.59	111.20	$T_2(0)$ — $O_C(m)$ — $T_1(m)$	131.23	
O_C — T — O_D	109.11	108.23	111.21	113.71	$T_1(0)$ — $O_D(0)$ — $T_2(m)$	141.21	
					$T_2(0)$ — $O_D(m)$ — $T_1(m)$	142.68	
Mean	109.45	109.49	109.43	109.41	Mean	141.83	

0.026 Å. Bond lengths involving these five atoms deviate the most from the previous values.

The mean values of the T —O bond lengths for the four tetrahedra have changed only in the third decimal place. But the changes are consistent in indicating a smaller degree of Si,Al order than previously, *i.e.* both T_1 tetrahedra have decreased in size and both T_2 tetrahedra have increased. Si,Al contents of the tetrahedra, as indicated by the graphs of Smith and Bailey (1963), Jones (1968), and Ribbe and Gibbs (1969) are listed in Table 4.

Because of the consistent direction of the change in size of the tetrahedra, the effect on the long-range order parameter of Smith and MacKenzie (1961) is cumulative. Even though the Al content of an in-

TABLE 4. DEGREE OF Si, Al ORDER

Tetrahedron	Al—contents			
	Jones (1968)	Ribbe & Gibbs (1969)	Smith and Bailey (1963) ^a	
			Rounded values	Unrounded values
$T_1(0)$	57.6	58.6	60.0	58.3
$T_1(m)$	24.9	24.7	23.2	24.2
$T_2(0)$	9.6	8.9	6.1	8.3
$T_2(m)$	8.1	7.2	4.3	6.6
Σ	100.2	99.4	93.6	97.4
Degree of order	43%	45%	52%	47%

^a These authors state that, in their graph of mean $T-O$ bond length vs. tetrahedral Al-content, a straight line through the three points with the smallest standard errors extrapolates to $Si-O=1.606 \text{ \AA}$ and $Al-O=1.757 \text{ \AA}$. In the text they recommend the rounded values of 1.61 and 1.75 \AA , respectively.

dividual tetrahedron has changed by only 0.03 to 0.04 Al, the degree of order has decreased from its former value of approximately 61 percent to approximately 45 percent, with some variation depending on the graph used to obtain the Si,Al values.

The anisotropic thermal ellipsoids (Table 2) were not reported previously for Spencer U . The ellipsoid for potassium is disk-shaped with two long axes and one short axis. The orientation has started to shift away from that reported for monoclinic orthoclase (Jones and Taylor, 1961) towards those reported for triclinic maximum microcline (Brown and Bailey, 1964; Finney and Bailey, 1964). The minor axis is just off the XZ plane near the zone $[101]$ and about 19° from X^* . The major axis has moved away from Y about 18° in the YZ plane. The major axes for the ellipsoids of the tetrahedral cations are grouped between X and X^* and the minor axes between Z and Z^* . Most of the vibration, therefore, is along the direction of the Jacob's ladder chains. The oxygen ellipsoids in general have their maximum vibration normal to the linking $T-O$ bonds and minimum vibration parallel to these bonds.

ACKNOWLEDGMENTS

This study has been supported in part by the University of Wisconsin Research Committee. Use of the University of Wisconsin Computing Center was made possible through support, in part, from the National Science Foundation, other United States Government agencies, and the Wisconsin Alumni Research Foundation (WARF) through the University of Wisconsin Research Committee. The writer expresses his appreciation to Mrs. C. G. Cinnamon for assistance in keypunching of data cards.

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Manuscript received, July 21, 1969; accepted for publication, July 28, 1969.