

Analysis of $P\bar{1}$, $I\bar{1}$ and $C\bar{1}$ plagioclase structures

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Abstract. — The paper reports the refinement of five plagioclase structures from different geological settings. Compositions and space groups of the samples are An0 ($C\bar{1}$), An66 ($I\bar{1}$), An91 ($I\bar{1}$), An94 ($I\bar{1}$), and An94 ($P\bar{1}$). Emphasis is on calcic plagioclases with highly significant results for 'a', 'b', 'c', and 'd' type reflections. The structural contribution to 'b', 'c', and 'd' type superstructure reflections is investigated with Fourier analysis. The resolution of the X-ray determination of the Al, Si tetrahedral site occupancies is explored. The Na, Ca positions are refined as split sites and found to be differently occupied by Na and Ca atoms, respectively. Individual tetrahedral bond lengths are shown to be highly correlated to their structural environment. Average tetrahedral bond lengths indicate that those four tetrahedra which represent an "albite-like" structural unit in a four-ring chain extending along *z* in $I\bar{1}$ anorthite maintain their identity also at intermediate compositions while the other four non-equivalent tetrahedra gradually change their Al content from an "anorthite-like" to an "albite-like" ordering pattern.

Key words : plagioclase, crystal structure, superstructure, antiphase domains, bonding.

Analyses des structures $P\bar{1}$, $I\bar{1}$ et $C\bar{1}$ des plagioclases.

Résumé. — Cette note est relative à l'affinement de la structure de cinq plagioclases de différents contextes géologiques. Les compositions et groupes spatiaux des échantillons sont An0 ($C\bar{1}$), An66 ($I\bar{1}$), An91 ($I\bar{1}$), An94 ($I\bar{1}$) et An94 ($P\bar{1}$). Une importance particulière est attachée aux plagioclases calciques pour lesquels des résultats significatifs sont donnés pour les réflexions de type 'a', 'b', 'c' et 'd'. La contribution structurale aux réflexions de surstructure de type 'b', 'c' et 'd' est étudiée par analyse de Fourier. On explore la résolution de la détermination par rayons X de l'occupation Al, Si des sites tétraédriques. L'affinement de la position des Na, Ca montre que les sites sont dédoublés, avec un taux d'occupation différent en atomes Na et Ca. Les longueurs de liaison individuelles dans les tétraèdres sont corrélées à l'environnement structural. Les longueurs de liaison moyennes dans les tétraèdres montrent que les quatre tétraèdres qui représentent une unité structurale de "type albite" dans une chaîne à quadruple cycle le long de *z* dans l'anorthite $I\bar{1}$, gardent leur identité même à des compositions intermédiaires tandis que les quatre tétraèdres non équivalents modifient progressivement leur contenu en Al depuis un arrangement de "type-anorthite" jusqu'à un arrangement de "type-albite".

Mots-clés : plagioclase, structure cristalline, surstructure, domaines d'antiphase, liaison interatomique.

INTRODUCTION

The crystal structure of plagioclase feldspars has been the subject of numerous studies since it was first proposed by Taylor *et al.* (1934). For a discussion of its features the reader is referred to Smith (1974, Vol. 1, Chapters 3, 4 and 5) and to Ribbe (1983, Chapters 1, 2, 4 and 9). These authors indicate that several features of the plagioclase structure (Figure 1) remain puzzling, and we have found that after conclusion of this work many questions are still open. Our main purpose is to contribute more accurate structural data. According to Jagodzinski and Korekawa (1976) previous determinations of the anorthite structure may be incorrect, because excessively high R-factors for 'c' and 'd' type superstructure

reflections suggest that the primitive ($P\bar{1}$) anorthite structure has not yet been correctly resolved.

The new refinements emphasize superstructures of calcic plagioclase. We consider :

— direct refinements of Al, Si tetrahedral (T) site occupancies and their relationship to average T-O distances,

— the relation between the lengths of individual T-O bonds and their structural environment,

— structural changes during the $C\bar{1} \rightarrow I\bar{1}$ and $I\bar{1} \rightarrow P\bar{1}$ transitions,

— the relation between these changes and the occurrence of superstructure reflections and antiphase vectors,

— the splitting of the large Na, Ca (A) cation sites,

— changes caused by chemical substitution.

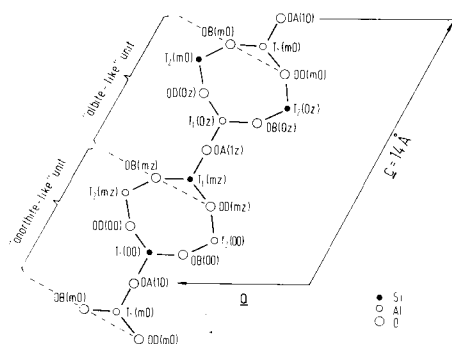


FIG. 1. — Sketch of a tetrahedral four-ring chain in the structure of anorthite. Only atoms in the vicinity of the xz section at y near 0 are shown. A similar chain with atoms labeled i which is not equivalent in space group $P\bar{1}$ exists at y near 0.5.

Schéma d'une chaîne d'anneaux à quatre tétraèdres dans la structure de l'anorthite. Seuls sont indiqués les atomes à proximité de la section xz à y voisin de 0. Une chaîne semblable avec des atomes i , qui n'est pas équivalente dans le groupe spatial $P\bar{1}$, existe à y voisin de 0,5.

SAMPLES AND METHODS OF ANALYSIS

The five plagioclase samples originate from a variety of geological settings described in table I.

Chemical compositions are summarized in table II. Small fragments were used for X-ray data collection applying essentially the same procedures as used by Wenk *et al.* (1980).

Lattice parameters were first determined by automatic centering of about 30 reflections on the diffractometer. They were later refined from Jagodzinski-type Guinier films (Table III). Assuming that the material is homogeneous the latter are more accurate, and they were used in the calculation of interatomic distances. It should be pointed out, however, that they were done on crystal fragments different from those used for the structure refinements which may be significant in the case of heterogeneous samples such as Verzasca anorthite.

Raw intensities were corrected for L-p effects, and — for Cazadero albite — also for absorption, although the latter correction was found to be insignificant. Weighting of reflections was based on individual standard deviations. To avoid overweighting of intense reflections, weights were chosen to be $w = 1/\sigma^2$ where $\sigma^2 = \sigma_c^2 + 0.0025^2 F_o$, and σ_c is the standard deviation based on counting statistics. Scattering factors of Cromer and Mann (1968) for half ionized atoms were used, except in the low albite refinement in which different assumptions were

Code	Locality	Geological unit	Reference
Grass Valley anorthite	Grass Valley, California	Anorthosite, Sierra Nevada Batholith	Wenk and Wenk (1973)
Grass Valley 1200 anorthite	Grass Valley, California	heated at 1200°C for 10 days	Wenk and Wenk (1973)
Verzasca anorthite	Val Carochio, Switzerland	Calcsilicate rocks of amphibolite facies in Lepontine complex	Wenk, E. and Wenk, H.-R. (1977)
Lake County labradorite	Plush, Oregon	Andesitic lava flow	Wenk et al. (1980)
Cazadero low albite	Cazadero, California	Veins in blueschists of Franciscan formation	Foley and Lee (1963)

TABLE I. — Geological setting of plagioclase samples.

Origine géologique des échantillons de plagioclase.

Code	Weight percent					An content (based on Ca, Na)
	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	
Grass Valley anorthite	43.6	35.3	18.8	0.62	0.02	An ₉₄ Ab ₆
Verzasca anorthite	46.5	35.1	18.0	0.95	0.02	An ₉₁ Ab ₉
Lake County labradorite	52.2	30.9	13.7	4.0	0.12	An ₈₆ Ab ₁₄
Cazadero low albite	69.3	19.9	0.03	12.1	0.04	An _{0.1} Ab _{99.7} Or _{0.2}

TABLE II. — Chemical composition of plagioclase samples determined by microprobe analysis.

Composition chimique des échantillons de plagioclase déterminées par microsonde électronique.

Code	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
Grass Valley anorthite	8.1784(7)	12.8736(8)	14.1765(12)	93.187(5)	115.938(5)	91.142(5)
Grass Valley 1200 anorthite	8.1826(12)	12.8727(7)	14.1794(9)	93.222(6)	115.871(7)	91.159(5)
Verzasca anorthite	8.1805(6)	12.8738(6)	14.1838(10)	93.258(6)	115.984(6)	91.055(5)
Lake County labradorite	8.1747(9)	12.8708(6)	14.2030(12)	93.461(5)	116.086(5)	90.514(6)
Cazadero low albite	8.1354(7)	12.7052(7)	7.1582(7)	94.274(6)	116.600(5)	87.685(6)

TABLE III. — Lattice parameters of plagioclases. Estimated standard deviations in parentheses refer to the last digit(s).

Paramètres réticulaires des plagioclases. Les déviations standards estimées, entre parenthèses, se rapportent au(x) dernier(s) chiffre(s).

tested. The influence of ionicity was generally found to be negligible, even in refining multipliers. All reflections with $F > 3\sigma$ were used in the least-squares refinements which were done with the program NUCLS 6, a modified version of ORFLS (Busing *et al.*, 1962). Positional and anisotropic thermal parameters and multipliers for cations were refined simultaneously with full matrix inversions. An isotropic extinction coefficient was refined to correct for secondary extinction (Zachariasen, 1968). In the case of $P\bar{1}$ anorthite 514 parameters were varied. All refinements converged satisfactorily at R-factors between 2 % and 5 % (Table IV). Atomic parameters are given in tables V - VII, bond lengths and angles in tables X - XIV.

At first $P\bar{1}$ anorthite did not refine when using Wainwright and Starkey's (1971) coordinates as starting parameters. Difference Fourier maps had to be used until the R-factor reached 8 %. In the end all atoms refined to within 0.1 Å of

Wainwright and Starkey's positions, except for $T_2(000)$, which was at a distance of 0.3 Å, a highly significant difference. R-factors were calculated separately for 'a', 'b', 'c' and 'd' type reflections. 'a' reflections show the best agreement. Larger R-factors for weaker superstructure reflections are due to counting statistics and not to uncertainties in the resolution of the superstructure. It appears that the data for Grass Valley ($P\bar{1}$) anorthite may constitute the first published statistically significant refinement of the $P\bar{1}$ superstructure (cf. Jagodzinski and Korekawa, 1976).

REFINEMENT OF TETRAHEDRAL SITE OCCUPANCIES

The distribution of Al and Si atoms over the 16 tetrahedral sites in space group $P\bar{1}$, 8 sites in $I\bar{1}$, and 4 sites in $C\bar{1}$ is one of the most

	Grass Valley An 94	Grass Valley 1200 An 94	Verzasca An 91	Lake County An 66	Cazadero An 0,1
Total number of reflections	4015	1574	2052	3115	2528
a-reflections	1357	1156	1526	2303	
b-reflections	1039	418	526	812	
c-reflections	1120				
d-reflections	499				
R tot	2.85	2.90	4.52	2.93	2.82
R tot weighted	4.27	3.33	3.95	3.94	3.67
R_a	2.64	2.44	4.10	2.48	
R_a weighted	4.59	2.97	3.70	3.46	
R_b	3.52	6.38	7.51	7.10	
R_b weighted	3.97	5.84	5.74	6.47	
R_c	4.59				
R_c weighted	5.74				
R_d	8.73				
R_d weighted	9.19				

TABLE IV. — R-factors for refinements of plagioclase structures.

Facteurs R pour l'affinement des structures de plagioclase.

		Grass Valley		Grass Valley 1200	Verzasca	Lake County	Cazadero
		An 94		An 94	An 91	An 86	An 04
		O	i				
A{00}	x	.26569(14)	.7681(6)	.2663(11)	.2672(4)	.2670(2)	.2670(2)
	y	.26400(9)	.4887(4)	.2650(12)	.2667(5)	.2631(2)	.2679(2)
	z	.08789(9)	.5855(4)	.0863(9)	.0863(4)	.0850(2)	.1450(3)
A{04}	x	.2729(5)	.77371(12)	.2745(6)	.2748(4)	.27456(18)	.282(2)
	y	.0278(4)	.53570(7)	.0353(6)	.0345(5)	.03304(16)	.074(2)
	z	.0513(5)	.54266(8)	.0438(6)	.0444(5)	.04677(15)	.142(4)
A{20}	x	.2666(20)	.7640(3)	.266(4)	.264(2)	.2641(3)	
	y	.0177(12)	.5024(2)	.015(4)	-.007(3)	-.0059(11)	
	z	.5644(11)	.0769(2)	.564(4)	.562(3)	.5772(7)	
A{24}	x	.2681(4)	.7668(5)	.267(6)	.2667(3)	.2696(3)	
	y	.0308(2)	.5288(3)	.032(4)	.0288(6)	.0270(3)	
	z	.5435(2)	.0495(3)	.542(4)	.5477(6)	.5474(2)	
T ₁ {00}	x	.00842(12)	.49310(11)	.0072(5)	.00743(19)	.00762(7)	.00895(6)
	y	.15890(6)	.34295(6)	.1581(3)	.15843(11)	.16079(4)	.16843(3)
	z	.10407(7)	.39578(7)	.1044(3)	.10435(10)	.10511(4)	.20810(6)
T ₁ {02}	x	.00517(12)	.50020(12)	.0033(7)	.0028(8)	.00400(8)	
	y	.16241(7)	.33428(7)	.1638(3)	.1649(1)	.16475(4)	
	z	.61142(7)	.88771(7)	.6119(4)	.6115(1)	.60990(4)	
T ₁ {04}	x	.00571(12)	.50480(13)	.9997(7)	.9996(2)	.00071(7)	.00383(5)
	y	.18476(7)	.31479(7)	.8148(3)	.8155(1)	.81565(4)	.82064(3)
	z	.88166(7)	.62032(7)	.1195(4)	.1188(1)	.11783(4)	.23733(5)
T ₁ {02}	x	.99407(12)	.50473(12)	.0046(5)	.00564(19)	.00469(7)	
	y	.18369(6)	.31902(6)	.8173(3)	.81742(11)	.81718(4)	
	z	.38675(7)	.11093(7)	.6119(3)	.61246(10)	.61340(4)	
T ₂ {00}	x	.68558(12)	.81005(13)	.6877(5)	.6873(2)	.68774(7)	.69156(5)
	y	.11272(7)	.38898(7)	.1125(3)	.1117(2)	.11092(4)	.11027(3)
	z	.15344(7)	.33611(7)	.1594(3)	.1574(1)	.15841(4)	.31476(6)
T ₂ {02}	x	.68007(12)	.82683(12)	.6770(6)	.6777(2)	.68090(7)	
	y	.10455(6)	.39354(6)	.1057(3)	.1059(1)	.10676(4)	
	z	.66269(7)	.84725(7)	.6574(3)	.6590(1)	.65872(4)	
T ₂ {04}	x	.32489(12)	.17694(12)	.6759(6)	.6772(2)	.67851(7)	.68139(5)
	y	.11724(6)	.38026(6)	.8815(3)	.8815(1)	.88083(4)	.88194(3)
	z	.81420(7)	.67660(7)	.1810(3)	.1822(1)	.18039(4)	.36077(6)
T ₂ {02}	x	.31815(13)	.18471(13)	.6834(7)	.6828(2)	.68331(7)	
	y	.12677(7)	.37660(7)	.8751(3)	.8750(1)	.87650(4)	
	z	.32619(7)	.17968(7)	.6774(4)	.6755(1)	.67724(4)	
0A{10}	x	.0211(3)	.4949(3)	.0068(13)	.0106(5)	.0071(2)	.00445(14)
	y	.1252(2)	.6248(2)	.1254(7)	.1261(2)	.1284(1)	.13086(8)
	z	.3948(2)	.4882(2)	.9912(6)	.9924(2)	.9910(1)	-.03341(15)
0A{12}	x	.9840(3)	.5086(3)	.9984(13)	.9911(5)	.9981(2)	
	y	.1256(2)	.6251(2)	.1263(7)	.1259(2)	.1279(1)	
	z	.4847(2)	.9935(2)	.4894(7)	.4873(2)	.4887(1)	
0A{20}	x	.5759(3)	.0743(3)	.5753(11)	.5776(4)	.57981(17)	.58170(13)
	y	.9908(2)	.4888(2)	.9894(6)	.9901(2)	.99098(10)	.99748(8)
	z	.1423(2)	.6368(2)	.1393(6)	.1405(2)	.13964(10)	.28022(15)
0A{22}	x	.5723(3)	.0721(3)	.5728(10)	.5730(4)	.57736(18)	
	y	.9904(2)	.4818(2)	.9908(6)	.9919(2)	.99173(10)	
	z	.6377(2)	.1378(2)	.6380(7)	.6373(2)	.63817(10)	
0B{00}	x	.8162(3)	.3272(3)	.8220(13)	.8192(5)	.8190(2)	.81223(14)
	y	.1012(2)	.5977(2)	.0996(6)	.1007(2)	.1031(1)	.11008(9)
	z	.0834(2)	.5994(2)	.0921(8)	.0899(5)	.0928(1)	.18994(17)
0B{02}	x	.8086(3)	.2905(3)	.7990(14)	.8025(5)	.8051(2)	
	y	.0580(2)	.6002(2)	.1016(6)	.1019(2)	.1033(1)	
	z	.6022(2)	.0849(2)	.5926(8)	.5970(5)	.5949(1)	
0B{04}	x	.8151(3)	.3016(3)	.8073(14)	.8113(5)	.8105(2)	.82038(15)
	y	.8544(2)	.3563(2)	.8561(7)	.8555(3)	.8539(1)	.85108(9)
	z	.1392(2)	.6166(2)	.1255(8)	.1307(5)	.1262(1)	.25869(19)
0B{02}	x	.8139(3)	.3330(3)	.8223(13)	.8197(5)	.8192(2)	
	y	.8535(2)	.3573(2)	.8555(8)	.8554(3)	.8541(1)	
	z	.6067(2)	.1756(2)	.6165(8)	.6124(3)	.6173(1)	
0C{00}	x	.0135(3)	.5107(3)	.0129(14)	.0127(4)	.0130(2)	.01304(14)
	y	.2795(2)	.7781(2)	.2798(7)	.2795(2)	.2841(1)	.30236(8)
	z	.1356(2)	.6357(2)	.1367(7)	.1353(2)	.1373(1)	.27027(16)
0C{02}	x	.0180(3)	.5108(3)	.0165(12)	.0149(5)	.0149(2)	
	y	.2923(2)	.7963(2)	.2932(6)	.2951(3)	.2942(1)	
	z	.6476(2)	.1499(2)	.6495(7)	.6481(3)	.6457(1)	
0C{04}	x	.0029(3)	.5131(3)	.0073(15)	.0096(4)	.0114(2)	.02183(14)
	y	.6807(2)	.1797(2)	.6801(7)	.6807(2)	.6826(1)	.69372(8)
	z	.1059(2)	.6093(2)	.1076(8)	.1084(2)	.1087(1)	.22945(16)
0C{02}	x	.0081(3)	.5074(3)	.0069(13)	.0091(5)	.0116(2)	
	y	.6905(2)	.1942(2)	.6916(7)	.6920(3)	.6905(1)	
	z	.6006(2)	.0986(2)	.5995(8)	.6003(2)	.6030(1)	
0D{00}	x	.1843(3)	.6961(3)	.1915(14)	.1884(5)	.1935(2)	.20750(14)
	y	.1088(2)	.6071(2)	.1063(6)	.1066(3)	.1077(1)	.10874(9)
	z	.1904(2)	.6820(2)	.1856(7)	.1883(2)	.1895(1)	.38895(15)
0D{02}	x	.2118(3)	.6949(3)	.2023(16)	.2037(5)	.2015(2)	
	y	.1029(2)	.6037(2)	.1031(7)	.1044(3)	.1052(1)	
	z	.6858(2)	.1947(2)	.6925(8)	.6902(2)	.6921(1)	
0D{04}	x	.2022(3)	.6929(3)	.1969(14)	.1995(5)	.1951(2)	.18396(15)
	y	.8121(2)	.3646(2)	.8169(7)	.8167(3)	.8168(1)	.81605(9)
	z	.2128(2)	.7271(2)	.2205(7)	.2180(4)	.2178(1)	.43611(16)
0D{02}	x	.1757(3)	.6952(3)	.1855(14)	.1816(5)	.1851(2)	
	y	.8583(2)	.3670(2)	.8618(7)	.8615(3)	.8636(1)	
	z	.7169(2)	.2030(2)	.7096(7)	.7124(3)	.7130(1)	

Gross Valley			Gross Valley 1200			Verzasca			Lake County				
An 94			An 94			An 91			An 56				
D			i										
A(00)	0 ₁₁	110(15)	123(14)	222(51)	479(50)	496(25)	0A(20)	0 ₁₁	303(42)	321(40)	246(88)	552(79)	473(27)
	0 ₂₂	214(7)	92(6)	521(34)	535(34)	737(19)	0 ₁₂	0 ₁₂	99(13)	75(13)	101(22)	90(22)	144(6)
	0 ₃₃	83(7)	82(6)	201(23)	245(25)	329(12)	0 ₁₃	0 ₁₃	130(15)	19(15)	173(26)	183(22)	189(9)
	0 ₁₂	-63(7)	65(7)	-112(28)	-80(27)	-220(14)	0 ₁₂	0 ₁₂	22(17)	23(17)	-5(31)	62(31)	46(11)
	0 ₁₃	64(8)	4(7)	121(28)	174(26)	207(13)	0 ₁₃	0 ₁₃	44(21)	83(21)	43(41)	139(35)	84(13)
	0 ₂₃	-75(5)	-24(4)	-203(23)	-234(23)	-315(13)	0 ₂₃	0 ₂₃	28(10)	42(11)	21(18)	13(17)	47(6)
A(40)	0 ₁₁	532(71)	901(92)	251(43)	377(62)	363(22)	0A(22)	0 ₁₁	282(41)	230(39)	320(88)	308(72)	487(28)
	0 ₂₂	760(32)	1090(50)	169(16)	198(34)	273(11)	0 ₂₂	0 ₂₂	88(13)	87(13)	131(23)	164(22)	151(8)
	0 ₃₃	403(31)	422(32)	150(18)	130(29)	192(10)	0 ₃₃	0 ₃₃	145(15)	180(15)	182(27)	150(22)	191(9)
	0 ₁₂	262(40)	2(51)	71(18)	26(30)	85(10)	0 ₁₂	0 ₁₂	18(17)	1(17)	34(32)	26(31)	-37(11)
	0 ₁₃	-30(41)	261(52)	39(21)	106(32)	54(11)	0 ₁₃	0 ₁₃	61(21)	55(20)	77(41)	48(33)	88(13)
	0 ₂₃	-359(21)	-341(31)	-40(13)	-10(25)	-59(7)	0 ₂₃	0 ₂₃	20(11)	25(11)	40(18)	29(18)	6(7)
A(20)	0 ₁₁	181(22)	352(41)	345(55)	204(140)	451(34)	0B(00)	0 ₁₁	383(39)	479(41)	441(76)	502(72)	668(28)
	0 ₂₂	78(6)	209(19)	764(34)	269(83)	107(53)	0 ₂₂	0 ₂₂	129(13)	123(13)	179(22)	171(23)	207(9)
	0 ₃₃	59(9)	201(20)	537(35)	73(71)	357(26)	0 ₃₃	0 ₃₃	227(15)	283(16)	358(28)	340(24)	313(10)
	0 ₁₂	50(8)	122(22)	141(35)	-23(72)	-137(26)	0 ₁₂	0 ₁₂	-50(18)	-25(17)	-33(31)	-54(31)	-82(12)
	0 ₁₃	22(12)	40(21)	-27(36)	182(21)	182(21)	0 ₁₃	0 ₁₃	182(20)	247(22)	29(39)	242(35)	258(15)
	0 ₂₃	-10(8)	-27(12)	-516(23)	0(84)	-395(34)	0 ₂₃	0 ₂₃	-15(11)	-33(11)	-23(20)	-46(19)	-22(7)
A(24)	0 ₁₁	385(14)	145(22)	209(98)	389(28)	327(16)	0B(02)	0 ₁₁	554(43)	478(41)	653(81)	682(74)	761(30)
	0 ₂₂	1235(12)	130(13)	94(34)	250(22)	243(9)	0 ₂₂	0 ₂₂	127(13)	121(13)	134(22)	174(23)	198(8)
	0 ₃₃	449(86)	131(13)	28(31)	189(21)	154(8)	0 ₃₃	0 ₃₃	246(16)	358(16)	387(27)	369(25)	333(10)
	0 ₁₂	277(12)	41(14)	138(33)	131(15)	39(8)	0 ₁₂	0 ₁₂	-50(18)	-25(17)	-33(31)	-54(31)	-82(12)
	0 ₁₃	-11(18)	31(15)	-4(35)	28(17)	44(8)	0 ₁₃	0 ₁₃	358(40)	335(22)	29(39)	242(35)	258(15)
	0 ₂₃	-466(7)	-73(86)	135(26)	-73(18)	-61(6)	0 ₂₃	0 ₂₃	-35(11)	-13(11)	-46(20)	-8(19)	-24(7)
T ₁ (00)	0 ₁₁	243(16)	216(15)	204(30)	410(29)	404(10)	JB(m0)	0 ₁₁	623(43)	519(41)	649(91)	785(81)	688(33)
	0 ₂₂	89(5)	74(5)	113(8)	135(9)	155(3)	0 ₂₂	0 ₂₂	195(15)	187(14)	180(23)	249(24)	272(10)
	0 ₃₃	74(5)	80(5)	87(9)	89(9)	106(3)	0 ₃₃	0 ₃₃	409(18)	368(17)	627(38)	583(30)	504(13)
	0 ₁₂	-10(7)	-9(6)	-18(11)	-4(12)	-42(4)	0 ₁₂	0 ₁₂	59(19)	41(18)	-26(36)	68(34)	31(14)
	0 ₁₃	64(8)	65(8)	45(14)	73(13)	92(5)	0 ₁₃	0 ₁₃	353(24)	296(22)	464(49)	485(42)	452(18)
	0 ₂₃	8(4)	7(4)	20(6)	7(8)	2(3)	0 ₂₃	0 ₂₃	-21(13)	-13(12)	-76(23)	-55(22)	-40(8)
T ₁ (02)	0 ₁₁	220(17)	219(17)	303(36)	409(32)	351(11)	0B(m2)	0 ₁₁	507(41)	794(48)	698(93)	733(78)	701(30)
	0 ₂₂	72(5)	66(5)	90(88)	140(10)	123(3)	0 ₂₂	0 ₂₂	134(13)	105(13)	126(20)	132(21)	234(9)
	0 ₃₃	71(6)	62(6)	77(9)	98(8)	93(3)	0 ₃₃	0 ₃₃	215(14)	524(19)	488(32)	443(26)	461(12)
	0 ₁₂	-15(7)	-10(7)	-45(13)	-33(4)	-33(4)	0 ₁₂	0 ₁₂	108(17)	58(21)	167(36)	76(34)	70(13)
	0 ₁₃	66(8)	46(8)	76(17)	80(14)	76(5)	0 ₁₃	0 ₁₃	208(20)	528(26)	433(47)	378(39)	361(16)
	0 ₂₃	7(4)	7(4)	11(7)	0(8)	11(3)	0 ₂₃	0 ₂₃	50(11)	-8(14)	40(22)	-12(21)	-38(8)
T ₁ (m0)	0 ₁₁	229(17)	280(18)	323(39)	396(34)	340(12)	0C(00)	0 ₁₁	550(43)	427(41)	502(79)	671(74)	700(29)
	0 ₂₂	88(6)	57(6)	108(9)	141(10)	133(3)	0 ₂₂	0 ₂₂	95(14)	109(13)	156(21)	122(21)	156(8)
	0 ₃₃	67(6)	76(6)	66(10)	89(9)	66(3)	0 ₃₃	0 ₃₃	204(15)	242(15)	201(24)	202(21)	242(9)
	0 ₁₂	42(7)	31(7)	52(14)	8(14)	58(5)	0 ₁₂	0 ₁₂	-32(18)	-34(17)	-54(31)	-54(31)	-82(12)
	0 ₁₃	60(8)	82(9)	83(17)	72(15)	59(5)	0 ₁₃	0 ₁₃	163(22)	178(21)	145(37)	184(33)	205(14)
	0 ₂₃	8(4)	6(4)	20(8)	7(8)	-1(3)	0 ₂₃	0 ₂₃	-22(11)	-9(11)	-21(18)	-24(17)	9(7)
T ₁ (m2)	0 ₁₁	237(16)	259(15)	243(33)	464(32)	423(11)	0C(02)	0 ₁₁	498(43)	447(42)	556(77)	553(71)	608(27)
	0 ₂₂	86(5)	87(5)	104(8)	131(9)	155(3)	0 ₂₂	0 ₂₂	107(14)	111(13)	128(20)	164(21)	201(8)
	0 ₃₃	71(6)	62(6)	77(9)	98(8)	93(3)	0 ₃₃	0 ₃₃	202(15)	202(15)	202(15)	201(21)	247(9)
	0 ₁₂	-15(7)	-10(7)	-45(13)	-33(4)	-33(4)	0 ₁₂	0 ₁₂	-36(18)	-70(17)	4(31)	-13(31)	-101(12)
	0 ₁₃	50(8)	51(7)	48(15)	85(14)	89(6)	0 ₁₃	0 ₁₃	155(22)	148(21)	145(37)	148(33)	149(13)
	0 ₂₃	15(4)	6(4)	36(7)	10(7)	13(2)	0 ₂₃	0 ₂₃	-5(11)	-38(11)	15(18)	-26(18)	-44(7)
T ₂ (00)	0 ₁₁	187(17)	196(16)	172(33)	356(33)	268(11)	0C(m0)	0 ₁₁	320(40)	350(39)	546(82)	504(72)	544(27)
	0 ₂₂	66(5)	50(5)	101(9)	95(9)	91(3)	0 ₂₂	0 ₂₂	134(13)	105(13)	126(20)	132(21)	234(9)
	0 ₃₃	85(6)	122(6)	135(10)	137(9)	107(3)	0 ₃₃	0 ₃₃	176(16)	136(14)	176(23)	184(22)	191(9)
	0 ₁₂	0(7)	2(7)	22(13)	14(13)	7(4)	0 ₁₂	0 ₁₂	84(17)	27(17)	115(32)	56(31)	104(12)
	0 ₁₃	41(8)	44(8)	35(15)	66(15)	50(5)	0 ₁₃	0 ₁₃	68(21)	45(20)	98(36)	85(33)	65(13)
	0 ₂₃	12(4)	2(4)	7(7)	-12(8)	9(2)	0 ₂₃	0 ₂₃	4(11)	0(11)	22(17)	-14(17)	-25(7)
T ₂ (02)	0 ₁₁	209(15)	244(15)	246(30)	385(31)	376(11)	0C(m2)	0 ₁₁	446(41)	502(42)	336(74)	654(75)	739(29)
	0 ₂₂	63(5)	57(5)	76(8)	112(9)	113(3)	0 ₂₂	0 ₂₂	132(14)	134(13)	161(22)	170(22)	170(22)
	0 ₃₃	108(6)	108(6)	178(9)	148(3)	105(3)	0 ₃₃	0 ₃₃	127(14)	164(15)	129(23)	150(22)	195(9)
	0 ₁₂	0(6)	7(6)	3(12)	36(12)	-2(4)	0 ₁₂	0 ₁₂	78(18)	64(18)	50(31)	65(31)	124(12)
	0 ₁₃	67(8)	62(8)	69(14)	81(14)	81(5)	0 ₁₃	0 ₁₃	67(21)	56(21)	52(34)	84(34)	84(14)
	0 ₂₃	2(4)	6(4)	0(7)	-11(7)	-7(2)	0 ₂₃	0 ₂₃	15(11)	2(11)	-7(18)	-21(18)	-7(6)
T ₂ (m0)	0 ₁₁	229(15)	230(15)	219(31)	409(30)	365(11)	0C(00)	0 ₁₁	508(42)	436(42)	411(83)	690(78)	684(29)
	0 ₂₂	61(5)	69(5)	78(8)	109(9)	113(3)	0 ₂₂	0 ₂₂	162(14)	161(14)	212(23)	236(24)	223(8)
	0 ₃₃	119(5)	121(6)	149(9)	174(9)	143(3)	0 ₃₃	0 ₃₃	131(14)	141(15)	179(25)	162(22)	167(8)
	0 ₁₂	17(6)	35(6)	42(12)	53(13)	25(4)	0 ₁₂	0 ₁₂	60(18)	67(18)	98(35)	16(33)	40(12)
	0 ₁₃	65(8)	43(8)	43(14)	90(14)	81(5)	0 ₁₃	0 ₁₃	-14(38)	-14(38)	-14(38)	46(34)	153(13)
	0 ₂₃	10(4)	24(4)	21(7)	28(7)	24(2)	0 ₂₃	0 ₂₃	21(11)	12(11)	9(20)	-5(19)	27(7)
T ₂ (m2)	0 ₁₁	244(16)	196(17)	231(34)	339(32)	275(11)	0C(02)	0 ₁₁	512(43)	441(42)	562(88)	512(74)	674(29)
	0 ₂₂	64(5)	76(5)	123(10)	96(3)	96(3)	0 ₂₂	0 ₂₂	129(13)	127(13)	191(24)	164(23)	219(9)
	0 ₃₃	100(6)	106(6)	158(9)	105(3)	105(3)	0 ₃₃	0 ₃₃	157(14)	179(15)	176(26)	201(23)	174(9)
	0 ₁₂	23(7)	22(7)	21(13)	25(14)	7(5)	0 ₁₂	0 ₁₂	40(18)	63(18)	37(37)	60(32)	26(12)
	0 ₁₃	79(8)	61(8)	70(15)	84(15)	64(5)	0 ₁₃	0 ₁₃	25(21)	-17(21)	-93(39)	-91(33)	9(13)
	0 ₂₃	19(4)	18(4)	31(7)	4(8)	10(3)	0 ₂₃	0 ₂₃	236(11)	7(11)	-14(21)	-25(19)	19(7)
0A(10)	0 ₁₁	618(42)	828(47)	836(103)	980(85)	1005(33)	0D(m0)	0 ₁₁	421(42)	661(47)	560(89)	556(72)	729(30)
	0 ₂₂	162(14)	157(14)	236(23)	209(24)	280(10)	0 ₂₂	0 ₂₂	159(14)	175(15)	183(25)	252(25)	247(9)
	0 ₃₃	112(14)	95(14)	113(23)	146(21)	147(9)	0 ₃₃	0 ₃₃	40(18)	18(20)	43(37)	67(33)	29(13)
	0 ₁₂	-39(18)	86(20)	43(37)	32(35)	33(13)	0 ₁₂	0 ₁₂	23(21)	-52(23)	-139(43)	-120(33)	-46(14)
	0 ₁₃	155(20)	204(21)	179(42)	220(35)	240(14)	0 ₁₃	0 ₁₃	-14(38)	-14(38)	-14(38)	46(34)	153(13)

important aspects of feldspar structures, yet its experimental determination is difficult. Because of the great similarity in the shape of the scattering factor curves for Al and Si, a direct refinement from X-ray diffraction data is not very accurate. We experimented with two different methods.

The second approach to refine T site occupancies follows the procedure that Fischer and Zehme (1964) used for low microcline. It is based on the different shapes of the Al and Si scattering factor curves. We used this method for Cazadero low albite only. First, positional and thermal parameters for all atoms were refined

	Gross Valley		Gross Valley 1200		Verzasca	Lake County	
	An 94		An 94		An 91	An 66	
	0	1					
A(00)	.701(3)	.224(4)	.969	.408(4)	.983	.567(10)	.491(40)
A(04)	.253(4)	.745(3)		.575(4)		.379(10)	.472(50)
A(20)	.180(5)	.581(4)	.994	.990(7)	1.001	.160(33)	.375(15)
A(24)	.818(5)	.413(4)		.321(6)		.837(33)	.635(15)
T ₁ (00)	1.015(2)	1.012(2)		1.018(3)		1.000(5)	1.000(3)
T ₁ (02)	.985(2)	.961(2)		.959(3)		.952(5)	.984(3)
T ₁ (m0)	.955(2)	.953(2)		.958(3)		.960(5)	.973(3)
T ₁ (mz)	1.017(3)	1.015(3)		1.017(3)		.998(5)	.992(3)
T ₂ (00)	.950(2)	.953(2)		.962(3)		.967(5)	.975(3)
T ₂ (02)	1.014(3)	1.014(3)		1.013(3)		1.013(3)	1.003(5)
T ₂ (m0)	1.019(3)	1.027(3)		1.015(3)		1.008(5)	.994(3)
T ₂ (mz)	.959(2)	.954(2)		.961(3)		.967(5)	.973(3)

TABLE VII. — Multipliers for A and T sites. Constants and conditions for refinement are described in the text. Estimated standard deviations in parentheses refer to the last digit(s).

Coefficients d'occupation pour les sites A et T. Les constantes et les conditions d'affinement sont décrites dans le texte.

The first approach is based on the total number of scattering electrons (11.5 for Al^{1.5+} and 12 for Si²⁺). Assuming a disordered distribution of Al and Si over all tetrahedral sites an average scattering factor was calculated corresponding to the bulk composition of the crystal (e.g., $f = (1.66 f_{Al} + 2.34 f_{Si})/4$ for An66). While multipliers of oxygen atoms were held constant at 1.0 those of T and A cations were refined (Table VII). If the average scattering factor is applied to a site which is preferentially occupied by Si the multiplier will increase because of the higher effective electron density. Such a refinement of multipliers with a combined scattering factor is, of course, not strictly correct, because X-ray form factors, in contrast to neutron scattering lengths, have a characteristic angle dependence. The combined scattering factor applies neither to a pure Si nor to a pure Al site, but it was found that if all reflections, particularly low angle reflections, are included, the error introduced is insignificant. T site occupancies have previously been inferred from average $\langle T-O \rangle$ distances (e.g., Ribbe and Gibbs, 1969) and in fact the multipliers do show an inverse correlation with average $\langle T-O \rangle$ distances (Figure 2).

with the entire data set. Then the overall scale factor was refined with low angle reflections ($\sin \theta/\lambda < 0.30$). In the next step anisotropic temperature factors of all atoms were refined with high angle reflections ($\sin \theta/\lambda > 0.65$). As can be seen in table VIII, these temperature factors are not very sensitive to ionicity and gene-

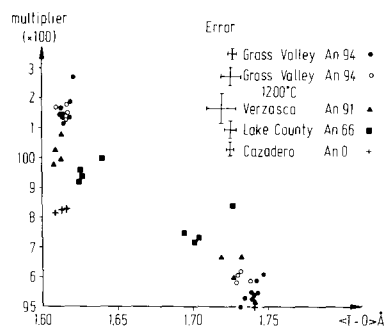


FIG. 2. — Multipliers refined from X-ray data (Table VII) versus $\langle T-O \rangle$ distances (Table X).

Coefficients d'occupation affinés à partir des données de rayons X (Tableau VII) en fonction des distances $\langle T-O \rangle$ (Tableau X).

rally are within 1 or 2 standard deviations of those obtained with all reflections. In the last step of the refinement oxygen occupancies were held constant at 1.0, two atoms (Al and Si) were assigned to each T site, and multipliers of both were refined independently without constraints with reflections $0.40 < \sin \theta/\lambda < 0.65$ for which the shape of the Al and Si scattering factor curves differs significantly. The multipliers were found to be very sensitive to ionic charge (Table IX). R-factors decrease slightly, but not significantly, with increasing charge. For neutral scattering factors no negative occupancies are observed. In contrast, atomic positions and temperature factors (Table VIII) are barely affected by charge assumptions except for the Na split-position which is ill-defined in any case. Al and Si are easily separated, but the uncertainty of ± 0.1 is rather high. Note that the sum of the two tetrahedral atoms on each site is less than 1.0, which may be due to a correlation with the temperature factor or the extinction coefficient.

The structure of the Lake County labradorite has been refined both with X-ray and neutron diffraction data (Tagai *et al.*, 1980). The goal of the neutron refinement was to obtain more accurate direct site occupancies for Al and Si, since neutron scattering lengths for the two elements are considerably more different than scattering factors (compare Table 2 in Wenk *et al.*, 1980).

Figure 3 compares T site occupancies refined from neutron and X-ray data. X-ray occupancies were obtained from multipliers (Table VII) by linear interpolation, assuming that the site with the largest multiplier is pure Si and that with the smallest one pure Al. Surprisingly, resolution in refinements with X-ray data is only slightly worse than in those with neutron data, probably due to the larger number of data (3115 versus 1099). The study demonstrates that Al, Si site occupancies can be refined both with X-ray and neutron diffraction data, but resolution with both techniques is not very satisfactory.

STRUCTURAL CONTRIBUTION TO SUPERSTRUCTURE REFLECTIONS

The structure of primitive anorthite was determined by Kemster *et al.* (1962) and discussed by Megaw *et al.* (1962) in great detail. Later refinements include those by Wainwright and

		Ionic all reflections	Neutral all reflections	Neutral $\sin \theta/\lambda > 0.65$
A(0)	0 ₁₁	577 (58)	257 (65)	304 (15)
	0 ₂₂	493 (62)	480 (45)	519 (12)
	0 ₃₃	1347 (105)	1405 (73)	1515 (40)
	0 ₁₂	-150 (41)	-112 (20)	-160 (11)
	0 ₁₃	387 (64)	331 (49)	425 (20)
A(s)	0 ₂₃	-445 (57)	-454 (41)	-489 (17)
	0 ₁₁	-29 (86)	67 (100)	-223 (34)
	0 ₂₂	1115 (179)	1039 (123)	817 (53)
	0 ₃₃	2136 (202)	1901 (207)	1506 (122)
	0 ₁₂	13 (70)	271 (57)	-218 (21)
T ₁ (0)	0 ₁₃	49 (102)	503 (83)	348 (51)
	0 ₂₃	-1242 (174)	1000 (127)	-833 (66)
	0 ₁₁	233 (7)	235 (6)	256 (8)
	0 ₂₂	76 (2)	74 (2)	77 (3)
	0 ₃₃	257 (9)	253 (8)	276 (10)
T ₁ (n)	0 ₁₂	-20 (3)	-18 (2)	-20 (3)
	0 ₁₃	123 (6)	119 (5)	127 (6)
	0 ₂₃	0 (3)	2 (3)	-1 (3)
	0 ₁₁	217 (6)	210 (5)	236 (7)
	0 ₂₂	70 (2)	69 (2)	71 (3)
T ₂ (0)	0 ₃₃	203 (8)	203 (7)	229 (10)
	0 ₁₂	20 (2)	22 (2)	21 (2)
	0 ₁₃	107 (5)	100 (4)	117 (5)
	0 ₂₃	10 (3)	9 (2)	19 (2)
	0 ₁₁	206 (6)	194 (5)	211 (8)
T ₂ (n)	0 ₂₂	65 (2)	60 (2)	62 (3)
	0 ₃₃	327 (8)	318 (7)	340 (10)
	0 ₁₂	-4 (2)	-5 (2)	-4 (2)
	0 ₁₃	98 (5)	93 (4)	99 (5)
	0 ₂₃	1 (3)	1 (2)	4 (2)
0A(1)	0 ₁₁	192 (5)	180 (5)	198 (8)
	0 ₂₂	60 (2)	56 (2)	59 (3)
	0 ₃₃	313 (8)	305 (7)	323 (10)
	0 ₁₂	12 (2)	12 (2)	10 (2)
	0 ₁₃	105 (5)	99 (4)	102 (5)
0A(2)	0 ₂₃	14 (3)	12 (2)	9 (2)
	0 ₁₁	615 (18)	635 (15)	655 (18)
	0 ₂₂	138 (6)	160 (5)	157 (6)
	0 ₃₃	367 (20)	413 (17)	396 (19)
	0 ₁₂	-8 (8)	-9 (7)	-10 (7)
0A(3)	0 ₁₃	255 (15)	309 (13)	311 (14)
	0 ₂₃	19 (8)	19 (7)	25 (7)
	0 ₁₁	250 (14)	318 (12)	323 (14)
	0 ₂₂	70 (5)	87 (4)	84 (5)
	0 ₃₃	559 (20)	616 (17)	579 (19)
0B(0)	0 ₁₂	3 (6)	2 (5)	-4 (6)
	0 ₁₃	118 (13)	163 (12)	145 (12)
	0 ₂₃	30 (7)	34 (5)	36 (7)
	0 ₁₁	443 (17)	475 (14)	462 (16)
	0 ₂₂	152 (6)	176 (5)	179 (6)
0B(n)	0 ₃₃	768 (23)	833 (20)	818 (23)
	0 ₁₂	-86 (8)	-85 (7)	-84 (7)
	0 ₁₃	388 (16)	422 (14)	429 (15)
	0 ₂₃	-47 (9)	-46 (8)	-44 (8)
	0 ₁₁	467 (17)	517 (15)	541 (18)
0C(0)	0 ₂₂	215 (7)	232 (6)	230 (7)
	0 ₃₃	1054 (26)	1100 (23)	1123 (28)
	0 ₁₂	102 (8)	101 (7)	108 (9)
	0 ₁₃	532 (18)	558 (15)	588 (18)
	0 ₂₃	35 (10)	35 (9)	41 (10)
0C(n)	0 ₁₁	376 (16)	444 (14)	413 (16)
	0 ₂₂	93 (5)	106 (5)	96 (5)
	0 ₃₃	703 (21)	763 (19)	768 (21)
	0 ₁₂	-44 (7)	-46 (6)	-49 (6)
	0 ₁₃	240 (15)	251 (13)	225 (14)
0C(s)	0 ₂₃	-28 (8)	-35 (7)	-33 (7)
	0 ₁₁	367 (16)	405 (14)	410 (16)
	0 ₂₂	84 (5)	100 (5)	94 (5)
	0 ₃₃	688 (21)	748 (19)	709 (21)
	0 ₁₂	37 (7)	37 (6)	42 (6)
0D(0)	0 ₁₃	156 (15)	176 (13)	145 (14)
	0 ₂₃	20 (8)	24 (7)	25 (7)
	0 ₁₁	460 (17)	494 (14)	484 (17)
	0 ₂₂	158 (5)	172 (5)	176 (6)
	0 ₃₃	364 (20)	421 (17)	398 (19)
0D(n)	0 ₁₂	40 (8)	45 (7)	47 (7)
	0 ₁₃	49 (14)	80 (12)	64 (13)
	0 ₂₃	21 (8)	25 (7)	23 (7)
	0 ₁₁	532 (17)	567 (15)	537 (17)
	0 ₂₂	166 (6)	182 (5)	184 (6)
0D(s)	0 ₃₃	404 (20)	453 (17)	440 (21)
	0 ₁₂	-23 (8)	-50 (7)	-56 (8)
	0 ₁₃	5 (15)	24 (13)	-15 (14)
	0 ₂₃	-33 (8)	-35 (7)	-36 (8)

TABLE VIII. — Anisotropic temperature factors for Cazadero low albite refined with different models, $\beta_{ij} \times 10^5$. Estimated standard deviations in parentheses refer to the last digit(s).

Facteurs de température anisotropes pour l'albite BT de Cazadero affinée avec différents modèles, $\beta_{ij} \times 10^5$.

		neutral		1/2 ionic		ionic
$T_1(O)$	Si	0.10(10)		0.27(10)		0.47(11)
	Al	0.86(11)	.96	0.67(11)	.94	0.45(11)
$T_1(O)$	Si	0.93(10)		1.14(10)		1.39(10)
	Al	0.05(11)	.98	-0.19(11)	.93	-0.47(11)
$T_2(O)$	Si	1.09(10)		1.30(10)		1.55(10)
	Al	-0.11(11)	.98	-0.35(11)	.95	-0.63(12)
$T_2(O)$	Si	0.97(10)		1.21(10)		1.48(10)
	Al	0.00(11)	.97	-0.26(11)	.95	-0.57(11)
A(9)		0.621(7)		0.619(6)		0.618(6)
A(4)		0.359(7)	.98	0.358(6)	.98	0.357(6)
R		2.66		2.46		2.30
R_w		3.94		3.70		3.52

TABLE IX. — T and A site occupancies for Cazadero low albite as a function of ionic charge. 1030 reflections in the range $0.40 < \sin \theta/\lambda < 0.65$ were used, oxygen atoms were held constant at occupancy 1.0.

Occupation des sites T et A pour l'albite BT de Cazadero en fonction de la charge ionique. 1030 réflexions du domaine $0.40 < \sin \theta/\lambda < 0.65$ ont été utilisées, et le taux d'occupation des atomes d'oxygène a été supposé constant et égal à 1.0.

Starkey (1971), Czank (1973) and Kalus (1978). The asymmetric unit contains 16 tetrahedra. They can be viewed as an arrangement of four-membered rings to chains which extend parallel to z and are linked into a three dimensional framework. It is standard to use Megaw's (1956) nomenclature to describe atomic positions. T_1 and OA atoms are on the axis of the chain (Figure 1); T_2 , OB, and OD atoms form the four-membered rings, and OC atoms link two chains into a framework.

In the basic structure of albite with space group $C\bar{1}$ all four-ring units are identical within a chain. In the superstructure of body-centered anorthite ($I\bar{1}$), two rings along z are no longer equivalent by translation. There is a reverse Al, Si distribution in the two ring units to satisfy the Al-O-Al avoidance rule (Loewenstein, 1954). This causes a doubling of the z axis and the occurrence of 'b' superstructure reflections in

	Gross Valley		Gross Valley 1200	Verrescoe	Lake County	Cazadero
	An 94		An 94	An 91	An 65	An 0.1
	0	1				
$T_1(OO)-OA$	1.637	1.634	1.634	1.630	1.648	
-OB	1.623	1.615	1.614	1.621	1.639	
-OC	1.586	1.593	1.602	1.590	1.620	
-OD	1.619	1.628	1.629	1.624	1.652	
Average	1.617	1.618	1.620	1.616	1.640	
$T_1(Oz)-OA$	1.764	1.767	1.759	1.763	1.737	1.744
-OB	1.742	1.751	1.742	1.739	1.723	1.740
-OC	1.708	1.723	1.707	1.715	1.702	1.735
-OD	1.771	1.764	1.758	1.759	1.741	1.745
Average	1.746	1.752	1.741	1.744	1.726	1.741
$T_1(Ox)-OA$	1.769	1.763	1.768	1.755	1.720	
-OB	1.698	1.736	1.707	1.707	1.683	
-OC	1.737	1.743	1.738	1.740	1.715	
-OD	1.752	1.698	1.717	1.720	1.695	
Average	1.739	1.735	1.733	1.731	1.703	
$T_1(Oz)-OA$	1.645	1.644	1.638	1.639	1.643	1.601
-OB	1.616	1.590	1.606	1.606	1.616	1.597
-OC	1.621	1.608	1.619	1.616	1.632	1.624
-OD	1.674	1.614	1.589	1.579	1.610	1.617
Average	1.614	1.614	1.613	1.610	1.625	1.610
$T_2(OO)-OA$	1.756	1.761	1.750	1.741	1.718	
-OB	1.751	1.738	1.747	1.732	1.703	
-OC	1.730	1.742	1.735	1.722	1.694	
-OD	1.699	1.703	1.695	1.691	1.666	
Average	1.734	1.736	1.734	1.721	1.695	
$T_2(Oz)-OA$	1.637	1.634	1.640	1.629	1.644	1.632
-OB	1.623	1.629	1.625	1.613	1.631	1.595
-OC	1.614	1.615	1.618	1.610	1.619	1.615
-OD	1.606	1.588	1.593	1.596	1.604	1.617
Average	1.620	1.617	1.619	1.612	1.625	1.615
$T_2(Ox)-OA$	1.636	1.642	1.635	1.637	1.644	1.646
-OB	1.591	1.612	1.613	1.593	1.610	1.621
-OC	1.607	1.601	1.602	1.598	1.613	1.597
-OD	1.639	1.628	1.626	1.634	1.634	1.602
Average	1.618	1.620	1.619	1.616	1.626	1.617
$T_2(Oz)-OA$	1.755	1.753	1.749	1.755	1.720	
-OB	1.738	1.711	1.717	1.726	1.688	
-OC	1.717	1.730	1.713	1.713	1.694	
-OD	1.750	1.765	1.764	1.747	1.707	
Average	1.740	1.740	1.733	1.736	1.702	
Standard Deviation	.002 - .003		.007 - .011	.001 - .002	.001 - .002	.001 - .002

TABLE X. — T-O distances of plagioclases in $\bar{A}$.
Distances T-O (en Å), dans les plagioclases.

	Greas Valley		Greas Valley 1200	Verzasca	Lake County	Cazadero
	An 94		An 94	An 91	An 66	An 0,1
	0	1				
OA(10)	138,0	139,2	139,2	135,6	140,5	141,3
OA(12)	137,1	136,2	137,8	137,1	138,7	
OA(20)	126,2	123,5	124,9	125,8	126,3	130,0
OA(22)	123,7	124,8	124,4	124,4	125,5	
OB(OO)	130,8	136,4	133,9	133,7	135,9	139,6
OB(Oz)	137,3	129,5	133,7	136,0	135,8	
OB(m0)	166,5	149,3	155,7	160,0	157,7	161,2
OB(mz)	146,2	160,3	153,3	150,6	153,7	
OC(OO)	132,8	130,9	131,9	132,1	131,3	129,8
OC(Oz)	131,6	130,6	131,9	131,1	131,1	
OC(m0)	130,6	130,9	130,3	131,3	131,5	135,9
OC(mz)	127,9	130,0	128,5	129,7	130,6	
OD(OO)	135,3	128,8	131,5	133,8	133,2	133,9
OD(Oz)	124,5	132,5	129,7	128,2	130,4	
OD(m0)	142,3	158,7	151,0	148,3	149,9	151,8
OD(mz)	160,8	142,2	151,3	156,0	152,2	
Standard Deviation	0,1 - 0,2		0,5 - 0,8	0,1 - 0,2	0,2 - 0,3	0,1 - 0,2

TABLE XI. — T-O-T angles of plagioclases in degrees.

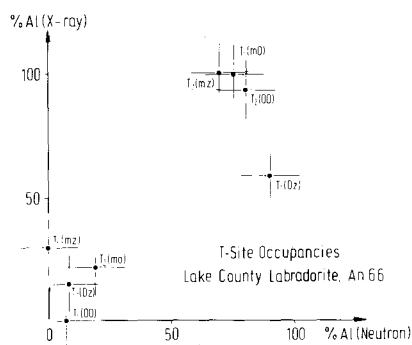
Angles T-O-T (en degrés) dans les plagioclases.

FIG. 3. — Al, Si occupancies of T sites in Lake County labradorite. Comparison of neutron (Tagai *et al.*, 1978) and X-ray diffraction data. X-ray data obtained from multipliers (Table VII) are normalized so that the largest multiplier corresponds to pure Si and the smallest to pure Al occupancy.

Occupation Al, Si des sites T dans la labradorite de Lake County. Comparaison des données de diffraction des neutrons (Tagai et al., 1978) et de rayons X. Les données de rayons X obtenues à partir des coefficients d'occupation (Tableau VII) sont normalisées de manière à ce que le coefficient le plus grand corresponde à une occupation totale par Si et le plus petit par Al.

the diffraction pattern ($h + k = \text{odd}$, $l = \text{odd}$) in addition to the basic 'a' reflections of albite ($h + k = \text{even}$, $l = \text{even}$). Pairs of atoms separated by the vector $\sim 1/2 \mathbf{c}$ are distinguished by indices O and z (Figure 1). In space group $\bar{1}1$ the body-centering vector relates the z -atoms to symmetrically identical atoms displaced by

$\sim 1/2(\mathbf{a} + \mathbf{b})$ from the O -atoms. Shifts of atoms from their average positions in $C\bar{1}$ to the new positions in $\bar{1}1$ are particularly large for OB and OC atoms with little separations between corresponding T atoms (Table XV). These shifts of OB and OC atoms and occupancies of T and A sites provide the main contribution to the intensity of 'b' reflections as shown by concentrations on a 'b' Fourier map (Figure 4 and Table XVI).

When the symmetry is further reduced from $\bar{1}1$ to $P\bar{1}$ two parallel chains extending along z and located at $x, y \sim 0$ and $x, y \sim 1/2$ are no longer equivalent. Atoms in the chain at $x, y \sim 1/2$ which are related to O - and z -atoms in the chain at $x, y \sim 0$ by the pseudo body-centering (i) vector are distinguished by indices i and zi , respectively. The loss of the translation $\mathbf{R} = 1/2(\mathbf{a} + \mathbf{b} + \mathbf{c})$ gives rise to extra superstructure reflections: 'c' reflections ($h + k = \text{even}$, $l = \text{odd}$) and 'd' reflections ($h + k = \text{odd}$, $l = \text{even}$). For 'c' reflections there is a translational symmetry $1/2[\mathbf{a} + \mathbf{b}]$, while for 'd' reflections it is $1/2 \mathbf{c}$. Atomic shifts from average positions in $\bar{1}1$ to new positions in $P\bar{1}$ are largest for OB and OD atoms and moderate for OA(1) and T_2 atoms (Table XV). Intensity contributions are again best evaluated on Fourier maps with 'c' and 'd' reflections (Figure 4 and table XVI). The main contribution for 'c' and 'd' reflections comes from Ca occupancies. 'c' reflections also are significantly linked to OB, OD, OA(1) and T_2 atoms, 'd' reflections to T_1 , $T_2(m)$ and OB(m) atoms. Notice the distinct difference of the two

	Grass Valley		Grass Valley 1200	Verrucosa	Lake County	Cazadero
	An 94		An 94	An 91	An 66	An 0.1
	O	i				
$T_1(OO)$						
OA-OB	2.5229	2.5344	2.5231	2.5294	2.5620	2.7217
OA-OC	2.7161	2.7530	2.7670	2.7427	2.7837	2.9502
OA-OD	2.5313	2.5373	2.5296	2.5403	2.5805	2.7507
OB-OC	2.6526	2.6388	2.6547	2.6503	2.6663	2.8836
OB-OD	2.7119	2.7145	2.7171	2.7130	2.7480	2.8752
OC-OD	2.6291	2.6460	2.6506	2.6354	2.6601	2.8541
Average	2.6348	2.6373	2.6404	2.6352	2.6734	2.8392
$T_1(Oz)$						
OA-OB	2.6626	2.6424	2.6493	2.6525	2.6466	
OA-OC	2.9798	3.0318	2.9893	3.0025	2.9532	
OA-OD	2.6745	2.6464	2.6618	2.6653	2.6602	
OB-OC	2.9763	2.9919	2.9716	2.9788	2.8508	
OB-OD	2.9740	2.9774	2.9681	2.9516	2.9099	
OC-OD	2.8807	2.8832	2.8574	2.8763	2.8381	
Average	2.8412	2.8472	2.8329	2.8373	2.8097	
$T_1(mO)$						
OA-OB	2.7777	2.6878	2.7093	2.7370	2.6929	2.6124
OA-OC	2.9118	2.9259	2.9177	2.9112	2.8604	2.6815
OA-OD	2.6992	2.7646	2.7318	2.7197	2.6898	2.5897
OB-OC	2.8703	2.9084	2.8854	2.8805	2.8223	2.6095
OB-OD	2.8673	2.8792	2.8653	2.8561	2.8202	2.6962
OC-OD	2.8787	2.8078	2.8391	2.8304	2.7883	2.6533
Average	2.8342	2.6290	2.8248	2.8225	2.7791	2.6338
$T_1(mz)$						
OA-OB	2.5253	2.5539	2.5322	2.5300	2.5624	
OA-OC	2.7295	2.7090	2.7161	2.7153	2.7295	
OA-OD	2.5942	2.5508	2.5598	2.5698	2.5698	
OB-OC	2.6765	2.6629	2.6790	2.6771	2.6898	
OB-OD	2.6720	2.6678	2.6713	2.6612	2.6919	
OC-OD	2.6626	2.6486	2.6208	2.6090	2.6453	
Average	2.6334	2.6329	2.6315	2.6271	2.6523	
$T_2(OO)$						
OA-OB	2.8344	2.7299	2.7757	2.7759	2.7492	2.6635
OA-OC	2.7363	2.6945	2.7120	2.7089	2.6661	2.5644
OA-OD	2.7830	2.7932	2.7962	2.7733	2.7367	2.6123
OB-OC	2.9040	2.8962	2.8997	2.8738	2.8203	2.6598
OB-OD	2.8206	2.8972	2.8551	2.8216	2.7852	2.6569
OC-OD	2.8905	2.9288	2.9103	2.8834	2.8272	2.6212
Average	2.8281	2.8236	2.8248	2.8062	2.7641	2.6297
$T_2(Oz)$						
OA-OB	2.5959	2.6420	2.6288	2.6057	2.6397	
OA-OC	2.5140	2.5279	2.5261	2.5130	2.5397	
OA-OD	2.6572	2.6536	2.6535	2.6451	2.6580	
OB-OC	2.6933	2.7028	2.6978	2.6844	2.6979	
OB-OD	2.6767	2.6796	2.6424	2.6365	2.6646	
OC-OD	2.7094	2.6820	2.6955	2.6881	2.6962	
Average	2.6401	2.6375	2.6407	2.6290	2.6494	
$T_2(mO)$						
OA-OB	2.6674	2.6429	2.6466	2.6468	2.6560	2.6307
OA-OC	2.5683	2.5874	2.5854	2.5698	2.5975	2.5883
OA-OD	2.6678	2.6504	2.6543	2.6029	2.6508	2.6376
OB-OC	2.6542	2.6663	2.6628	2.6482	2.6655	2.6392
OB-OD	2.6151	2.6460	2.6381	2.6194	2.6492	2.6433
OC-OD	2.8799	2.6774	2.6701	2.6756	2.6925	2.6908
Average	2.6421	2.6449	2.6429	2.6373	2.6536	2.6383
$T_2(mz)$						
OA-OB	2.8319	2.8318	2.8150	2.8235	2.7659	
OA-OC	2.7658	2.7617	2.7476	2.7661	2.7171	
OA-OD	2.7627	2.8216	2.7888	2.7842	2.7439	
OB-OC	2.8457	2.8444	2.8302	2.8327	2.7883	
OB-OD	2.8879	2.8540	2.8724	2.8703	2.8064	
OC-OD	2.9308	2.9210	2.9105	2.9116	2.8432	
Average	2.8375	2.8391	2.8274	2.8314	2.7774	
Standard Deviation	.003 = .005		.008 = .013	.001 = .003	.002 = .003	.001 = .003

TABLE XII. — O-O distances of plagioclases in Å.

Distances O-O (en Å) dans les plagioclases.

Fourier maps which both originate from the same symmetry reduction $I\bar{1} \rightarrow P\bar{1}$.

RESULTS

a) $P\bar{1}$ plagioclase

Comparing O-T-O angles in the *O*- tetrahedron with those in the corresponding *i*- tetrahedron, we notice very close agreement (Table XIII) in general, the largest difference being 6° [$T_1(mO)$: OA-OB and OA-OD]. This suggests that during the $I\bar{1} \rightarrow P\bar{1}$ transition there is little distortion of tetrahedra. T-O-T angles (Table XI) on the other hand show much larger differences between

the *O*- and the *i*- chains particularly around OB(m) and OD(m) atoms, where they amount to more than 15°. Therefore, the $I\bar{1} \rightarrow P\bar{1}$ transition mainly involves a displacive distortion of the framework, with individual tetrahedra remaining fairly rigid. This is quite different for the transition $C\bar{1} \rightarrow I\bar{1}$. If we compare T-O-T angles at *O*- and corresponding *z*- oxygen atoms, e.g., for Grass Valley 1200 anorthite or Lake County labradorite, we notice very small angular differences.

The A positions were refined as four sites, each split into *O*- and Δ - sites, resulting in eight atoms with individual coordinates, anisotropic

	Grass Valley		Grass Valley 1200	Verzasca	Lake County	Cazadero
	An 94		An 94	An 91	An 86	An 8,1
	0	1				
$T_1(00)$ OA-OB	101.37	102.51	101.94	102.14	102.45	102.73
OA-OC	117.05	117.12	117.54	116.62	116.85	115.99
OA-OD	102.01	102.14	101.62	102.54	102.35	104.07
OB-OC	111.48	110.67	111.36	111.26	111.05	112.18
OB-OD	113.50	113.63	113.81	113.44	113.27	111.19
OC-OD	110.21	110.47	110.23	110.19	110.02	110.23
Distortion Index	6.52	6.01	6.42	5.90	5.72	5.06
$T_1(0z)$ OA-OB	98.82	97.35	98.38	96.46	98.50	
OA-OC	116.15	120.60	119.23	119.34	118.35	
OA-OD	98.32	97.06	98.38	98.34	99.81	
OB-OC	112.95	113.27	112.72	112.72	112.64	
OB-OD	115.57	115.70	115.99	115.08	114.32	
OC-OD	111.76	111.51	111.10	111.77	111.05	
Distortion Index	8.59	9.83	8.91	8.83	8.11	
$T_1(m0)$ OA-OB	106.54	100.40	102.44	104.48	104.59	109.54
OA-OC	112.34	113.17	112.64	112.78	112.71	112.52
OA-OD	100.15	106.02	103.23	103.00	103.93	107.16
OB-OC	113.35	113.47	113.73	113.36	112.29	108.23
OB-OD	112.44	113.96	113.59	112.93	113.26	111.45
OC-OD	111.18	109.38	110.50	109.76	109.71	107.56
Distortion Index	5.11	5.37	5.19	4.58	4.18	2.12
$T_1(mz)$ OA-OB	101.50	104.29	102.62	102.44	103.66	
OA-OC	113.39	112.79	113.02	113.03	112.90	
OA-OD	107.37	103.29	105.55	105.95	105.79	
OB-OC	111.56	112.71	112.34	112.36	111.83	
OB-OD	113.77	112.72	113.44	113.33	113.11	
OC-OD	109.09	110.55	109.56	109.46	109.36	
Distortion Index	4.61	4.43	4.45	4.42	3.95	
$T_2(00)$ OA-OB	107.85	102.58	104.64	106.14	106.95	111.24
OA-OC	103.42	100.57	101.78	102.95	102.78	104.32
OA-OD	107.31	107.51	108.04	107.81	107.95	107.05
OB-OC	113.08	112.76	112.81	112.66	112.25	111.89
OB-OD	109.70	114.71	112.12	111.08	111.54	111.63
OC-OD	114.92	116.46	116.12	115.34	114.61	110.37
Distortion Index	4.16	6.60	5.42	4.55	4.29	3.06
$T_2(0z)$ OA-OB	105.59	108.12	107.24	106.98	107.45	
OA-OC	101.34	102.18	101.66	101.74	102.25	
OA-OD	113.09	113.68	110.28	110.26	109.85	
OB-OC	112.66	112.86	112.59	112.81	112.27	
OB-OD	111.64	109.00	110.38	110.52	110.92	
OC-OD	114.63	113.72	114.15	113.96	113.57	
Distortion Index	4.96	4.15	4.45	4.45	4.08	
$T_2(m0)$ OA-OB	111.48	108.63	109.15	110.04	109.40	107.24
OA-OC	104.72	105.85	106.04	105.17	105.74	105.88
OA-OD	109.09	108.40	109.02	109.00	108.48	108.56
OB-OC	112.16	112.08	111.83	112.26	111.59	110.17
OB-OD	108.09	108.59	108.08	108.55	109.49	110.15
OC-OD	111.27	112.12	111.64	111.77	112.01	114.50
Distortion Index	2.80	2.40	2.12	2.57	2.27	3.00
$T_2(mz)$ OA-OB	108.35	109.65	108.64	108.40	108.50	
OA-OC	105.63	104.50	105.10	105.78	105.50	
OA-OD	104.04	106.65	105.52	105.31	106.41	
OB-OC	110.94	111.52	111.23	110.87	111.07	
OB-OD	111.80	110.40	111.67	111.44	111.50	
OC-OD	115.44	113.41	114.17	114.55	113.46	
Distortion Index	4.21	3.15	3.62	3.57	3.12	
Standard Deviation	0.11 - 0.14		0.4 - 0.6	0.07 - 0.09	0.16 - 0.19	0.06 - 0.08

TABLE XIII. — O-T-O angles and distortion indices of plagioclases in degrees.
Angles O-T-O et indices de distorsion (en degrés) dans les plagioclases.

temperature factors and multipliers. All parameters converged, but occupancies of the two-split positions are very different except for the zOi -site (Table VII, figure 5). The sum of the multipliers is close to unity. A(z) sites are slightly more occupied than A(O) sites which is also the case in all $\bar{1}\bar{1}$ structures and may indicate that Na substitutes preferentially on A(O).

The 'd' type reflections in Grass Valley anorthite were much weaker than the 'c' type reflections, whereas they are of comparable intensity in pure anorthite. During heat treatment and during substitution of NaSi for CaAl, 'd' reflections disappear first. Diffuse 'c' reflections are still present in more sodic pla-

gioclases, such as Lake County labradorite, while 'd' reflections are absent. The $P\bar{1} \rightarrow \bar{1}\bar{1}$ transition may therefore start with lattice distortions that affect $T_1(m)$ and $T_2(m)$ atoms which have a large contribution to the intensity of the 'd' reflections (Table XVI and figure 4).

In space group $\bar{1}\bar{1}$ the vectors $1/2\ c$ and $1/2\ [a+b]$ point to atoms which are translation-equivalent due to the body-centering vector. They are no longer equivalent in space group $P\bar{1}$ where they are distinguished by indices z and zi as noted above. Table XVII documents that during the $\bar{1}\bar{1} \rightarrow P\bar{1}$ transition distances between O- and z-atoms or i- and zi-atoms which are separated by $\sim 1/2\ c$ change by a larger amount

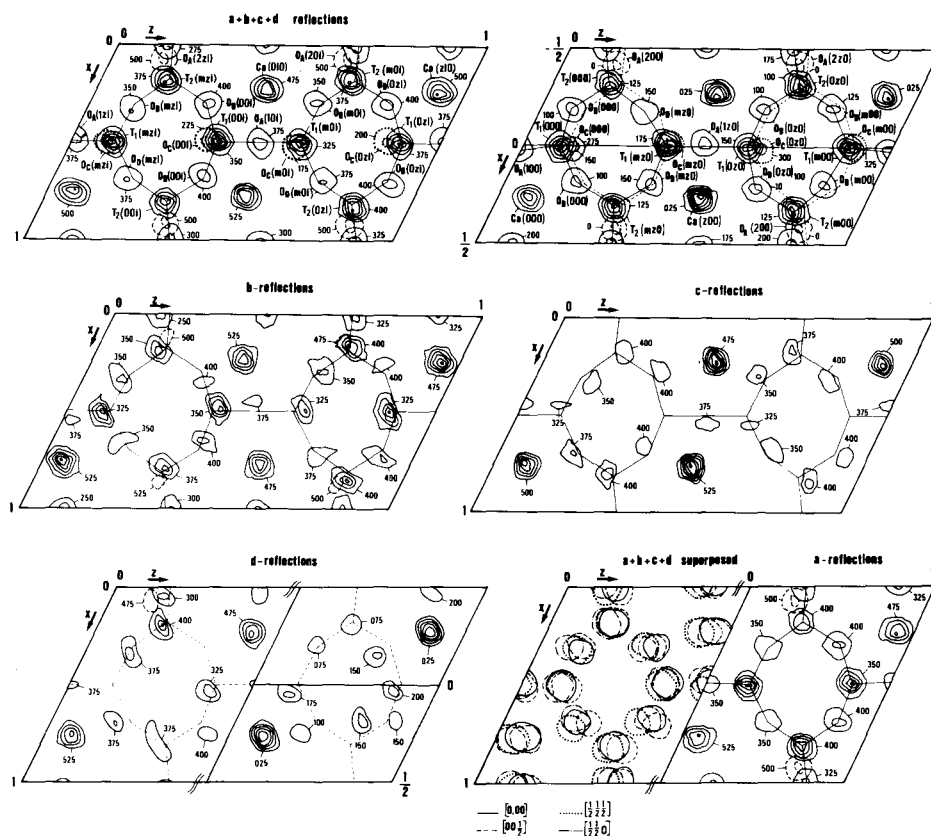


FIG. 4. — Fourier maps of Grass Valley primitive anorthite, calculated for 'a', 'b', 'c', 'd' and 'a' + 'b' + 'c' + 'd' reflections. y coordinates of peaks in that xz section where they are maximal are indicated ($\times 1000$).

Cartes de Fourier de l'anorthite primitive de Grass Valley, calculée pour les réflexions 'a', 'b', 'c', 'd', et 'a' + 'b' + 'c' + 'd'. Les coordonnées y des pics sont indiquées ($\times 1000$) dans cette section où elles sont maximales.

than do distances between O- and z-atoms or z- and i-atoms which are separated by $\sim [\mathbf{a} + \mathbf{b}]$. This is of some significance with regards to 'b' antiphase boundaries (APB's). Anorthite generally contains 'c' APB's ($R = 1/2[\mathbf{a} + \mathbf{b} + \mathbf{c}]$) but occasionally — particularly in lunar rocks as well as in synthetic crystals — also 'b' APB's. They are thought to arise during Al, Si ordering in the $C\bar{1} \rightarrow \bar{1}\bar{1}$ transition (Kroll and Müller, 1980). In body-centered anorthite the displacement across a boundary is either $1/2 \mathbf{c}$ or $1/2[\mathbf{a} + \mathbf{b}]$ with no distinction between the two. In primitive anorthite it was observed that 'b' APB's generally had a displacement vector $R = 1/2[\mathbf{a} + \mathbf{b}]$ (Müller *et al.*, 1973; Heuer *et al.*, 1976), which is structurally sensible because distortions across such an interface, and thus strain energies, are smaller than across an interface with $R = 1/2 \mathbf{c}$.

b) $\bar{1}\bar{1}$ plagioclase

The $\bar{1}\bar{1}$ structures refined satisfactorily with least-squares methods, using coordinates of average $C\bar{1}$ structures as starting parameters. Contrasting to Grass Valley ($P\bar{1}$) anorthite there was no need to rely on Fourier techniques in this case (however, cf. Tagai *et al.*, 1980).

The two Ca-rich crystals yielded structures very similar to primitive anorthite. The Al, Si distribution, determined both from $\langle \text{T-O} \rangle$ bond lengths and occupancy factors (Tables VII and X), conforms with that of pure anorthite, with $T_1(\text{Oz})$, $T_1(\text{mO})$, $T_2(\text{OO})$ and $T_2(\text{mz})$ occupied by Al. More sodic plagioclases such as Lake County labradorite display some distinctly different features. Based on average $\langle \text{T-O} \rangle$ bond lengths (Table X) it appears that the distribution of Al and Si on the four sites $T_1(\text{Oz})$,

		Grass Valley		Grass Valley 1200	Verzasca	Lake County	Caradere
		An 94		An 94	An 91	An 56	An 0,1
		0	i				
A(000)-0A(10)	0	2,675	2,773	2,742	2,713	2,769	2,671
	Δ	2,288	2,403	2,339	2,323	2,357	2,526
-0A(10)	0	2,476	2,365	2,403	2,447	2,423	2,515
	Δ	2,893	2,859	2,919	2,937	2,932	2,824
-0A(20)	0	2,305	2,282	2,300	2,307	2,322	2,377
	Δ	2,313	2,339	2,341	2,346	2,340	2,264
-0A(20)	0	4,029	3,914	3,967	3,965	3,936	3,728
	Δ	3,469	3,280	3,326	3,337	3,347	3,594
-0A(2z)	0	3,511	3,542	3,532	3,539	3,553	3,730
	Δ	4,042	4,184	4,160	4,160	4,124	3,802
-0B(00)	0	2,409	2,564	2,484	2,472	2,487	2,449
	Δ	2,305	2,401	2,365	2,353	2,410	2,579
-0B(m0)	0	3,750	3,431	3,569	3,511	3,592	3,473
	Δ	2,987	2,558	2,679	2,753	2,763	3,222
-0C(0z)	0	3,095	3,199	3,153	3,136	3,093	2,960
	Δ	3,595	3,769	3,751	3,705	3,673	3,179
-0C(mz)	0	3,274	3,164	3,224	3,216	3,250	3,277
	Δ	2,697	2,570	2,577	2,599	2,622	2,932
-0D(00)	0	2,379	2,246	2,312	2,344	2,377	2,437
	Δ	2,548	2,471	2,521	2,569	2,535	2,354
-0D(m0)	0	2,557	2,891	2,729	2,702	2,722	2,988
	Δ	3,346	3,777	3,642	3,588	3,583	3,279
Average CN(A)=7	0	2,555	2,612	2,589	2,589	2,599	2,628
	Δ	2,576	2,514	2,534	2,554	2,564	2,665
O-A Average		2,566	2,563	2,562	2,572	2,582	2,647
A(00z)-0A(1z)	0	2,563	2,536	2,511	2,733	2,693	
	Δ	2,473	2,318	2,371	2,432	2,421	
-0A(1z)	0	2,559	2,527	2,616	2,364	2,436	
	Δ	2,736	2,803	2,821	2,734	2,799	
-0A(2z)	0	2,292	2,289	2,283	2,296	2,316	
	Δ	2,338	2,326	2,360	2,332	2,332	
-0A(2z)	0	3,637	3,429	3,634	3,494	3,424	
	Δ	3,355	3,463	3,343	3,409	3,376	
-0A(20)	0	3,786	3,672	3,823	3,589	3,637	
	Δ	4,089	4,072	4,151	4,055	4,080	
-0B(0z)	0	2,546	2,454	2,455	2,577	2,564	
	Δ	2,421	2,354	2,368	2,432	2,399	
-0B(mz)	0	2,857	3,282	2,968	3,295	3,307	
	Δ	2,520	2,767	2,577	2,626	2,702	
-0C(00)	0	3,653	3,479	3,607	3,374	3,320	
	Δ	3,832	3,795	3,851	3,794	3,704	
-0C(m0)	0	2,717	2,876	2,720	3,008	3,026	
	Δ	2,565	2,553	2,530	2,584	2,624	
-0D(0z)	0	2,203	2,359	2,351	2,257	2,231	
	Δ	2,400	2,558	2,540	2,451	2,512	
-0D(mz)	0	3,359	2,782	3,188	2,860	2,898	
	Δ	3,702	3,315	3,581	3,540	3,521	
Average CN(A)=7	0	2,534	2,546	2,558	2,585	2,599	
	Δ	2,493	2,526	2,510	2,513	2,541	
O-A Average		2,514	2,536	2,534	2,549	2,570	
Standard Deviation		.005 - .007		.010 - .025	.002 - .005	.003 - .005	.002 - .004

TABLE XIV. — A-O distances of plagioclases in Å (assuming that the A position is the weighted average of the two-split positions).

Distances A-O (en Å) dans les plagioclases (en prenant comme position A la moyenne pondérée des positions dédoublées).

$T_1(mz)$, $T_2(Oz)$, $T_2(mO)$ is still largely ordered, while it is partially disordered in case of the other four sites ($T_1(OO)$, $T_1(mz)$, $T_2(OO)$, $T_2(mz)$). See figure 6. This tendency is already, though barely, present in Verzasca anorthite (An91) and in bytownite (An85) (Chiari *et al.*, in press) when compared with pure anorthite of Wainwright and Starkey (1971). The four sites with the more ordered Al, Si distribution correspond to those four sites in the anorthite structure whose occupancy is like that of low albite (Fi-

gure 1). The four sites with the less ordered Al, Si distribution are those sites which in pure ordered anorthite are occupied by one Si atom surrounded by three Al atoms, and this arrangement can not occur in low albite but is typical of anorthite. Thus it seems that substitution of Si for Al affects the "albite-like" unit to a lesser extent than the "anorthite-like" unit which with increasing Ab-content resembles more and more that of low albite. Notice that the terms "albite-like" and "anorthite-like" refer to small seg-

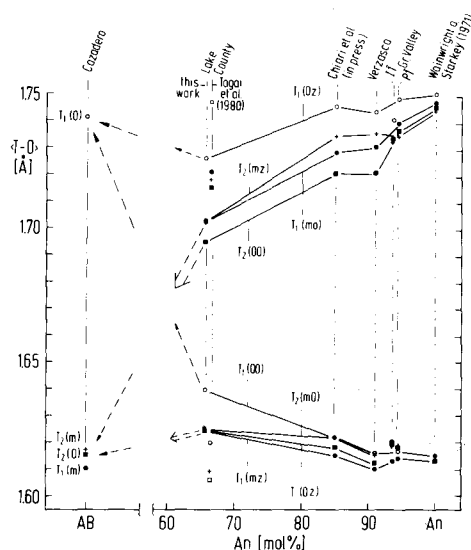


FIG. 6. — Average tetrahedral $\langle T-O \rangle$ distances versus An content of several refined plagioclase structures.

Distances moyennes $\langle T-O \rangle$ des tétraèdres en fonction du contenu en An de structures affinées de plagioclases.

feldspar is primarily dependent on the tetrahedral Al-content. To some extent, however, it is also related to the specific environment of the pair of bond-forming atoms. This has been documented and quantified in several papers by Ribbe, Phillips and Gibbs: for anorthite compare Phillips *et al.* (1973) and Ribbe *et al.* (1974). Their statistical studies of bond length variation in feldspars produced three factors which perturb T-O bond lengths:

(1) Linkage: Si-O $\rightarrow$ Si bonds are ~ 0.03 Å longer than Si-O $\rightarrow$ Al bonds.

(2) Bonds to Na,K,Ca: the coordination number (2, 3 or 4 in feldspars) of the oxygen atom is related directly to T-O distance.

(3) T-O-T angle: longer T-O distances are associated with narrower T-O-T angles.

Figure 7 is a sketch of the environment of a T-O bond. In anorthite and An-rich structures — such as our An94 and An91 crystals — all T-O linkages are predominantly of the type Si-O-Al. Thus we did not consider the linkage factor (1) in our analysis.

	'a'+ 'b'+ 'c'+ 'd'	'a'	'b'	'c'	'd'
A(000)	27.2	21.0	4.9	11.1	2.3
A(200)	34.3	21.0	7.5	10.6	2.3
A(010)	24.7	21.0	4.9	10.6	1.8
A(210)	26.3	21.0	7.5	11.1	1.8
T ₁ (000)	31.5	28.7	4.9		
T ₁ (020)	26.3	28.7	5.4		
T ₁ (001)	34.0	28.7	4.9		0.8
T ₁ (021)	26.0	28.7	5.4		0.8
T ₁ (m00)	29.3	27.6	3.5		1.1
T ₁ (m20)	27.4	27.6	5.3		1.1
T ₁ (m01)	28.6	27.6	3.5		1.3
T ₁ (m21)	30.6	27.6	5.3		1.3
T ₂ (000)	25.2	23.2	3.9	4.2	
T ₂ (020)	29.4	23.2	4.9	4.4	
T ₂ (001)	26.4	23.2	3.9	4.4	
T ₂ (021)	26.6	23.2	4.9	4.2	
T ₂ (m00)	27.1	25.8	4.6	2.9	1.3
T ₂ (m20)	30.3	25.8	4.4	3.4	1.3
T ₂ (m01)	26.4	25.8	4.6	3.4	1.4
T ₂ (m21)	27.7	25.8	4.4	2.9	1.4
OA(100)	10.5	11.1	1.4		0.8
OA(120)	11.3	11.1		2.8	0.8
OA(101)	11.7	11.1	1.4	2.8	
OA(121)	11.3	11.1			
OA(200)	10.1	9.9			
OA(220)	10.3	9.9			
OA(201)	9.8	9.9			
OA(221)	10.1	9.9			
OB(000)	13.1	10.4	2.7	2.1	
OB(020)	13.4	10.4	2.2	2.5	
OB(001)	10.3	10.4	2.7	2.5	
OB(021)	11.6	10.4	2.2	2.1	
OB(m00)	10.2	8.4	2.3	2.5	0.9
OB(m20)	12.7	8.4	2.3	3.2	0.9
OB(m01)	10.7	8.4	2.3	3.2	0.9
OB(m21)	9.3	8.4	2.3	2.5	0.9
OC(000)	11.6	9.2	2.8		0.8
OC(020)	11.2	9.2	2.6		0.8
OC(001)	11.7	9.2	2.8		
OC(021)	12.4	9.2	2.6		
OC(m00)	12.4	11.5	2.3		
OC(m20)	12.1	11.5	2.1		
OC(m01)	12.6	11.5	2.3		
OC(m21)	12.6	11.5	2.1		
OD(000)	10.2	9.9		2.2	
OD(020)	12.1	9.9	1.4	2.3	
OD(001)	12.1	9.9		2.3	
OD(021)	11.9	9.9	1.4	2.2	
OD(m00)	10.5	8.4	1.6	3.4	0.8
OD(m20)	8.5	8.4		2.6	0.8
OD(m01)	9.5	8.4	1.6	2.6	
OD(m21)	9.8	8.4		3.4	

TABLE XVI. — Maximum electron density contribution (in $\bar{e}/\text{\AA}^3$) from 'a', 'b', 'c' and 'd'-type reflections to various atoms in Grass Valley (P1) anorthite. (Since positions do not coincide - Figure 4 - 'a'+ 'b'+ 'c'+ 'd' is not the sum of the individual contributions).

Contribution de densité électronique maximale (en $\bar{e}/\text{\AA}^3$) pour les réflexions de type 'a', 'b', 'c' et 'd' à divers atomes de l'anorthite de Grass Valley (P1). (Du fait que les positions ne coïncident pas - figure 4 - 'a'+ 'b'+ 'c'+ 'd' n'est pas la somme des contributions individuelles).

The second factor — A-O bonding — was treated in the following way. A T-O bond is weakened and thus lengthened when Ca is bonded to the oxygen atom. The influence that Ca exerts was taken to be proportional to the bond strength donated to the oxygen neighbour. Since oxygen atoms may be bonded to 0, 1 or 2 Ca-atoms, the sum of bond strengths, $\sum_i s_A$ ($i = 0, 1, 2$), has to be taken; this corresponds to a similar parameter used by Phillips *et al.* (1973).

The bond strengths were calculated using the Brown and Wu (1976) formulae :

$$S_{\text{Na-O}} = ((\text{Na-O})/1.622)^{-4.29}, \quad \text{and}$$

$$S_{\text{Ca-O}} = ((\text{Ca-O})/1.909)^{-5.4}.$$

Because all the structures were refined with two-split Ca positions, we used the average distance between an oxygen atom and its two-split Ca neighbours weighted by the Ca multiplicities*.

When oxygen atoms are to be assigned to the irregular A cation coordination sphere, there is always the question whether more distant A atoms should be considered as being bonded or not. We followed the advice of Allmann (1975) : When the A-O distance exceeds the sum of the van der Waals radii, the oxygen atom should not be taken as being bonded. The limiting distances for Na-O and Ca-O bonds are 3.30 Å and 3.37 Å, respectively (Pauling, 1968, p. 379).

Figure 8 demonstrates that there is a strong correlation between T-O distances and A-O bond strength sums in each of the three anorthite structures. Instead of the individual values, we have plotted the difference between individual and tetrahedral mean values in order to rule out the effect of different Al, Si site occupancies on T-O distances.

The third perturbation factor is the T-O-T angle. Its influence on T-O bond lengths has been the subject of some debate, but its significance has recently been confirmed in a review by Gibbs *et al.* (1981). The authors state, that "the Si-O bond length is observed to shorten by

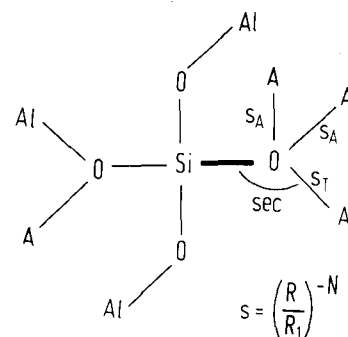


FIG. 7. — Sketch of the atomic environment of a T-O bond.

Schéma de l'environnement atomique d'une liaison T-O.

a small but significant amount, when the Si-O-Si angle widens". Molecular orbital calculations show that T-O bond overlap populations increase

pair	0 = z	0 = zi	1 = zi	1 = z
ps.-transl.	$\sim \frac{1}{2} c$	$\sim \frac{1}{2} (a+b)$	$\sim \frac{1}{2} c$	$\sim \frac{1}{2} (a+b)$
A(00)	0.015	0.189	0.236	0.029
A(04)	0.101	0.056	0.133	0.023
T ₁ (0)	0.005	0.010	0.018	0.006
T ₁ (m)	0.240	0.193	0.264	0.128
T ₂ (0)	0.140	0.007	0.109	0.003
T ₂ (m)	0.259	0.025	0.055	0.067
0A(1)	0.007	0.031	0.023	0.005
0A(2)	0.043	0.004	0.032	0.004
0B(0)	0.204	0.021	0.188	0.006
0B(m)	0.276	0.071	0.194	0.032
0C(0)	0.016	0.006	0.030	0.028
0C(m)	0.020	0.038	0.018	0.026
0D(0)	0.222	0.007	0.166	0.020
0D(m)	0.276	0.026	0.239	0.030
average	0.130	0.049	0.120	0.029

TABLE XVII. — Difference of distances between pseudo-translation-related atomic pairs in $P\bar{1}$ and $I\bar{1}$ Grass Valley anorthites, e.g., distance between T₁(mOO) and T₁(mzi) atoms in $P\bar{1}$ anorthite minus corresponding distance in $I\bar{1}$ anorthite = 0.193 Å. Columns 1 and 3 refer to atoms separated by $\sim 1/2 c$, columns 2 and 4 refer to atoms separated by $\sim 1/2 (a+b)$.

Différence des distances entre les paires atomiques reliées par pseudo-translation dans les anorthites $P\bar{1}$ et $I\bar{1}$ de Grass Valley, par exemple distance entre atomes T₁(mOO) et T₁(mzi) dans l'anorthite $P\bar{1}$ moins la distance correspondante dans l'anorthite $I\bar{1}$ = 0.193 Å. Les colonnes 1 et 3 correspondent aux atomes séparés par $\sim 1/2 c$, les colonnes 2 et 4 à ceux séparés par $\sim 1/2 (a+b)$.

* It may be mentioned that bond strengths can also be calculated in a graphical way from Voronoi polyhedra centered by the cations. In addition to the simple inverse relationship between bond strengths and bond lengths, as given by the Brown and Wu (1976) curves, this method also accounts for the modifying effects of oxygen-cation-oxygen angles (Kroll, 1980).

nonlinearly with increasing T-O-T angle (Gibbs *et al.*, 1972 ; Kroll and Phillips, 1976). The relationship can be linearized when the overlap populations are plotted versus $\sec(\text{T-O-T})$ (Gibbs *et al.*, 1972) or versus $(1-\sec(\text{T-O-T}))^{-1}$ (Newton and Gibbs, 1980).

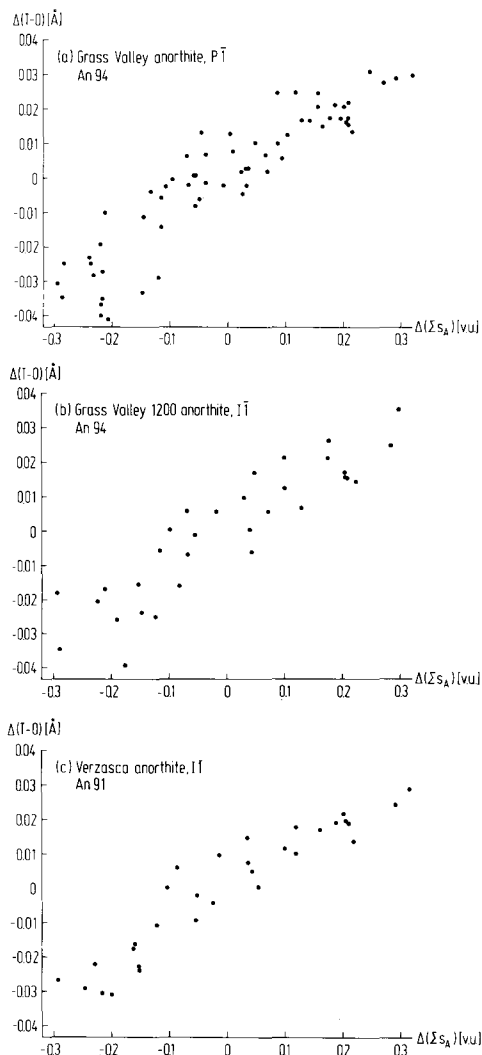


FIG. 8. — Plot of the differences between individual and tetrahedral mean values of T-O distances and bond strength sums received by oxygen atom O from its Ca neighbours : $\Delta\text{T-O} = \text{T-O} - \langle\text{T-O}\rangle$, $\Delta\sum s_A = \sum_i s_{Ai} - \langle\sum_i s_{Ai}\rangle$, where $i = 0, 1, 2$.

Différences entre valeurs individuelles et valeurs moyennes dans le tétraèdre, des distances T-O en fonction de la somme des forces de liaison reçues par un atome d'O des Ca voisins.

Figure 9 shows that the correlation between T-O bond lengths and $\sec(\text{T-O-T})$ is not as good as with A-O bonding. Nevertheless, it is clearly developed, especially when T-O bonds with two-, three-, or four-coordinated oxygen atoms are considered separately.

In the final regression analysis we regarded the A-O bonding and T-O-T angle factors as the independent variables :

$$\text{T-O} - \langle\text{T-O}\rangle = C_1(\sum_i s_{Ai} - \langle\sum_i s_{Ai}\rangle) + C_2(\sec(\text{T-O-T}) - \langle\sec(\text{T-O-T})\rangle).$$

In addition to the two Grass Valley crystals (An94($P\bar{1}$) and An95($I\bar{1}$) and the Verzasca crystal (An91($I\bar{1}$)) we included into the regression analysis the anorthite (An100) data of Wainwright and Starkey (1971) such that the total data set consisted of 192 equations. The results of the regression analysis are :

	Coefficient	Std. Error	t-value
C_1	0.10075	0.00359	28.1
C_2	-0.02442	0.00292	8.4
Coefficient of determination $r^2 = 0.87$			
Standard error of estimate $\sigma = 0.007\text{\AA}$			

As is expected from figures 8 and 9, the A-O bonding factor dominates over the angle factor, which is reflected in their respective standard |t|-values.

In figure 10 we have plotted the individual T-O distances as calculated from the regression analysis versus their respective observed values. Comparing the two $P\bar{1}$ structures, it can be seen that the overall fit of the Grass Valley data is superior to the data of Wainwright and Starkey (1971), especially for Si-O distances. However, we noticed that certain observed T-O distances deviate significantly from their expected values in both structures, which apparently points to a lack of adequacy of the regression model. This is not surprising in view of the simple model which we applied to the true complex bonding situation.

The quality of fit of the two $I\bar{1}$ structures is also distinctly different. However, this probably reflects merely the different precision of the two refinements. The mean standard error of the T-O

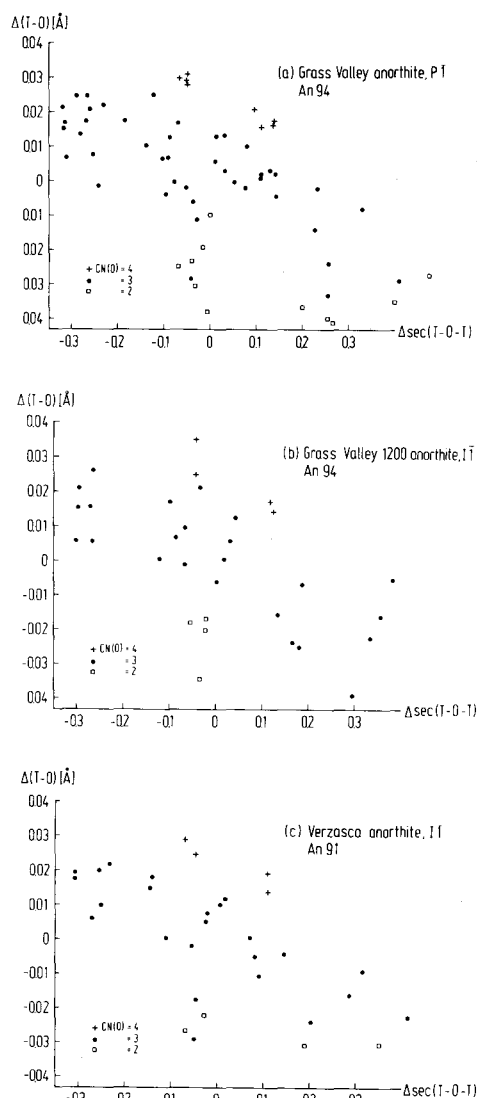


FIG. 9. — Plot of the differences between individual and tetrahedral mean values of T-O distances and T-O-T angles, given as $\sec(T-O-T) = (\cos(T-O-T))^{-1}$: $\Delta T-O = T-O - \langle T-O \rangle$, $\Delta\sec(T-O-T) = \sec(T-O-T) - \langle \sec(T-O-T) \rangle$.

Différences entre valeurs individuelles et valeurs moyennes dans le tétraèdre, des distances T-O en fonction des angles T-O-T.

distances is 0.008 Å for the Grass Valley 1200 crystal compared to only 0.002 Å for the Verzasca crystal.

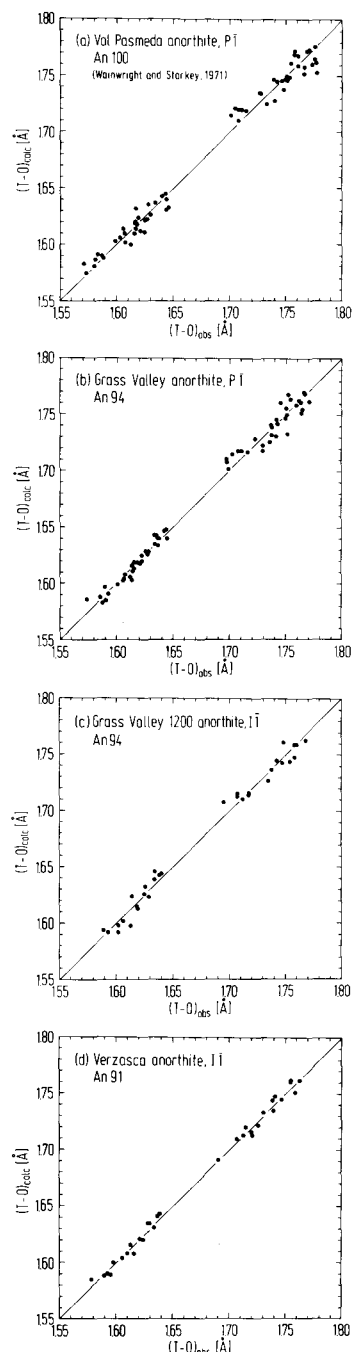


FIG. 10. — Plot of the individual T-O distances calculated from the regression equation versus the observed T-O distances.

Distances T-O individuelles calculées d'après l'équation de régression en fonction des distances T-O observées.

b) A-splitting

In all space groups, $C\bar{1}$, $I\bar{1}$, and $P\bar{1}$, the A-atoms were refined as two-split atoms, and the pattern is always quite similar with two partially occupied sites 0.7 - 0.8 Å apart in a direction close to $[01\bar{1}]$. Since shifts of A-atoms in superstructures from average positions are small (Table XV), splitting is still visible in average structures (compare figure 5 in Wenk *et al.*, 1980). However, occupancy of the split sites is different. Since splitting is present in $I\bar{1}$ and $P\bar{1}$ anorthite, it is not simply due to averaging of superstructures in space groups $C\bar{1}$ and $I\bar{1}$.

In $I\bar{1}$, $A(z\Delta)$ is more heavily occupied than the corresponding split position $A(zO)$ except for the heated Grass Valley crystal with a reverse pattern. Heating at 1 200 °C did not affect the Al, Si distribution, but destroyed the memory for the A site preference. Upon cooling, sites were "assigned" differently than in the original structure. In volcanic and heat-treated crystals, the two split positions are occupied more equally than in metamorphic and plutonic plagioclase (Figure 11). Differences in occupancy are naturally largest in space group $P\bar{1}$ with no averaging effects. The sum of two split positions is nearly unity, but the total occupancy of the Ca(O) sites is consistently smaller than that of the Ca(z) sites (Table VII) suggesting that Na may be concentrated on the former. However, occupancies are not uncorrelated with thermal parameters and some of the differences may be an artifact of refinement.

Splitting of the A position is likely to present a statistical distribution over two (or in anorthite, four) energetically different sites with only short range order which cannot be resolved in space group $P\bar{1}$. The site energies are determined by the geometry of the framework and thus by the Al, Si distribution. The A cations can vibrate freely between the two split positions at temperatures above 240 °C — thus minimizing the intensity of 'c' reflections (e.g., Laves *et al.*, 1970 ; Czank, 1973 ; Adlhart *et al.*, 1980) — but return to their initial position upon cooling after heating below 800 °C, which is indicated by the identical morphology of c antiphase boundaries (Müller and Wenk, 1973 ; Heuer *et al.*, 1976). This memory is lost at higher temperatures, such as in the Grass Valley anorthite heated at 1 200 °C, where the distribution over the split

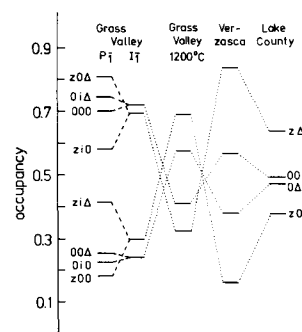


FIG. 11. — Site occupancies of the split A atoms.

Occupation des sites des atomes A dédoublés.

sites has switched.

The space around the A atoms, measured as average $\langle A-O \rangle$ distances, systematically decreases with increasing An-content. The framework expands at the same time, as is illustrated by the increasing cell volume and average $\langle T-O \rangle$ distances. A atoms are therefore less constrained in albite than in anorthite.

c) Structural units

An interesting result of this study is the establishment of "albite-like" and "anorthite-like" structural units in chemically intermediate plagioclases with body-centered structure (Figure 1). The "albite-like" unit has the composition $AlSi_3$ which is common to the whole plagioclase solid solution series. The "anorthite-like" unit has the composition Al_3Si in pure anorthite changing continuously to $AlSi_3$ as the An-content decreases. It is presumably always ordered on a local scale, such that Al_3Si units would be arranged in a framework of $AlSi_3$ units. On the average, both units alternate regularly in body-centered plagioclase and are only now and then interrupted by an antiphase offset. Similar units were found in structure determinations of intermediate plagioclases with a periodic superstructure expressed by satellites in the diffraction pattern (Korekawa *et al.*, 1979 ; Horst *et al.*, 1981). In this latter case, the regular stacking is interrupted by periodic APB's. As has been shown by Wenk and Nakajima (1980), such a model for intermediate plagioclase is compatible with microstructural observations which docu-

ment frequent pairwise recombinations of APB's to relieve local strain concentrations.

It ought to be pointed out that the division into the two units is not only apparent in tetrahedral T-O bond lengths, but also in the distortion pattern of the whole unit as expressed in T-O-T bond angles (Table XI). However, here the division is considerably less regular. The largest distortions in the structure occur at those oxygen atoms [OB(mO), OB(mz), OD(mO), OD(mz)] where the two units meet. These oxygen atoms also show the largest angular differences in the $\bar{1}\bar{1}$ - $P\bar{1}$ related frameworks and are not bonded to A atoms.

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