Is each analcime different?

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Abstract

Preceding studies assigned a cubic symmetry (*Ia3d*) to analcime, even if possible lower symmetries are suggested from contradictory evidence: *e.g.*, the occurrence of optical anomalies and the presence of forbidden reflections in X-ray photographs.

In an attempt to check the true symmetry of analcime, the crystal structures of seven optically anisotropic and apparently untwinned crystals from various localities were refined (final R from 0.02 to 0.07 for the observed reflections). They were tetragonal ($I4_1/acd$, with cell edges: $a > c$ in four samples and $a < c$ in one sample) and orthorhombic (*Ibca*). These different symmetries follow from the different ordering of Al in each of three tetrahedra and from the related different occupancy of the nearest Na site. Neither tetrahedra occupied only by Al (maximum Al fraction 0.5), nor complete occupancies of Na sites (maximum 0.84) were observed.

Simple relationships were obtained between Al fractions in tetrahedra and (1) occupancies of the nearest Na sites, (2) lattice parameters, and (3) intensities of triplets of X-ray reflections.

A hypothesis is given regarding the possible derivation of all the crystal structures of analcime from the superposition of three different orientations of one basic tetragonal structure, with an Al fraction of 0.5 in two equivalent tetrahedra and no Al in the third.

Introduction

The crystal structure of analcime, $NaAlSi_2O_6 \cdot H_2O$, was determined by Taylor (1930) and refined many times (Calleri and Ferraris, 1964; Knowles *et al.*, 1965; Ferraris *et al.*, 1972), but always with reference to the cubic space group *Ia3d*, although it has been known for a long time that many analcimes exhibit some deviation from cubic symmetry (Coombs, 1955; Harada and Sudo, 1976; and quoted references).

Before our work little was known about the real symmetry of non-cubic analcime. Mazzi *et al.* (1976) showed the symmetry of non-cubic leucite to be tetragonal $I4_1/a$ and considered it a possible symmetry also for non-cubic analcime. Harada and Sudo (1976) suggested a monoclinic symmetry as probable for analcime, because the extrapolation of β values in the wairakite–analcime series gives $\beta = 90°12'$ for pure analcime. We therefore considered non-cubic anal-cimes worthy of a detailed X-ray single-crystal investigation.

Experimental

Thick sections without coverglass were prepared from nearly thirty analcime samples, and we selected with the polarizing microscope those samples which were definitely anisotropic at least in some parts. These non-cubic crystals were always poly-synthetically twinned, and hence we were forced to select portions of twins with single individuals large enough for single-crystal diffractometry and with sharp composition planes.

As shown by Mazzi *et al.* (1976) for the related mineral leucite, both merohedric and pseudo-me-rohedric twins are possible, and only the latter can be recognized and avoided during the data collection.

The following seven samples were selected for the

complete collection of intensity data, as typical representatives of about thirty specimens submitted to a preliminary X-ray single-crystal examination (the number of the specimen in the "Museo di Mineralogia dell'Università di Modena" is in parentheses):

ANA 1: Veselí near Ústí nad Labem (also known in German as "Wesseln bei Aussig"), Bohemia, Czechoslovakia (16-2-21, 47). Crust of vitreous transparent crystals, up to 5 mm, intergrown and twinned, filling the veins and covering a free surface of an albitized basaltic rock (Rammelsberg, 1858).

ANA 2: Val di Fassa, Trento, Italy (16-2-21, 21). Crust of milky white and pale pink crystals, up to 1 cm across, densely intergrown with calcite on a weathered alkali–basaltic rock (Braccio, 1951).

ANA 3, ANA 4, ANA 5 and ANA 7: Alta Val Duron, Val di Fassa, Trento, Italy (all from specimen 16-2-21, 100). Vitreous colorless transparent crystals, featuring irregular prisms up to 7 mm long, in radial fibrous aggregates filling the cavities of a Middle Triassic weathered basaltic andesite (Monese and Sacerdoti, 1970; Vezzalini and Alberti, 1975).

ANA 6: Isola dei Ciclopi, Catania, Sicily, Italy (16-2-21, 46). Vitreous transparent euhedral trapezohedron, 2 cm across, in a basaltic rock (Di Franco, 1926; Knowles *et al.*, 1965; Ferraris *et al.*, 1972).

The crystals for X-ray measurements were ground into spheres, whose dimensions are given in Table 1 together with other experimental conditions.

Unit-cell dimensions and diffraction intensities were measured at room temperature with a Philips 1100 automatic single-crystal diffractometer and graphite-monochromatized radiation. The lattice parameters given in Table 2 were obtained by least-squares refinement of the adjusted angular settings of 18 reflections.

Diffraction intensities were measured in the ω-scan mode, and background measurements were made at both sides of each reflection. Three standard reflections, monitored at three-hour intervals, did not show significant changes in their intensities during the data collection. Intensities were corrected for Lorentz-polarization effects and for absorption, then converted to $|F_{obs}|$ and $\sigma(F_{obs})$ according to Davies and Gatehouse (1973). The reflections with $|F_{obs}|^2$ less than $3\sigma(F_{obs}^2)$ were considered as "not observed".

The symmetry of the intensities and systematic extinctions led to space group $I4_1/acd$ for samples ANA 1, ANA 2, ANA 3, ANA 5 and ANA 6, and to space group $Ibca$ for ANA 4 and ANA 7. These space groups are compatible with the presence of diffractions ($hlh: 2h + l = 4n + 2$) observed in the powder patterns and also detected in some single-crystal photographs. These reflections violate $Ia3d$ symmetry and were considered for a long time to be evidence of deviation from cubic symmetry. Actually the majority of these reflections were "unobserved" in all examined crystals; when present they were in agreement with the corresponding space group (*e.g.* 020. 0100, 424 were present both in the tetragonal and orthorhombic crystals, whereas 002, 0010, 442 were absent in tetragonal crystals, but present in the orthorhombic ones) with no evidence of broadening or splitting.

Following the X-ray data collection, electron microprobe analyses were made on the same crystals with an ARL-SEMQ instrument operated in the wavelength dispersive mode at 15 kV, 0.1 μA beam current (10 nA sample current) and using a defocused beam (spot size ~50 μm), yielding the atomic proportions reported in Table 2. On-line data processing based upon ZAF corrections (Ziebold and Ogilvie, 1964) used Albee and Ray (1970) correction factors. Synthetic plagioclase glass, natural albite, and microcline were used as standards for Si, Al, Ca, Na, and K. Fe, Mg, Sr, and Ba were also analyzed for but found to be absent. The values given in Table 2 are the averaged analyses of three points for each specimen, which were homogeneous throughout. Water loss was not determined because of the paucity of the available material.

Refinements

The atomic parameters given by Ferraris *et al.* (1972), properly adapted to the $I4_1/acd$ and $Ibca$ space groups, were used as starting coordinates of the refinements carried out with a modified version of the least-squares program ORFLS (Busing *et al.*, 1962). The scattering-factor curves were calculated from the values given in *International Tables for X-Ray Crystallography* (1974, p. 99–101) for neutral atoms. A secondary extinction correction (Zachariasen, 1963) was included in the refinements of the form:

$$F_{calc}(\text{corr}) = F_{calc}/(1 + \beta g I_{obs})$$

where F_{calc} is the calculated structure factor, $F_{calc}(\text{corr})$ the value corrected for the secondary extinction, I_{obs} the observed intensity and g the ex-

Table 1. Summary of experimental and refinement data

	ANA 1	ANA 2	ANA 3	ANA 4	ANA 5	ANA 6	ANA 7
Sphere diameter (mm)	0.084	0.114	0.174	0.236	0.192	0.198	0.236
Radiation	MoKα	CuKα	MoKα	MoKα	MoKα	CuKα	MoKα
μR (cm^{-1})	0.030	0.408	0.063	0.085	0.069	0.709	0.085
Maximum 2θ(°)	60	130	60	60	60	130	60
Scan width (°)	1.0	2.5	1.0	1.4	1.2	2.5	1.0
Scan speed (°/sec)	0.025	0.05	0.0333	0.05	0.025	0.0625	0.05
Time for each background (sec)	5	10	5	7	5	8	5
Total measurements	1100	670	1106	4491	1111	1263	2630
Total unique reflections	938	551	941	1912	942	554	1874
Observed reflections ($F^2 \geqslant 3\sigma(F^2)$)	483	434	662	1392	677	453	1352
Maximum percent variation in standard reflection intensities	2.9	2.1	3.6	3.5	3.3	1.7	2.5
Anisotropic refinement cycles	28	28	28	28	28	28	28
Extinction parameter (g x 10^8)	67(49)	635(73)	1060(31)	1874(18)	1510(23)	16031(233)	506(9)
Final R (All unique reflections)	0.151	0.064	0.061	0.041	0.052	0.042	0.048
Final R (Observed reflections)	0.067	0.043	0.037	0.024	0.030	0.033	0.029

E.s.d.'s on the last significant digit in parentheses.

tinction parameter to be refined (Table 1). Because of the use of a graphite monochromator the expression for β given by Zachariasen (1963) was modified as follows:

$$\beta = \frac{1}{A^*} \frac{dA^*}{d\mu} \frac{1}{\sin 2\theta} \frac{Q + \cos^4 2\theta}{Q + \cos^2 2\theta}$$

where A^* is the absorption factor, μ the linear absorption coefficient (for analcime: $\mu(\text{Mo}) = 7.19 \text{ cm}^{-1}$ and $\mu(\text{Cu}) = 71.58 \text{ cm}^{-1}$), Q is the cosine of the diffraction angle in the graphite monochromator (0.95563 for Mo and 0.80028 for Cu) and θ is the Bragg angle.

Nine least-squares cycles for diffractions with $F^2 > 12\sigma(F^2)$ were run in groups of three. The first cycle refined the scale factor, the atomic coordinates and the occupancies of Na and H$_2$O-oxygen; the second one refined the extinction parameter and the third again refined the atomic parameters and the anisotropic temperature factors. At this stage the Al/Si ratios for single tetrahedral sites were calculated according to Jones (1968) from the T–O bond distances, to introduce more suitable scattering factor curves in the subsequent least-squares cycles.

Nine more cycles were calculated in the same way for the diffractions with $F^2 > 4\sigma(F^2)$; at this stage the refinements of the population parameters for water showed full occupancy in all samples and this parameter was fixed in subsequent cycles. The new Al/Si ratios, calculated according to Jones (1968) from the updated average T–O distance in each tetrahedron, gave a sum of the products (Al fraction) × (multiplicity) much lower than the unit-cell content of 16 Al; hence a new line for the deduction of the Al fraction from the T–O distances was drawn through the points 1.609 (Al fraction = 0 in quartz after Zachariasen and Plettinger, 1965) and 1.648A (Al fraction = 0.333 in cubic analcime after Ferraris et al., 1972). The use of this function allowed the deduction of Al fractions in accordance with the chemical composition.

Nine further least-squares cycles utilized all diffractions with $F^2 > 3\sigma(F^2)$ and were run in the same sequence as before. Refinements were thus completed with the final shifts in the parameters less than the standard deviations. A last cycle (with positional and temperature parameters as variables) was run to calculate standard deviations for distances, bond angles, and thermal ellipsoid parameters.

Difference electron density maps were carefully inspected to search for hydrogen atoms of the water molecule, but without reliable results in most cases. Only in ANA 1 and ANA 2 did the difference syntheses show a diffuse maximum at about 0.12 0.21 0.15 (multiplicity 36 in space group $I4_1/acd$). It corresponds to the site H(2) 0.1098 0.1952 0.1494 (multiplicity 96 in space group $Ia3d$) given by Ferraris et al. (1972).

The observed and calculated structure factors are compared in Table 3[1]. Final atomic parameters and equivalent isotropic temperature factors are listed in Table 4. Anisotropic thermal parameters are given in Table 5[1], and thermal ellipsoids data in Table 6[1]. Bond distances and angles are listed in Table 7 (Si,Al–O framework), 9, and 10 (Na octahedra).

The results of the refinements are in good agreement with the stoichiometric formula, with the exception of samples ANA 1 and ANA 2, which show a lower Na and Al content both from the microprobe analyses and from the refinements (Tables 2 and 8).

Discussion of the structure

The crystal structure of non-cubic analcime (Fig. 1) is topologically identical to that of the cubic phase described by Taylor (1930), Calleri and Ferraris (1964), and Knowles *et al.* (1965).

None of the framework atoms shows significantly anisotropic thermal vibration. The Na atoms display marked anisotropy, with the maximum displacement in the direction of the water molecules and the minimum one towards the nearest *T* sites. The thermal vibrations of the water molecule give an elongated rotation ellipsoid with the longest axis perpendicular to the plane of the three nearest Na atoms.

[1] To receive a copy of Tables 3, 5, and 6, order Document AM-78-071 from the Business Office, Mineralogical Society of America, Suite 1000 lower level, 1909 K Street, NW, Washington, DC 20006. Please remit $1.00 in advance for the microfiche.
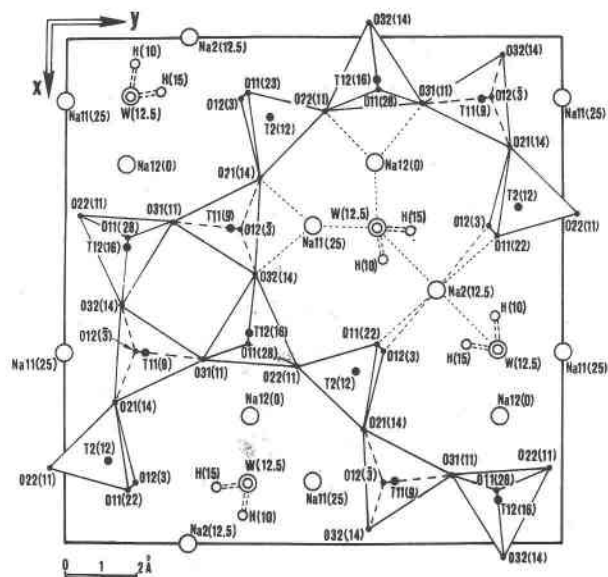

Fig. 1. The lower part (from $z \sim 0$ to $z \sim 1/4$) of the unit cell of non-cubic analcime, projected along *c*. Atoms are coded according to an orthorhombic structure; numbers in parentheses give the *z* parameters ($\times$ 100). The H positions are those assumed for the tetragonal samples ANA 1 and ANA 2, where the Na 2 site is nearly empty.

All the interatomic distances and angles agree well with the values given in the literature. The Na–O distances range from 2.469 to 2.555A, the Na–*W* distances from 2.319 to 2.478A (Table 9). When the Na-site occupancy (Table 8) approaches 100 percent (for example Na 2 in ANA 7, Na 1 in ANA 1 and ANA 2), the Na–O and Na–*W* distances tend to

Table 2. Crystal data

	ANA 1	ANA 2	ANA 3	ANA 4	ANA 5	ANA 6	ANA 7
Crystal system	Tetrag.	Tetrag.	Tetrag.	Orthorh.	Tetrag.	Tetrag.	Orthorh.
$\underline{a}$ (Å)	13.723(7)	13.727(2)	13.729(3)	13.733(1)	13.728(1)	13.721(1)	13.727(2)
$\underline{b}$ (Å)				13.729(1)			13.714(2)
$\underline{c}$ (Å)	13.686(10)	13.686(3)	13.709(4)	13.712(1)	13.722(1)	13.735(1)	13.740(2)
Volume (Å³)	2577.4	2578.9	2583.9	2585.3	2586.0	2585.8	2586.6
Space group	I4₁/acd	I4₁/acd	I4₁/acd	Ibca	I4₁/acd	I4₁/acd	Ibca
Atomic ratios*							
Si	32.74	32.85	31.94	32.31	32.06	31.65	32.34
Al	15.44	15.25	16.14	15.66	16.06	16.33	15.59
Na	14.78	14.88	15.74	15.67	15.41	15.15	15.71
K	0.02	0.02	0.05	0.06	0.06	0.05	0.08
Ca	tr	tr	0.03	0.03	0.08	0.60	0.03

*Calculated on the basis of 96 oxygens. Ba, Sr, Mg and Fe were also analyzed but found to be absent. Water loss was not determined. (Analysts: R.Rinaldi and G.Vezzalini).

E.s.d.'s on the last significant digit in parentheses.

Table 4. Final atomic coordinates and equivalent isotropic temperature factors (Å^2)

Atom	Type*	x	y	z	Beq.**
ANA 1					
T 1	32(g)	0.1264(1)	0.1617(1)	0.4118(1)	0.76
T 2	16(f)	0.1631(1)	0.4131	1/8	0.77
O 1	32(g)	0.1050(4)	0.3705(4)	0.2186(3)	2.40
O 2	32(g)	0.2218(3)	0.1028(3)	0.3633(4)	1.86
O 3	32(g)	0.3631(3)	0.2182(3)	0.1051(3)	1.84
Na 1	16(e)	0.1246(4)	0	1/4	2.80
Na 2	8(b)	0	1/4	1/8	2.84
W	16(f)	0.1195(6)	0.1305	1/8	6.03
ANA 2					
T 1	32(g)	0.1264(1)	0.1618(1)	0.4117(1)	1.05
T 2	16(f)	0.1632(1)	0.4132	1/8	0.98
O 1	32(g)	0.1055(3)	0.3712(3)	0.2191(2)	2.64
O 2	32(g)	0.2211(2)	0.1027(2)	0.3638(3)	2.18
O 3	32(g)	0.3634(3)	0.2190(2)	0.1056(2)	2.22
Na 1	16(e)	0.1242(3)	0	1/4	2.76
Na 2	8(b)	0	1/4	1/8	2.88
W	16(f)	0.1194(4)	0.1306	1/8	6.29
ANA 3					
T 1	32(g)	0.1258(1)	0.1624(1)	0.4123(1)	0.78
T 2	16(f)	0.1625(1)	0.4125	1/8	0.80
O 1	32(g)	0.1050(2)	0.3680(2)	0.2190(2)	2.14
O 2	32(g)	0.2206(2)	0.1040(2)	0.3642(2)	2.13
O 3	32(g)	0.3649(2)	0.2188(2)	0.1043(2)	2.07
Na 1	16(e)	0.1242(3)	0	1/4	3.04
Na 2	8(b)	0	1/4	1/8	2.29
W	16(f)	0.1233(4)	0.1267	1/8	6.01
ANA 5					
T 1	32(g)	0.1251(0)	0.1623(0)	0.4122(0)	0.88
T 2	16(f)	0.1624(0)	0.4124	1/8	0.83
O 1	32(g)	0.1044(2)	0.3665(2)	0.2194(1)	2.30
O 2	32(g)	0.2196(1)	0.1041(2)	0.3649(2)	2.34
O 3	32(g)	0.3654(2)	0.2194(1)	0.1043(1)	2.23
Na 1	16(e)	0.1248(2)	0	1/4	3.14
Na 2	8(b)	0	1/4	1/8	2.80
W	16(f)	0.1238(3)	0.1262	1/8	6.59

Atom	Type*	x	y	z	Beq.**
ANA 4					
T 11	16(f)	0.1256(0)	0.1624(0)	0.4122(0)	0.87
T 12	16(f)	0.4124(0)	0.1243(0)	0.1623(0)	0.87
T 2	16(f)	0.1625(0)	0.4123(0)	0.1252(0)	0.88
O 11	16(f)	0.1048(1)	0.3676(1)	0.2189(1)	2.23
O 12	16(f)	0.3824(1)	0.1452(1)	0.4686(1)	2.23
O 21	16(f)	0.2207(1)	0.1040(1)	0.3641(1)	2.18
O 22	16(f)	0.1458(1)	0.4704(1)	0.3851(1)	2.23
O 31	16(f)	0.3650(1)	0.2189(1)	0.1043(1)	2.17
O 32	16(f)	0.4691(1)	0.3853(1)	0.1459(1)	2.14
Na 11	8(c)	0.1247(2)	0	1/4	2.87
Na 12	8(d)	1/4	0.1252(2)	0	2.91
Na 2	8(e)	0	1/4	0.1250(3)	2.55
W	16(f)	0.1236(2)	0.1268(2)	0.1252(3)	6.02
ANA 6					
T 1	32(g)	0.1244(1)	0.1624(1)	0.4124(1)	0.83
T 2	16(f)	0.1623(1)	0.4123(1)	1/8	0.82
O 1	32(g)	0.1038(3)	0.3640(3)	0.2200(2)	2.32
O 2	32(g)	0.2185(2)	0.1046(3)	0.3666(3)	2.33
O 3	32(g)	0.3663(3)	0.2202(2)	0.1048(2)	2.36
Na 1	16(e)	0.1252(4)	0	1/4	2.57
Na 2	8(b)	0	1/4	1/8	2.87
W	16(f)	0.1256(4)	0.1244	1/8	6.53
ANA 7					
T 11	16(f)	0.1240(0)	0.1621(0)	0.4125(0)	0.89
T 12	16(f)	0.4124(0)	0.1254(0)	0.1626(0)	0.87
T 2	16(f)	0.1622(0)	0.4123(0)	0.1254(0)	0.87
O 11	16(f)	0.1039(1)	0.3632(2)	0.2206(1)	2.14
O 12	16(f)	0.3861(2)	0.1459(1)	0.4698(1)	2.14
O 21	16(f)	0.2181(1)	0.1046(1)	0.3658(2)	2.17
O 22	16(f)	0.1450(1)	0.4682(1)	0.3825(2)	2.20
O 31	16(f)	0.3676(2)	0.2197(1)	0.1047(1)	2.27
O 32	16(f)	0.4704(1)	0.3845(2)	0.1459(1)	2.22
Na 11	8(c)	0.1257(2)	0	1/4	2.92
Na 12	8(d)	1/4	0.1248(3)	0	2.52
Na 2	8(e)	0	1/4	0.1246(2)	2.88
W	16(f)	0.1271(3)	0.1239(3)	0.1238(3)	6.03

*Number of positions and Wyckoff notation. **Equivalent isotropic temperature factor after Hamilton (1959). Na-occupancy factors are given in Table 8. W = water molecule. E.s.d.'s on the last significant digit in parentheses.

become equal ($\sim$2.48Å). When the occupancy of the Na sites is low (for example Na 2 in ANA 1 and ANA 2) the Na–W distances (2.32Å) are smaller than the Na–O ones (2.55Å), and the water molecules are shifted towards the vacant Na positions. Of the three Na sites (Na 11, Na 12, Na 2) surrounding each water position, one must be empty to account for the stoichiometric unit; very likely the H_2O hydrogens face this latter Na site (Fig. 1). When the Na vacancies are variously distributed among the three Na sites (cubic analcime, ANA 5), the H atoms are also spread among the 96 positions corresponding to the H(2) parameters (Ferraris et al., 1972) in the cubic analcime. On the contrary, when the vacancies are concentrated only on one Na site (say Na 2 in tetragonal ANA 1 and ANA 2), all the H atoms occupy only the 32 equivalent positions which face this empty site, thus producing an appreciable maximum in the difference maps. This could be the explanation of the experimental evidence described in the preceding section.

A linear relationship (Fig. 2) exists between lattice constants and Al fraction in the T sites, so that an approximate determination of the Al occupancies is possible without any structural refinement, using the lattice dimensions only. The explanation of this simple relationship becomes clear from Figure 1: there is only one tetrahedral edge parallel to the a axis

Table 7. Interatomic distances (A) and angles (°) within the framework*

Atoms	T - O	Atoms	O - O	O - T - O	Atoms	T - O	Atoms	O - O	O - T - O	Atoms	T - O - T
ANA 1											
T1-O1'	1.656(5)	O1'-O2	2.751(7)	111.4(3)	T2-O1		O1-O1'	2.578(9)	105.7(4)	T1'-O1-T2	146.4(4)
T1-O2	1.675(5)	O1'-O3	2.658(6)	106.1(3)	T2-O1'	1.618(5)	O1-O2	2.653(7)	110.9(2)	T1-O2-T2	142.8(3)
T1-O3	1.671(5)	O1'-O3'	2.738(6)	111.7(3)	T2-O2		O1'-O2'			T1-O3-T1'	143.6(3)
T1-O3'	1.653(5)	O2-O3	2.752(7)	110.7(2)	T2-O2'	1.603(5)	O1-O2'	2.664(7)	111.6(3)		
Mean	1.664	O2-O3'	2.613(6)	103.5(2)	Mean	1.611	O1'-O2				
		O3-O3'	2.782(7)	113.7(3)			O2-O2'	2.563(8)	106.2(4)		
ANA 2											
T1-O1'	1.649(4)	O1'-O2	2.727(5)	110.7(2)	T2-O1		O1-O1'	2.594(6)	106.6(3)	T1'-O1-T2	147.4(3)
T1-O2	1.667(4)	O1'-O3	2.654(5)	106.7(2)	T2-O1'	1.617(3)	O1-O2	2.661(5)	111.0(2)	T1-O2-T2	142.9(2)
T1-O3	1.660(4)	O1'-O3'	2.733(5)	111.5(2)	T2-O2		O1'-O2'			T1-O3-T1'	144.2(2)
T1-O3'	1.657(4)	O2-O3	2.740(5)	110.9(2)	T2-O2'	1.612(4)	O1-O2'	2.663(5)	111.1(2)		
Mean	1.658	O2-O3'	2.616(5)	103.8(2)	Mean	1.615	O1'-O2				
		O3-O3'	2.771(6)	113.3(2)			O2-O2'	2.575(7)	106.0(3)		
ANA 3											
T1-O1'	1.648(3)	O1'-O2	2.744(5)	111.9(2)	T2-O1		O1-O1'	2.590(6)	105.2(2)	T1'-O1-T2	145.7(2)
T1-O2	1.665(3)	O1'-O3	2.645(4)	106.5(2)	T2-O1'	1.630(3)	O1-O2	2.680(5)	110.7(2)	T1-O2-T2	143.3(2)
T1-O3	1.656(3)	O1'-O3'	2.731(5)	111.5(2)	T2-O2		O1'-O2'			T1-O3-T1'	144.1(2)
T1-O3'	1.652(3)	O2-O3	2.735(5)	111.1(2)	T2-O2'	1.628(3)	O1-O2'	2.701(5)	112.0(2)		
Mean	1.655	O2-O3'	2.608(4)	103.5(2)	Mean	1.629	O1'-O2				
		O3-O3'	2.751(5)	112.5(2)			O2-O2'	2.608(6)	106.4(2)		
ANA 4											
T11-O12	1.657(2)	O12-O21	2.704(3)	111.9(1)	T2-O11	1.631(2)	O11-O12	2.584(3)	104.8(1)	T11-O12-T2	145.4(1)
T11-O21	1.669(2)	O12-O31	2.648(3)	106.3(1)	T2-O12	1.631(2)	O11-O21	2.683(3)	110.9(1)	T11-O21-T2	143.4(1)
T11-O31	1.652(2)	O12-O32	2.741(3)	111.4(1)	T2-O21	1.627(2)	O12-O22	2.687(3)	110.9(1)	T11-O31-T12	144.0(1)
T11-O32	1.661(2)	O21-O31	2.737(3)	111.0(1)	T2-O22	1.633(2)	O11-O22	2.741(3)	111.8(1)	T11-O32-T12	143.8(1)
Mean	1.660	O21-O32	2.616(3)	103.6(1)	Mean	1.630	O12-O21	2.757(3)	112.2(1)	T12-O11-T2	145.3(1)
		O31-O32	2.757(3)	112.7(1)			O21-O22	2.611(3)	106.4(1)	T12-O22-T2	143.8(1)
T12-O11	1.651(2)	O11-O22	2.703(3)	111.7(1)							
T12-O22	1.660(2)	O11-O31	2.732(3)	111.4(1)							
T12-O31	1.656(2)	O11-O32	2.641(3)	106.3(1)							
T12-O32	1.649(2)	O22-O31	2.608(3)	103.7(1)							
Mean	1.654	O22-O32	2.728(3)	111.1(1)							
		O31-O32	2.751(3)	112.7(1)							
ANA 5											
T1-O1'	1.645(2)	O1'-O2	2.738(3)	112.1(1)	T2-O1		O1-O1'	2.601(4)	104.4(2)	T1'-O1-T2	144.8(2)
T1-O2	1.656(2)	O1'-O3	2.632(3)	106.2(1)	T2-O1'	1.646(2)	O1-O2	2.709(3)	111.0(1)	T1-O2-T2	143.8(2)
T1-O3	1.651(2)	O1'-O3'	2.723(3)	111.4(1)	T2-O2		O1'-O2'			T1-O3-T1'	144.2(2)
T1-O3'	1.646(2)	O2-O3	2.724(3)	111.1(1)	T2-O2'	1.641(2)	O1-O2'	2.727(3)	112.2(1)		
Mean	1.650	O2-O3'	2.603(3)	103.8(1)	Mean	1.644	O1'-O2				
		O3-O3'	2.739(4)	112.4(1)			O2-O2'	2.624(4)	106.2(2)		
ANA 6											
T1-O1'	1.638(3)	O1'-O2	2.746(5)	112.4(2)	T2-O1		O1-O1'	2.616(6)	103.3(3)	T1'-O1-T2	143.3(2)
T1-O2	1.640(4)	O1'-O3	2.619(5)	106.4(2)	T2-O1'	1.668(3)	O1-O2	2.724(5)	111.4(2)	T1-O2-T2	144.9(2)
T1-O3	1.633(4)	O1'-O3'	2.702(3)	110.7(2)	T2-O2		O1'-O2'			T1-O3-T1'	144.8(3)
T1-O3'	1.647(3)	O2-O3	2.699(5)	111.1(2)	T2-O2'	1.656(4)	O1-O2'	2.761(3)	112.3(2)		
Mean	1.640	O2-O3'	2.600(5)	104.6(2)	Mean	1.662	O1'-O2				
		O3-O3'	2.715(6)	111.8(3)			O2-O2'	2.651(7)	106.4(3)		
ANA 7											
T11-O12	1.638(2)	O12-O21	2.732(3)	112.7(1)	T2-O11	1.675(2)	O11-O12	2.624(3)	103.3(1)	T11-O12-T2	143.6(1)
T11-O21	1.644(2)	O12-O31	2.626(3)	106.4(1)	T2-O12	1.670(2)	O11-O21	2.753(3)	111.1(1)	T11-O21-T2	144.6(1)
T11-O31	1.642(2)	O12-O32	2.714(3)	111.2(1)	T2-O21	1.664(2)	O12-O22	2.750(3)	111.3(1)	T11-O31-T12	145.4(2)
T11-O32	1.653(2)	O21-O31	2.712(3)	111.3(1)	T2-O22	1.659(2)	O11-O22	2.770(3)	112.3(1)	T11-O32-T12	144.0(2)
Mean	1.644	O21-O32	2.596(3)	103.9(1)	Mean	1.667	O12-O21	2.772(3)	112.5(1)	T12-O11-T2	142.9(1)
		O31-O32	2.724(3)	111.5(1)			O21-O22	2.661(3)	106.4(1)	T12-O22-T2	145.3(2)
T12-O11	1.627(2)	O11-O22	2.709(3)	112.6(1)							
T12-O22	1.630(2)	O11-O31	2.684(3)	110.6(1)							
T12-O31	1.637(2)	O11-O32	2.608(3)	106.4(1)							
T12-O32	1.631(2)	O22-O31	2.588(3)	104.8(1)							
Mean	1.631	O22-O32	2.687(3)	111.0(1)							
		O31-O32	2.703(3)	111.6(1)							

* Interatomic distances and angles symmetrically equivalent are bracketed.

Atomic positions relationships in orthorhombic and in tetragonal are as follows: (T11,O11,O21,O31,Na11) orthorh. correspond to (T1,O1,O2,O3,Na1) tetrag. and (T12,O12,O22,O32,Na12) orthorh. correspond to (T1',O1',O2',O3',Na1') tetrag.

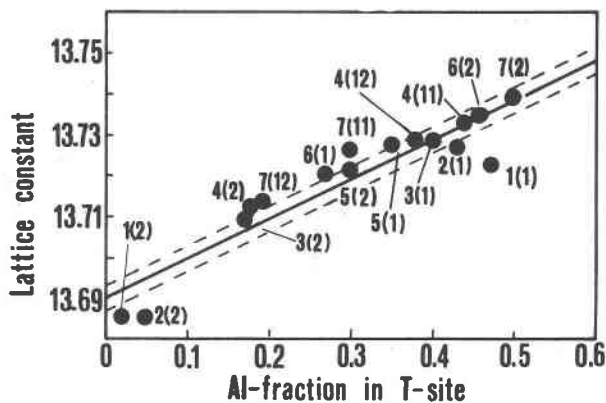E.s.d.'s on the last significant digit in parentheses.

Fig. 2. Linear relationship between Al fractions in tetrahedra and corresponding unit-cell edges; a is plotted versus Al in $T\,11$ (or $T\,1$ in tetragonal analcimes), b versus Al in $T\,12$ and c versus Al in $T\,2$. The numbers outside parentheses identify the samples, the numbers in parentheses are those of the T sites. The straight line allows a simple but reliable deduction of the Al fractions from the lattice parameters. The dashed lines are at one standard deviation.

and it pertains to $T\,11$ ($T\,1$ in tetragonal analcime); similarly one edge of $T\,12$ ($T\,1'$) is parallel to the b axis, and one edge of $T\,2$ is parallel to the c axis. Thus the Al occupancies of each of these may be determined from the corresponding length of a, b, and c.

Relationship between the fraction of Al in the T sites and the occupancy of the nearest Na sites

A simple relationship between the occupancies of the Na sites and the fraction of Al in the tetrahedra can be derived by applying a least-squares method to minimize the lack of balance of electrostatic charge on the oxygens of the framework.

Let r, s, and t be the Al fractions in $T\,11$, $T\,12$, and $T\,2$ respectively and let m, n, and p be the Na occupancies in Na 11, Na 12, and Na 2. The bond strength (S) which reaches one oxygen from $T\,11$ is $[4(1 - r) + 3r]/4 = 1 - (r/4)$, and similarly from $T\,12$ it is $1 - (s/4)$, and from $T\,2$ it is $1 - (t/4)$. The bond strength which reaches an oxygen from sodium is respectively $m/6$, or $n/6$, or $p/6$. The double negative charge of each oxygen is balanced by the bond strengths of the two nearest T sites and by one Na site. The degree of lack of balance is given by: $U = S(T) + S(T) + S(\text{Na}) - 2$. The actual imbalance for each oxygen is:

$$U(\text{O}\,11) = 2p - 3(s + t)/12$$

$$U(\text{O}\,12) = 2p - 3(r + t)/12$$

$$U(\text{O}\,21) = 2m - 3(r + t)/12$$

$$U(\text{O}\,22) = 2n - 3(s + t)/12$$

$$U(\text{O}\,31) = 2n - 3(r + s)/12$$

$$U(\text{O}\,32) = 2m - 3(r + s)/12$$

In applying the least-squares method, the function to be differentiated is:

$$f = \left[\sum_1^6 U^2(\text{O}) \right] + K[m + n + p - 2(r + s + t)]$$

where K is a constant to be determined and which derives from the procedure for the calculation of conditioned maxima and minima, and $m + n + p - 2(r + s + t) = 0$ is the condition that the sum of all Na's must equal the sum of all Al's (the coefficient 2 is the ratio between the multiplicity of the T sites and that of Na sites). By assuming m, n, and p to be independent variables, the system of the following four equations is obtained:

$$\delta f/\delta m = (4m - 6r - 3s - 3t)/36 + K = 0$$

$$\delta f/\delta n = (4n - 3r - 6s - 3t)/36 + K = 0$$

$$\delta f/\delta p = (4p - 3r - 3s - 6t)/36 + K = 0$$

$$m + n + p - 2(r + s + t) = 0$$

The solution of the system gives three similar equations:

$$m = (14r + 5s + 5t)/12$$

$$n = (5r + 14s + 5t)/12$$

$$p = (5r + 5s + 14t)/12$$

As the total Al: $(r + s + t) = 1$ for stoichiometric

Table 8. Al fraction in T sites and occupancy in Na sites

	ANA 1	ANA 2	ANA 3	ANA 4	ANA 5	ANA 6	ANA 7
Al-fraction	(× 100)						
T 1 (T 11)	47	42	40	44	35	27	30
T 12				38			19
T 2	2	5	17	18	30	45	50
Al total	96	89	97	100	100	99	99
Na occupancy	(× 100) §						
Na 1 (Na 11)	82	84	79	77	73	61	69
	85	*78*	*75*	*81*	*69*	*58*	*62*
Na 12				74			52
				73			*48*
Na 2	23	17	48	52	58	77	80
	25	*29*	*45*	*46*	*62*	*82*	*89*
Na total †	93	92	103	101	102	100	101
	97	*92*	*97*	*100*	*100*	*99*	*100*

§ Values obtained from the last refinement cycle; for all values the standard deviation is 1 on the last significant digit. The occupancies calculated from the equation: $m = 1.32r + 0.225$ (see text) are written in italics below each corresponding Na-occupancy.
† Na total values are half the sum of the occupancies of three sites because of the multiplicity of Na-positions (in tetragonal analcimes take the first value twice).

analcimes, the three equations are simplified as follows:

$$m = 0.75r + 5/12; \qquad n = 0.75s + 5/12;$$

$$p = 0.75t + 5/12$$

According to the above equations, the Na occupancy of an octahedron would depend only on the Al fraction in the tetrahedron which shares one edge with the Na octahedron. The plot of Na occupancy versus Al fraction of Figure 3 contains all points corresponding to the observed values and the calculated line: Na occupancy = 0.75(Al fraction) + 5/12 (line A). The agreement is fairly good, except for points with low Al fractions. Most likely this disagreement follows from actual more complex relationships than the simple ones assumed in the preceding derivation. For instance a possible weak hydrogen bond between water and oxygens of the

Table 9. Bond distances (A) in the Na-coordination polyhedra*

Sample	Bond	Distance	Bond	Distance
ANA 1	Na 1 – O 2	2.485(6)	Na 2 – O 1	
	Na 1 – O 3'	2.469(6)	Na 2 – O 1'	2.539(5)
	Na 1 – W	2.478(6)	Na 2 – W	2.319(11)
ANA 2	Na 1 – O 2	2.487(4)	Na 2 – O 1	
	Na 1 – O 3'	2.479(4)	Na 2 – O 1'	2.555(4)
	Na 1 – W	2.478(4)	Na 2 – W	2.319(8)
ANA 3	Na 1 – O 2	2.498(4)	Na 2 – O 1	
	Na 1 – O 3'	2.483(4)	Na 2 – O 1'	2.522(3)
	Na 1 – W	2.442(4)	Na 2 – W	2.395(8)
ANA 4	Na 11 – O 21	2.496(3)	Na 2 – O 11	2.518(3)
	Na 11 – O 32	2.487(3)	Na 2 – O 12	2.516(3)
	Na 11 – W	2.442(3)	Na 2 – W	2.398(3)
	Na 12 – O 22	2.502(3)		
	Na 12 – O 31	2.490(3)		
	Na 12 – W	2.443(3)		
ANA 5	Na 1 – O 2	2.494(2)	Na 2 – O 1	
	Na 1 – O 3'	2.496(2)	Na 2 – O 1'	2.508(3)
	Na 1 – W	2.438(3)	Na 2 – W	2.404(3)
ANA 6	Na 1 – O 2	2.503(5)	Na 2 – O 1	
	Na 1 – O 3'	2.516(5)	Na 2 – O 1'	2.485(4)
	Na 1 – W	2.421(4)	Na 2 – W	2.437(9)
ANA 7	Na 11 – O 21	2.490(3)	Na 2 – O 11	2.487(3)
	Na 11 – O 32	2.508(3)	Na 2 – O 12	2.483(3)
	Na 11 – W	2.427(4)	Na 2 – W	2.457(4)
	Na 12 – O 22	2.511(3)		
	Na 12 – O 31	2.524(3)		
	Na 12 – W	2.396(4)		

* Bond distances symmetrically equivalent are bracketed.
All the above distances repeated twice for symmetry.
For the meaning of the primed atoms see second footnote in Table 7.
E.s.d.'s on the last significant digit in parentheses.

Fig. 3. Plot of Na occupancy against the Al fraction in the nearest T site: Na 11 (or Na 1 in tetragonal analcimes) versus Al in T 11 (or T 1), Na 12 versus Al in T 12 and Na 2 versus Al in T 2. The A line, Na occupancy = 0.75(Al fraction) + 5/12, was calculated from the charge balance on oxygens without considering the H₂O hydrogens. The line of best fit (line B), Na occupancy = 1.32(Al fraction) + 0.23, corresponds to that calculated considering also the H₂O hydrogens; the dashed lines are at one standard deviation. Numbers outside parentheses correspond to samples, numbers in parentheses identify T and/or Na sites.

tetrahedral framework could be considered. Actually the W–O distances, which range from 3.336 to 3.574A (Table 10), are larger than the conventional ones for a hydrogen bond. Furthermore, they occur between two vertices of the same Na octahedron. However, the shortest distances (W–O 1 = 3.34A in ANA 1 and ANA 2) take place between vertices of an octahedron around Na 2, in which the cationic site is practically empty. One might infer that in the general case some hydrogen bonds would occur with oxygens O 11 (O 1) and O 12 (O 1') when the Na 2 position is vacant (Fig. 1) and, in the same way, with O 22 (O 2') and O 31 (O 3) or O 21 (O 2) and O 32 (O 3') when the Na 11 (Na 1) or Na 12 (Na 1') positions are empty.

Calling w the possible weak H-bond strength, which would reach one oxygen of the tetrahedral framework, the charge balance equations written above would be increased by a term, namely ½$(m + n - p)w$ for O 11 and O 12, ½$(m - n + p)w$ for O 22 and O 31, and finally ½$(-m + n + p)w$ for O 21 and O 32.

By the procedure followed in the preceding calcu-

Table 10. Distances (A) of water from framework oxygens*

	ANA 1	ANA 2	ANA 3	ANA 4	ANA 5	ANA 6	ANA 7
W – O 1 (O 11) } W – O 1' (O 12) }	3.336(9)	3.346(7)	3.390(6)	3.392(4) 3.387(4)	3.392(5)	3.411(7)	3.443(5) 3.414(5)
W – O 1 (O 11) } W – O 1' (O 12) }	3.539(9)	3.551(7)	3.564(7)	3.558(5) 3.564(5)	3.555(5)	3.549(7)	3.556(5) 3.563(5)
W – O 2 (O 21) } W – O 2' (O 22) }	3.500(11)	3.497(8)	3.440(8)	3.442(4) 3.441(4)	3.426(6)	3.393(9)	3.376(5) 3.374(5)
W – O 2 (O 21) } W – O 2' (O 22) }	3.570(7)	3.574(5)	3.554(5)	3.552(5) 3.566(5)	3.558(4)	3.565(5)	3.562(5) 3.556(5)
W – O 3 (O 31) } W – O 3' (O 32) }	3.379(5)	3.390(4)	3.393(4)	3.396(4) 3.394(4)	3.400(3)	3.421(5)	3.405(5) 3.437(5)
W – O 3 (O 31) } W – O 3' (O 32) }	3.563(7)	3.572(5)	3.561(5)	3.562(5) 3.564(5)	3.566(4)	3.566(5)	3.563(5) 3.558(5)

* Interatomic distances symmetrically equivalent are bracketed.
For the meaning of the primed atoms see second footnote in Table 7.
E.s.d.'s on the last significant digit in parentheses.

lation, the occupancy (say m) of a sodium site is:

$$m = \frac{9(1 - 6w)r + 6w(48w - 13) + 5}{144w(3w - 1) + 12} ,$$

when $r + s + t = 1$. This equation is obviously transformed into the preceding one, $m = (9r + 5)/12 = 0.75r + 5/12$, if $w = 0$. With $w = 0.072$, *i.e.* a weak interaction between oxygens and H_2O hydrogens, one obtains $m = 1.32r + 0.23$. This equation is the same as that of the regression line (Fig. 3, line B) drawn through the whole set of the experimental data (linear correlation coefficient: 0.96).

Order–disorder in (Al,Si) tetrahedra

As explained above, there is a definite relationship between the Na occupancy in one site and the Al fraction in the nearby tetrahedron. Because the upper limit of Na occupancy is obviously 100 percent, according to line B (Fig. 3) the Al fraction in any site should not be larger than 60 percent. As a matter of fact, no Al fraction larger than 50 percent has been found in this work.

The possible schemes of (Si,Al) ordering in analcime can be summarized as follows. In cubic analcime all 48 tetrahedra are symmetrically equivalent, and hence the 16 Al atoms must occupy at random one third of them. In the tetragonal space group $I4_1/acd$ the 48 tetrahedra are split into two groups: the T 1 sites (multiplicity 32) and T 2 sites (multiplicity 16). Two ordering schemes are possible: (1) the 16 Al

atoms occupy 50 percent of the 32 T 1 sites and no T 2 sites. Consequently the cubic cell is flattened with $a > c$; ANA 1, ANA 2 and, to a lesser extent, ANA 3 are good examples of this type. (2) The 16 Al atoms occupy no T 1 sites and 100 percent of the 16 T 2 sites. This second model was described for analcime by Meier (1973), but it actually conflicts with the upper limit for the Al fraction (60 percent) emphasized at the beginning of this section. Therefore the maximum allowed Al contents for this model would be 6.4 Al atoms in 20 percent of the T 1 sites, and 9.6 Al in 60 percent of T 2 sites, and, as a consequence, the cubic cell is elongated with $a < c$. ANA 6 has an Al distribution of this kind.

On the whole, the two ordering schemes in the tetragonal system are simple and clear; things are a little more complicated in the orthorhombic system, space group *Ibca*. First of all, the orientation is not obvious, because an interchange of the axes does not affect the style of the extinctions. Therefore we choose a "pseudotetragonal" orientation, a and b most similar, namely $|c - a| \geq |a - b| \leq |c - b|$; we also choose $a \geq b$.

What happens in the orthorhombic system is related to the two ordering schemes possible in the tetragonal system, namely in one case the unit cell is flattened with $(a + b)/2 > c$, and in the other one it is elongated with $(a + b)/2 < c$.

First case, $(a + b)/2 > c$: the tetragonal T 1 site is split into two sites, T 11 and T 12, each with multi-

plicity 16. The Al fraction, which is 50 percent in $T 1$ (ANA 1, ANA 2), is slightly different in $T 11$ and $T 12$ (44 percent and 38 percent), the remaining small fraction of Al being placed in $T 2$ (example ANA 4).

Second case, $(a + b)/2 < c$: the $T 1$ site is again split into two sites $T 11$ and $T 12$. The Al fraction which is 25 percent in $T 1$ (ANA 6), is not equal in the two new sites (30 percent and 19 percent), the remaining large fraction of Al (50 percent) being placed in $T 2$ (example ANA 7).

The difference between the two orthorhombic cases follows from the "pseudotetragonal" orientation of the crystallographic axes: the latter case vanishes if one retains only the conventional choice of the axes in the orthorhombic system $b > a > c$.

Interpretation of the different types of analcime as derived from a single basic tetragonal structure

The various crystal structures of analcime studied here can be considered as built upon one basic tetragonal structure 0.5/0.5/0, i.e., 0.5 is the Al fraction in $T 11$ and $T 12$ ($T 1$ and $T 1'$ in tetragonal analcime) and no Al is in $T 2$; this structure is very near to those of ANA 1 and ANA 2. The different analcimes would derive from the superposition of three portions (say d, e, and f, with $d + e + f = 1$) of the basic structure, such portions being rotated by 120° around a diagonal of the unit cell (3-fold axis of cubic analcime).

This interpretation makes it possible to devise a simple way of identifying the nature of a specimen of analcime through intensity measurements of only three reflections. If r, s, and t are the Al fractions in $T 11$, $T 12$, and $T 2$ respectively, the volume propor-

tions d, e, and f are easily obtained from $d = r + s - t$, $e = r - s + t$, and $f = -r + s + t$. The atomic parameters of the basic structure (Table 11) were calculated by linear extrapolation of the atomic parameters versus Al fraction in $T 2$ for the determined tetragonal structures (ANA 1, 2, 3, 5 and 6); obviously enough, they are very similar to those of ANA 1 and ANA 2. A recalculation of the atomic parameters for the various analcimes, starting from those of the basic structure and using the appropriate values for d, e, and f, gave results in agreement with those obtained from the structural determinations (standard deviations 0.0002 for T and Na sites, 0.0005 for O sites and 0.0009 for W sites). The occupancy of Na in Na 11 and Na 12 was fixed at 0.88 and that of Na 2 at 0.24 (Fig. 3, line B). The thermal factors for the atoms of the basic structure were an average of those in ANA 1 and ANA 2.

Any structure factor $Fc'(hkl)$ of an analcime defined by a triplet d, e, and f can be calculated from the structure factors $Fc(hkl)$, $Fc(lhk)$ and $Fc(klh)$ of the basic structure by means of the relations:

$$\begin{cases} Fc'(hkl) = d\ Fc(hkl) + e\ Fc(lhk) + f\ Fc(klh) \\ Fc'(lhk) = d\ Fc(lhk) + e\ Fc(klh) + f\ Fc(hkl) \\ Fc'(klh) = d\ Fc(klh) + e\ Fc(hkl) + f\ Fc(lhk) \end{cases}$$

On the other hand, if the Fc' values are replaced by the observed ones (Fo') for the actual structure of an analcime, the solution of the above system of three equations allows one to calculate d, e, and f from only one triplet of reflections, and hence the Al fractions r,

Table 11. Atomic coordinates and anisotropic temperature factors ($\times 10^4$) assigned to the basic structure

Atom	Type*	Occupancy	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T 11	32(g)	0.5 Al + 0.5 Si	0.1266	0.1619	0.4118	10	10	11	0	0	1
T 2	16(f)	0.0 Al + 1.0 Si	0.1632	0.4132	1/8	11	11	9	0	2	-2
O 1	32(g)	1.00	0.1052	0.3710	0.2187	37	42	17	-1	10	4
O 2	32(g)	1.00	0.2217	0.1026	0.3630	10	29	35	7	2	0
O 3	32(g)	1.00	0.3631	0.2183	0.1052	30	17	27	-6	-4	4
Na 11	16(e)	0.88	0.1242	0	1/4	36	38	38	0	0	-22
Na 2	8(b)	0.24	0	1/4	1/8	35	35	45	-30	0	0
W	16(f)	1.00	0.1194	0.1306	1/8	80	80	80	18	37	37

* Number of positions and Wyckoff notation.
The anisotropic temperature factor has the form:

$$\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$$

Table 12. Comparison between the observed and calculated quantities relevant to the interpretation of analcimes as domains of the basic structure with three different orientations

	BS[1]	ANA 1	ANA 2[2]	ANA 3	ANA 4	ANA 5	ANA 6	ANA 7
|Fo' (660)|[3]	107.3	107.6	106.5	129.9	131.2	141.5	157.5	163.9
|Fo' (606)|[3]	166.6	166.4	167.0	155.3	152.3	149.5	141.5	131.2
|Fo' (066)|[3]	=	=	=	=	156.9	=	=	145.3
d	100	92	79	63	64	40	9	0
		99	*101*	*62*	*60*	*42*	*15*	*4*
e	0	2	5	17	24	30	45	61
		<1	*<0*	*20*	*24*	*29*	*42*	*60*
f	=	=	=	=	12	=	=	39
					16			*36*
r	50	47	42	40	44	35	27	30
		50	*50*	*40*	*42*	*36*	*29*	*32*
s	=	=	=	=	38	=	=	19
					38			*20*
t	0	2	5	17	18	30	45	50
		0	*0*	*20*	*20*	*29*	*42*	*48*
|Fc' (2 0 0)|[4]	71	70 (71)	71 (71)	30 (64)	25 (65)	9 (60)	18 (54)	40 (57)
|Fo' (2 0 0)|		60	62	22	20	9	15	27
|Fc' (10 0 0)|[4]	48	47 (48)	48 (48)	20 (43)	17 (44)	6 (40)	12 (36)	27 (38)
|Fo' (10 0 0)|		41	40	25	19	7	15	27

[1] BS : "basic structure"; Fo'(660), Fo'(606) and Fo'(066) are in this case Fc values.
[2] Total aluminum is significantly less than 1.
[3] Fo' values normalized according to: Fo'(660)+Fo'(606)+Fo'(066) = Fc(660)+Fc(606)+Fc(066) = 440.5.
[4] Fc' (2 0 0) and Fc' (10 0 0) calculated by using d, e and f obtained from reflections 660, 606 and 066; calculated values for a twin of the "basic structure" in parentheses.
= Values equal to those of the preceding line because of the tetragonal symmetry.

d, e and f are the fractions (× 100) of the "basic structure"; r, s and t are the Al-fractions (× 100) in T 11, T 12 and T 2: values obtained from the crystal structure analyses are in roman, those obtained from reflections 660, 606 and 066 are in italics.
For the meaning of Fo' and Fc' see text.

s, and t. The following relations:

$$Fc'(hkl) + Fc'(lhk) + Fc'(klh) = Fc(hkl)$$
$$+ Fc(lhk) + Fc(klh) = K[Fo'(hkl) + Fo'(lhk) + Fo'(klh)]$$

obtained by summing the terms of the above system of equations can be used to put the Fo' values on an absolute scale through the determination of K.

The above system is much simplified if reflections such as hhl, lhh, and hlh are used. Because for the basic tetragonal structure $Fc(lhh) = Fc(hlh)$, and $d + e + f = 1$, each Fc' (KFo') value becomes dependent on only one variable d, or e, or f:

$$d = [KFo'(hhl) - Fc(lhh)]/[Fc(hhl) - Fc(lhh)]$$
$$e = [KFo'(hlh) - Fc(lhh)]/[Fc(hhl) - Fc(lhh)]$$
$$f = [KFo'(lhh) - Fc(lhh)]/[Fc(hhl) - Fc(lhh)]$$

Following several tests on various triplets of reflec-

tions, the observed structure factors of reflections 660, 606, and 066 resulted in the most suitable ones to give a good agreement between the fractions d, e, and f obtained from the structural studies and those from the application of the above equations (for their Fc values, see first column of Table 12). The errors are considerably reduced by using the above triplet of reflections rather than others, because in the basic structure only the atoms of one Na site and of one related T site give their maximum contributions to each of these three reflections: i.e., Na 2 and T 2 affect only 660, Na 11 and T 11 contribute uniquely to 066, whereas Na 12 and T 12 influence only 606. Table 12 shows the results of the calculations for the seven analcimes.

Perhaps the interpretation of the crystal structures of analcimes founded on the basic tetragonal structure 0.5/0.5/0 is more than formal: two out of seven of our specimens, from different localities (ANA 1

and ANA 2), have a crystal structure very near to the basic structure and actually, at least in the examined specimens, no Al fraction in each tetrahedron is larger than 0.5; such an amount is indeed the maximum allowable for the distribution of one Al atom in two equivalent sites (T 11 and T 12) in a tetragonal structure. Should this upper limit 0.5 be confirmed by successive studies, then the crystal structures of analcimes could be really built up by small domains of the basic tetragonal structure in three or fewer different orientations.

Of course only the above indirect evidence can support this interpretation, because when the domains are small enough no difference between a "structure with domains" and a "true single-crystal structure" can be seen by X-ray diffraction. A gradual increase of the dimensions of such domains would transform a "single crystal with domains" into a twin; in the extreme situation, the Fc and Fc' values in the preceding system of equations should be replaced by Fc^2 and Fc'^2. A calculation of the structure factors for the various analcimes, made on the hypothesis of the presence of twins of the basic structure, gave for nearly all reflections results very similar to those obtained for single crystals. Only the weak reflections 200, 020, 002, and 10 00, 0 10 0, 00 10 are sensitive in distinguishing the two possibilities. For instance in a set of tetragonal single crystals, $|Fc'(200)|$ decreases from 71 to 0 going from the basic structure (d:e:f = 1:0:0) to the cubic one (d:e:f = 1:1:1), then it increases again to 35 for a structure with d:e:f = 0:1:1. In the case of twinning that value decreases regularly from 71 to 50 along the entire set of such tetragonal structures. No indication of this kind of twinning was, however, detected in the structures here studied, as the observed structure factors for 200 and 10 00 were never larger than those calculated for a single crystal (Table 12) and no peak broadening or splitting was experimentally evidenced. Similarly, no twinning was determined optically in any of the crystal fragments selected for the present study.

Conclusions

Both analcime and the related mineral leucite show pseudo-merohedric twinning, detectable by optical methods and by the splitting of the X-ray reflections, with twin individuals often large enough to be examined separately by X-ray single-crystal methods. In leucite these apparent single individuals still show merohedric twinning, with domains large enough to be revealed during the resolution of the crystal struc-

ture. In analcime the individuals of the pseudo-merohedric twinning behave as a real single crystal. In high- and low-temperature leucite the Si–Al substitution is always disordered, whereas in analcime different degrees of ordering allow the existence of four main kind of symmetries: cubic ($Ia3d$), tetragonal ($I4_1/acd$) with $a > c$, tetragonal with $a < c$, and orthorhombic ($Ibca$), with all the possible intermediate varieties. This fact justifies the title of the paper, which is a paraphrase of a famous statement about feldspars by Fritz Laves.

However, the various types of analcime could be interpreted on the basis of only one basic tetragonal structure ($I4_1/acd$) in three different orientations, related by 120° rotation around [111], the single domains being small enough to simulate a real single crystal. If the volume proportions of the three orientations are called d, e, and f (Table 12), then when $d = e = f = 1/3$ the diffraction symmetry is cubic, when $e = f < 1/3$ the diffraction symmetry is tetragonal $a > c$, (Table 2), if $e = f > 1/3$ the diffraction symmetry is tetragonal $a < c$, and finally in general when $d \neq e \neq f$ the diffraction symmetry is orthorhombic.

If one wants to know the possible geological meaning of all these analcimes, the main problem is to find a routine identification procedure for them; powder diffractometry, the main tool of mineralogical identification, is clearly useless. At the present, the only possible way is X-ray single-crystal investigation, which however may be reduced to the accurate measurements of the lattice parameters and/or of the intensities of 600, 606, and 066 reflections. Of course such methods can be applied only in the presence of twin domains large enough to permit the detachment of a suitable untwinned fragment.

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