

## The crystal structure of natural monoclinic analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ )

František Pechar

Czechoslovak Academy of Sciences, Institute of Geology and Geotechnics,  
V Holešovičkách 41, CS-182 09 Praha 8

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### *Monoclinic analcime / Crystal structure / $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$*

**Abstract.** An X-ray and neutron diffraction analysis was performed on a single crystal of natural monoclinic analcime ( $\text{Na}_{15.04}\text{K}_{0.14}\text{Ca}_{0.12}$ ) ( $\text{Al}_{14.40}\text{Fe}_{0.26}\text{Si}_{32.39}\text{Sr}_{0.003}$ ) $\text{O}_{96} \cdot 16.62 \text{H}_2\text{O}$ ,  $I2/a$  (or general  $C2/c$ ),  $a = 13.689(2) \text{ \AA}$ ,  $b = 13.676(2) \text{ \AA}$ ,  $c = 13.665(2) \text{ \AA}$ ,  $\beta = 90.38(1)^\circ$ ,  $V = 2558.2 \text{ \AA}^3$ ,  $Z = 16$ ,  $D_{\text{obs.}} = 2.29$  (locality Husa u Marcínova, Bohemia).

Refinement of 1460 (X-ray) and 860 (neutron) independent reflections yielded  $R = 0.030$ . The mean distance Si(Al)–O and O–H are  $1.6512 \text{ \AA}$  and  $0.9624 \text{ \AA}$ . The aluminosilicate framework of monoclinic analcime is topologically the same as in the cubic modification.

### **Introduction**

The crystal structure of analcime  $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16 \text{H}_2\text{O}$  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; Mazzi and Galli, 1978).

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  $\beta$  values in the wairakite-analcime series gives  $\beta = 90.12^\circ$  for pure analcime.

Mazzi and Galli (1978) have shown the symmetry for non-cubic analcimes to be tetragonal ( $I4_2/acd$ ) and orthorhombic ( $Ibca$ ).

The purpose of this work was to determine the crystal structure of a monoclinic analcime (Husa u Marcínova, Bohemia) by the aid of an X-ray diffraction study.

## Experimental

The X-ray diffraction measurements were performed on a natural single crystal of  $0.3 \times 0.3 \times 0.4 \text{ mm}^3$  from the locality Husa u Marcínova, Bohemia. Its chemical composition expressed in oxides is 61.38%  $\text{SiO}_2$ , 19.36%  $\text{Al}_2\text{O}_3$ , 0.23%  $\text{CaO}$ , 10.46%  $\text{Na}_2\text{O}$ , 0.21%  $\text{K}_2\text{O}$ , 0.01%  $\text{TiO}_2$ , 0.07%  $\text{Fe}_2\text{O}_3$ , 0.007%  $\text{SrO}$  and 7.88%  $\text{H}_2\text{O}$ . The diffraction data were collected on the automatic four-circle X-ray diffractometer SINTOX P1 of the ÚMCH ČSAV Prague. The wavelength of the  $\text{MoK}\alpha$ -radiation was 0.71073 Å. The intensity data were measured in the  $\omega$ -scan mode, and background measurements were made at both sides of each reflection. Three standard reflections, monitored at 3-h intervals, did not show significant changes of their intensities during the data collection.

Intensities were corrected for Lp-factor and for absorption ( $\mu = 0.086 \text{ cm}^{-1}$ ). Reflections with  $|F_{\text{obs}}|^2 < 3 \sigma (F_{\text{obs}}^2)$  were considered unobserved. For a maximum value of  $2\theta = 65^\circ$  a total of 2680 reflections was recorded, yielding a set of 1460 unique reflections.

The neutron diffraction data were collected on the automatic four-circle neutron diffractometer NANCY at the DIDO research reactor, Kernforschungsanlage Jülich (W. Schäfer, Mineralogisches Institut der Universität Bonn). The wavelength was 1.287 Å [monochromator  $\text{Cu}(111)$ ]. The intensity data were collected by step scanning in the  $\theta - 2\theta$ -scan mode at intervals of  $\Delta(2\theta) = 0.1^\circ$  with a rate of  $2.2^\circ/25 \text{ min}$ . For a maximum value of  $2\theta = 65^\circ$  1845 independent reflections were recorded, 860 of which showed significant intensities. A weighting scheme according to  $w(F_o) = (\sigma_c^2 + 0.0001 F_o^2)^{-1}$  was applied, where  $\sigma_c$  is the experimental error from counting statistics.

From a transmission experiment a linear absorption coefficient of  $\mu = 0.88 \text{ cm}^{-1}$  was determined. A correction for absorption was therefore neglected.

## Lattice parameters and space group

The analcime of Husa u Marcínova crystallizes in a monoclinic lattice with 16 formula units of  $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$  per unit cell.

The lattice parameters were determined from the adjusted setting of 12 independent reflections by least-squares methods. Table 1 lists the results in comparison with previous publications.

**Table 1.** Comparison of lattice parameters for monoclinic analcime.

Locality source	Husa u Marcínova this work	Mazzi et al. (1978)		Harada et al. (1972) monoclin-analcime	Harada et al. (1976) wairakite
		$I4_1/acd$	$Ibca$		
$a$ (Å)	13.689(2)	13.727(2)	13.727(2)	13.69	13.65
$b$ (Å)	13.676(2)	—	13.714(2)	13.68	13.66
$c$ (Å)	13.665(2)	13.686(3)	13.740(2)	13.66	13.56
$\beta$ (°)	90.38(1)	—	—	90.20	90.23
$V$ (Å <sup>3</sup> )	2558.2	2578.9	2586.6	2558.2	2528.4

**Table 2.** Comparison of Si, Al and Na contents in analcime.

Atom	This work	Mazzi et al.		Harada et al. monoclin.	Theoretical
		$I4_1/acd$	$Ibca$		
Si	32.39	32.06	32.31	31.75	32.00
Al	14.40	16.06	15.66	16.29	16.00
Na	15.04	15.41	15.67	15.84	16.00
$R$	0.698	0.682	0.675	0.686	0.666

The observed systematic extinction of reflections is in agreement with space group  $I2/a$ . The pseudo-orthorhombic setting of  $I1\ 2/a\ 1$  for monoclinic analcime was given preference over the conventional setting  $C2/c$ .

### Structure refinement

The refinement of the crystal structure from X-ray data was done by full-matrix least-squares analysis (SHELXTL) using the parameters of an E-map as starting values. A  $1/(\text{SIGMA}^2(F_o) + \text{G.F.F.})$  weighting scheme was used. The refinement resulted in a final  $R$ -value of 0.036. Starting parameters for the neutron refinement were taken from the X-ray analysis. For all calculation the X-ray package of computer programs (XTAL) was used, employing the following neutron scattering lengths [ $10^{-15}$  m]:  $b_{\text{Na}} = 3.51$ ,  $b_{\text{Si}} = 4.1491$ ,  $b_{\text{Al}} = 3.449$ ,  $b_{\text{O}} = 5.803$ ,  $b_{\text{H}} = -3.7409$  (Koester, 1977). The hydrogen positions were determined from difference Fourier maps from the X-ray refinement. The final refinement converged to  $R(F) = 0.030$ . Table 3 lists atomic fractional coordinates and anisotropic thermal parameters. A list of bond distances and angles has been deposited.<sup>1</sup>

Figure 1 depicts a projection of the structure along the  $c$ -axis.

<sup>1</sup> Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 52539, the names of the authors and the title of the paper.

**Table 3.** Final atomic coordinates and thermal anisotropic parameters ( $U \times 100 \text{ \AA}^2$ ) defined by  $T = \exp[-2\pi^2(U_{11}a^*h^* + \dots + 2U_{23}b^*c^*kl)]$ .

Atom	W notation	$x$	$y$	$z$	Occu- pation
Si1	8f	0.1122(1)	0.1580(1)	0.4175(1)	1.0
Si2	8f	0.4221(1)	0.1310(1)	0.1599(1)	1.0
Si3	8f	-0.1286(1)	0.3381(1)	0.4056(1)	1.0
Si4	8f	-0.4029(1)	0.3728(1)	0.1682(1)	1.0
Al1	8f	0.1753(1)	0.4112(1)	0.1370(1)	0.9
Al2	8f	-0.1526(1)	0.0856(1)	0.1176(1)	0.9
O1	8f	0.1099(3)	0.3434(3)	0.2274(3)	1.0
O2	8f	-0.0905(3)	0.1464(3)	0.2150(3)	1.0
O3	8f	0.1166(3)	0.3624(3)	0.0340(3)	1.0
O4	8f	-0.0983(3)	0.1499(3)	0.0209(3)	1.0
O5	8f	0.2029(3)	0.1165(3)	0.3575(3)	1.0
O6	8f	-0.2237(3)	0.3999(3)	0.3796(3)	1.0
O7	8f	0.1645(3)	0.5357(3)	0.1452(3)	1.0
O8	8f	-0.1282(3)	0.9626(3)	0.1137(3)	1.0
O9	8f	0.3976(3)	0.2243(3)	0.0891(3)	1.0
O10	8f	-0.3556(3)	0.2780(3)	0.1144(3)	1.0
O11	8f	0.0132(3)	0.1104(3)	0.3720(3)	1.0
O12	8f	-0.0405(3)	0.3782(3)	0.3361(3)	1.0
O13	8f	0.1344(4)	0.1264(4)	0.1348(4)	1.0
O14	8f	0.8858(4)	0.3703(4)	0.1169(4)	1.0
Na1	8f	0.1318(1)	0.9997(1)	0.2561(1)	0.45
Na2	4e	0.2500	0.1203(4)	0.0	0.90
Na3	4e	0.7500	0.3763(4)	0.0	0.9
Na4	8f	0.0115(1)	0.2474(1)	0.1160(1)	0.45
H1	8f	0.0899(4)	0.0949(4)	0.0	1.0
H2	8f	0.1790(4)	0.1610(4)	0.0920(4)	1.0
H3	8f	0.8413(4)	0.3388(4)	0.0719(4)	1.0
H4	8f	0.9353(4)	0.4018(4)	0.0789(4)	1.0

## Discussion

The crystal structure of monoclinic analcime (Fig. 1) is topologically identical to that of the cubic analcime described by Calleri and Ferraris (1964) and Knowles et al. (1965).

According to the chemical analysis the order-disorder parameter of the Si, Al distribution expressed by the ratio  $\rho = \text{Si}/(\text{Si} + \text{Al} + \text{Fe}^{3+})$  is 0.698. With respect to the ordered character of the atomic distribution the analcime framework belongs to the second class of zeolites, the so-called "Intermediate zeolites", according to the classification of Gottardi (1979). Thus in the monoclinic framework 70% (33 sites) of the tetrahedral sites are represented by  $\text{SiO}_4$ -tetrahedra. The monoclinic analcime from Husa u Marcínova has a disordered distribution of Si, Al atoms in tetrahedral sites.

Table 3. (continued).

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Si1	0.64(6)	0.68(6)	0.61(6)	0.02(5)	-0.01(5)	-0.0(5)
Si2	0.49(7)	0.64(7)	0.75(7)	-0.02(5)	-0.03(5)	-0.10(5)
Si3	0.49(6)	0.64(6)	0.65(6)	-0.18(5)	0.09(5)	0.01(5)
Si4	0.65(6)	0.69(6)	0.62(6)	0.01(5)	-0.01(5)	-0.0(5)
Al1	0.58(8)	0.56(7)	0.72(7)	0.01(6)	0.05(6)	-0.04(6)
Al2	0.62(8)	0.53(7)	0.76(8)	-0.05(6)	0.08(6)	-0.03(6)
O1	1.72(5)	0.84(5)	0.79(5)	-0.06(4)	0.22(4)	0.18(4)
O2	1.97(6)	0.81(5)	1.12(5)	-0.05(4)	-0.27(4)	-0.28(4)
O3	0.54(5)	0.70(5)	1.31(5)	-0.13(4)	-0.11(4)	-0.11(4)
O4	0.70(5)	0.76(5)	1.40(5)	-0.22(4)	0.02(4)	0.06(4)
O5	1.10(5)	0.85(5)	1.29(5)	0.29(4)	-0.00(4)	-0.45(4)
O6	1.25(5)	1.10(5)	1.39(5)	0.29(4)	0.18(4)	0.50(4)
O7	0.82(5)	0.97(5)	1.54(5)	0.17(4)	-0.42(4)	-0.05(4)
O8	0.93(5)	1.26(5)	1.35(5)	0.30(4)	0.44(4)	0.07(4)
O9	0.95(5)	1.67(6)	1.21(5)	-0.19(4)	0.36(4)	0.16(4)
O10	0.79(5)	1.71(5)	0.87(4)	0.00(4)	-0.06(4)	-0.26(4)
O11	0.94(5)	1.28(5)	1.36(5)	0.32(4)	0.42(4)	0.08(4)
O12	0.71(5)	0.78(5)	1.42(5)	-0.24(4)	0.04(4)	0.08(4)
O13	2.80(8)	4.21(9)	2.07(7)	-0.68(7)	1.08(6)	-1.01(7)
O14	1.59(7)	1.37(7)	4.34(8)	0.05(5)	-0.44(6)	0.49(6)
Na1	1.00(7)	1.02(7)	1.21(7)	-0.08(5)	-0.13(5)	-0.17(5)
Na2	1.10(7)	0.85(7)	1.29(7)	0.29(5)	-0.00(5)	-0.45(5)
Na3	1.74(7)	0.86(7)	0.80(7)	-0.08(5)	0.24(5)	0.20(5)
Na4	1.25(7)	1.10(7)	1.38(7)	0.28(5)	0.12(5)	0.48(5)
H1	4.00(16)	5.34(17)	3.45(13)	-0.14(12)	1.80(12)	0.42(12)
H2	4.63(19)	6.81(20)	4.45(16)	-1.41(16)	0.53(14)	-1.72(15)
H3	2.62(16)	5.79(19)	6.81(21)	0.12(13)	0.31(14)	0.42(16)
H4	4.72(16)	2.05(13)	4.75(15)	0.20(11)	-0.87(12)	-0.01(11)

General symmetry coordinate:  $x, y, z$ ;  $-x, -y, -z$ ;  $1/2 + x, -y, z$ ;  $1/2 - x, y, z$ .

The Si, Al distribution effectuates a distortion of lattice parameters and angles of the cubic, orthorhombic and tetragonal modification of analcime (Table 1).

This deformation corresponds to mean interatomic distances  $d(\text{Si}-\text{O}) = 1.6122 \text{ \AA}$ , and  $d(\text{Al}-\text{O}) = 1.7291 \text{ \AA}$  which are smaller than the given by Baur (1981)  $1.623 \text{ \AA}$  and  $1.752 \text{ \AA}$  for tetrahedral bonds in silicates and theoretical values  $1.62 \text{ \AA}$  and  $1.74 \text{ \AA}$  ( $\sigma + \pi$  bond theory). The tetrahedral angles are deformed between  $109.43$  and  $110.46^\circ$ . All water molecules are connected via hydrogen bonds to the framework. There is one relatively strong bond between water molecule O(14) and O(3) with an O...O distance of  $2.6172 \text{ \AA}$ . Its second H bond, however, has to be classified as a weak interaction despite the O...O distance of  $3.3656 \text{ \AA}$ , due to the unfavourable angle of  $33.15^\circ$ . In this water molecule the H-O-H angle of  $107.89^\circ$  deviates considerably from the angle of  $\text{H}_2\text{O}$  in vapor which is  $104.5^\circ$ . It

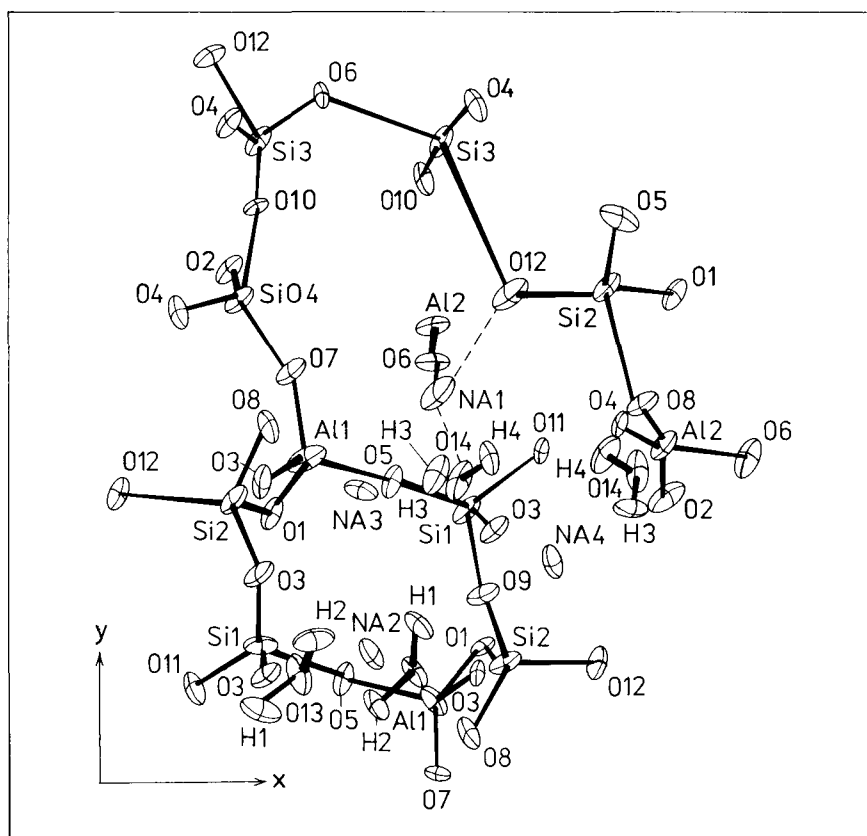


Fig. 1. Projection (ORTEP) of the monoclinic analcime structural motive on a (001) plane.

acts as a substitute in a vacant cationic site. The other water molecule is also distorted with an angle of  $103.22^\circ$ . The least distorted molecule O(13) shows the weakest hydrogen bonds to the framework. No hydrogen bonds exist between the molecules of crystal water. The coordination polyhedra of Na ions have coordination number 6, and consist of 2 oxygen atoms to the framework and 4 oxygen atoms to water molecules with mean interatomic distances  $d(\text{Na}-\text{O}) = 2.4919 \text{ \AA}$  and mean angle  $105.15^\circ$ .

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