Neutron diffraction study of the zeolite yugawaralite at 13 K*

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Abstract. The crystal structure of yugawaralite, $CaAl_2Si_6O_{16} \cdot 4H_2O$ [$Z = 2$; Pc, $a = 6.700(1)$, $b = 13.972(2)$, $c = 10.039(5)$ Å, $\beta = 111.07(2)°$] at 13 K was refined from neutron diffraction data. The mean $T-O$ distances in each tetrahedron ($Si-O = 1.609-1.618$ Å; $Al-O = 1.731-1.736$ Å) and the refinement of the neutron scattering lengths confirm complete Si, Al order in the framework. The Ca atom is coordinated to four framework oxygen atoms ($Ca-O = 2.480-2.558$ Å) and to four water oxygens ($Ca-O_w = 2.315-2.541$ Å). Three of the four water molecules show disorder with either multiple alternative oxygen or hydrogen sites, or both. Disorder of this type appears to be related to water molecules weakly bonded to framework oxygens, and is not necessarily related to Si/Al disorder in a zeolite framework. A water molecule in a partially occupied site (12% occupancy) was found to interact only via hydrogen bonding to the surrounding oxygen atoms and is not coordinated to the Ca atom. $H \cdots O$ contacts from 1.87 to 2.71 Å indicate a wide range of hydrogen oxygen interactions.

Introduction

The present work is part of a series of neutron diffraction studies of zeolite structures. The aim is to relate the stereochemical features to the zeolitic properties of these materials.

Zeolites with ordered frameworks from the fibrous group (natrolite: Artioli, Smith and Kvick, 1984; scolecite: Kvick, Ståhl and Smith, 1985; thomsonite: Pluth, Smith and Kvick, 1985) showed unique positions for the water oxygen and hydrogen atoms. A multi-temperature study of edingtonite (Kvick and Smith, 1986) shows that the ordered water structure at 298 K (Kvick and Smith, 1983) can change into multiple water sites upon cooling. Here, the water disorder can be related to a change in the position of the Ba cation presumably related to the effective enlargement of the cavities as a result of lower thermal motion. Unique water positions were also observed in leonhardite (Bartl, 1970) and bikitaite (Ståhl, Kvick and Ghose, 1984) whereas multiple hydrogen positions were observed in brewsterite (Artioli, Smith and Kvick, 1985), which has Si/Al disorder in the framework. Partially occupied oxygen and hydrogen positions have also been observed in analcime (Ferraris, Jones and Yerkess, 1972), heulandite (Hambley and Taylor, 1984) and stellerite (Miller and Taylor, 1985).

Yugawaralite is a rare zeolite first reported from Yugawara Hot Springs, Kanagawa Prefecture, Japan (Sakurai and Hayashi, 1952). A second locality in Heinabergsjökull, Iceland, supplied the crystals used for previous X-ray structure determinations (Barrer and Marshall, 1965; Kerr and Williams, 1967, 1969). Leimer and Slaughter (1969) studied a crystal from the type locality with X-rays but with lower precision. Yugawaralite has since been reported from Chena Hot Springs, Alaska (Eberlein, Erd, Weber and Beatty, 1971); from Osilo, Sardinia, Italy (Pongiluppi, 1977) and from Bombay, India (Wise, 1978). The crystal for this study is from a previously unreported locality at Hvalfjördur, Iceland (specimen Ni-6932 of the Icelandic Museum of Natural History, Reykjavik).

Experimental

An electron microprobe analysis by the WDS technique ($An_{80}Ab_{20}$ standard) on smaller crystal fragments from the present specimen yielded an almost pure composition: SiO_2 60.0%, Al_2O_3 17.1%, CaO 9.5%, Na_2O 0.1%. No K was detected within the precision of the analysis.

A crystal of volume 8 mm^3 was mounted on an aluminum pin with the ($\bar{1}02$) direction parallel to the ϕ axis of a four circle diffractometer at the Brookhaven National Laboratory High Flux Beam Reactor. The crystal was cooled to 13 K with a closed cycle DISPLEX CS-202 refrigerator and the temperature monitored by a calibrated Ge thermometer. The temperature was stablized at 13 $\pm$ 1 K and a least-squares fitting of 64 $\sin^2\theta$ values

for reflections with $39° < 2\theta < 54°$ was used to obtain the cell dimensions. A monochromatic neutron beam of wavelength $1.0505(1)$ Å from a Be monochromator was used for all measurements [the wavelength was calibrated by a standard KBr crystal; $a_0 = 6.6000(1)$ Å at 298 K].

The intensity data were obtained by a $\theta/2\theta$ scan technique, using between 60 to 100 steps per scan, with 10% on each side representing the background. The scan width was fixed ($\Delta 2\theta = 3.0°$) for $2\theta < 60°$ and variable ($\Delta 2\theta = K_2 + K_1 K_2 \tan\theta$) with $K_1 = 1.6$ and $K_2 = 1.4$ and 1.8 for $60° < 2\theta < 90°$ and $90° < 2\theta < 114°$, respectively. Each step was counted for about 2 s until a preset number of counts was accumulated in the direct beam monitor. Two standard reflections measured every 50 reflections showed a statistical variation of less than 2%. A total number of 4240 reflections out to $(\sin\theta/\lambda)_{max} = 0.785$ Å^{-1} ($\pm h + k + l$) were measured resulting in 3942 unique reflections ($R_{av} = 0.012$) out of which 3636 reflections above the 3σ level were used in the structure refinement. The intensities were corrected for background, Lorentz and absorption effects. The absorption correction was performed using a Gaussian grid of $6 \times 6 \times 6$ with a calculated absorption coefficient of $\mu = 0.5122$ cm^{-1}. The transmission factors were in the range of 0.86 to 0.95. The crystal plate (maximum dimensions of $4.9 \times 3.0 \times 0.9$ mm) had 12 well developed faces of the forms (100), (010), (001), (110), (211) and (201).

The refinement started using the coordinates for the framework atoms from Kerr and Williams (1969). The neutron scattering lengths were from Koester, Rauch, Herkens and Schröder (1981) except for the scattering length for Ca which was $b_{Ca} = 0.467 \times 10^{-14}$ m in close agreement with previously found values (Kvick, Ståhl and Smith, 1985). The space group Pc and complete order of the Si and Al atoms were assumed, and subsequently confirmed by the refinement. A difference Fourier synthesis after the first least-squares cycle indicated positions for the four main water oxygen sites, the Ca atom and eight hydrogen atoms. These hydrogen sites are very close to the hydrogen positions predicted by Baur (1972) from electrostatic calculations. A second cycle including these atoms gave $R(F^2) = 0.18$. The refinement was continued by successive least-squares cycles and difference Fourier syntheses. Two alternative sites were located for the oxygen atoms of water 1 and 4. One additional hydrogen site for water molecule 3 was found and one oxygen and two hydrogens for a low occupancy water molecule 5 were discovered. Two diffuse hydrogen sites close to the two alternative OW(1A) and OW(4A) positions were located. Introduction of the additional partial atoms reduced $R(F^2)$ to 0.08, which dropped to 0.05 after introduction of anisotropic temperature factors for these atoms.

Refined occupancy factors for the tetrahedral framework atoms were not significantly different from unity and were fixed during the final cycles. The occupancy factors for the water oxygen and hydrogen, although strongly correlated with the thermal parameters, converged to the values

reported in Table 1. The sum of the water oxygen occupancies: $\Sigma G_{OW} = 4.07$ is close to the expected value of 4, and within experimental error of half the sum of the total hydrogen atom occupancies: $\Sigma G_H = 7.94$.

An isotropic extinction correction for a type I crystal yielded a final extinction parameter of $g = 0.23(1) \times 10^4$ with no extinction correction larger than $1.18 \times F_o^2$. A total of 405 parameters (133 positional, 270 anisotropic thermal parameters, 1 scale factor and 1 isotropic extinction parameter) was refined in the last refinement cycle. All occupancy factors obtained from previous cycles were here fixed to the values given in Table 1. The final agreement factors were $R(F^2) = 0.0315$, $wR(F^2) = 0.0448$, $S = 1.18$ with $w^{-1} = \sigma(F^2)^2 + (0.02 \ F^2)^2 + 0.04$ where $\sigma(F^2)$ was based on counting statistics. The final difference Fourier synthesis only showed random peaks corresponding to less than 5% of an oxygen atom.

All calculations were performed on a VAX 11/730 computer at the Brookhaven National Laboratory with a crystallographic computer software package from the University of Uppsala, Sweden.

Discussion

The yugawaralite structure contains fully ordered Si and Al sites as well as an ordered Ca cation bonded to 4 framework oxygens and 4 water oxygens. The large zeolitic cavity, however, gives alternative sites for some of the water oxygen and hydrogen atoms. Water OW(2) and its two hydrogen atoms are ordered; OW(3) and H(33) are ordered but there are two alternative sites [H(31), H(32)] for the second hydrogen. Water molecules OW(1) and OW(2) are disordered with two alternative oxygen positions [OW(1), OW(1A) and OW(4), OW(4A)] and three alternative hydrogen sites [H(11), H(12), H(13)] and [H(41), H(42), H(43)] associated with each molecule. There is also a minor water site (occupancy 0.12) labelled OW(5) not coordinated by the cation. The OW(5) site is probably coupled to the occurrence of the alternative oxygen sites OW(1A) and OW(4A) as indicated by the population analysis.

The framework

The final coordinates are given in Table 1, and inter-atomic distances and angles are presented in Table 2. A list of structure factors may be ordered referring to the numbers CSD 51 688, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. The basic features of the framework closely agree with the result from the previous X-ray studies. The tetrahedral framework contains layers of edge-shared 5- and 4-membered rings lying parallel to the bc plane and interconnected by other 4-membered rings almost perpendicular to the plane. The framework can be constructed

Table 1. Atomic coordinates ($\times 10^5$), isotropic root-mean-square amplitude of displacement and occupancy factors

	x	y	z	U	G
Si1	34121(25)	14798(8)	98083(19)	0.056(2)	
Si2	71051(24)	3650(8)	19124(18)	0.057(2)	
Si3	40911(25)	12450(8)	69431(19)	0.053(2)	
Si4	2736(24)	47598(8)	43748(19)	0.053(2)	
Si5	36039(24)	37327(8)	96046(19)	0.055(2)	
Si6	74211(23)	49757(8)	62097(18)	0.055(2)	
Al1	0*	710(9)	0*	0.052(3)	
Al2	39614(28)	35598(9)	65361(20)	0.051(3)	
O1	10689(22)	10638(6)	94844(17)	0.083(2)	
O2	85591(23)	4834(6)	9817(17)	0.086(2)	
O3	19153(22)	7642(6)	59056(17)	0.078(2)	
O4	50365(22)	10778(6)	13425(16)	0.072(2)	
O5	43489(23)	11736(7)	86004(17)	0.091(2)	
O6	61915(23)	7317(6)	67971(17)	0.076(2)	
O7	84451(22)	6416(6)	35574(17)	0.075(2)	
O8	33904(23)	26252(6)	−394(18)	0.090(2)	
O9	39913(23)	23277(5)	63939(17)	0.077(2)	
O10	16380(23)	42664(6)	98834(17)	0.077(2)	
O11	83032(22)	48293(6)	49303(17)	0.079(2)	
O12	17154(22)	38236(6)	49904(17)	0.073(2)	
O13	57911(22)	41154(6)	8345(17)	0.078(2)	
O14	36053(23)	39320(6)	80583(17)	0.083(2)	
O15	62998(22)	40026(6)	64000(17)	0.078(2)	
O16	93634(22)	47014(6)	26478(16)	0.071(2)	
Ca	5134(24)	21654(7)	42364(19)	0.075(2)	
OW1	98759(34)	24929(13)	17041(25)	0.111(4)	0.774(39)
OW1A	4165(297)	27602(96)	20621(141)	0.219(50)	0.182(41)
H11	95821(60)	19582(22)	10667(37)	0.195(9)	0.825(14)
H12	3505(65)	30007(25)	12817(42)	0.212(11)	0.883(17)
H13	5913(412)	34986(134)	21315(240)	0.238(72)	0.157(16)
OW2	90310(24)	23331(7)	61844(18)	0.106(2)	
H21	87938(55)	18305(18)	67456(38)	0.203(9)	
H22	81676(40)	28638(15)	62799(32)	0.173(6)	
OW3	70811(23)	29016(7)	32835(18)	0.109(2)	0.978(7)
H31	59175(71)	27280(50)	34773(68)	0.195(16)	0.482(17)
H32	65286(127)	33338(60)	39098(76)	0.207(21)	0.417(17)
H33	66062(41)	32229(17)	23748(28)	0.171(6)	1.001(13)
OW4	36920(36)	15938(14)	36919(24)	0.125(4)	0.887(50)
OW4A	33283(237)	12668(97)	35814(155)	0.131(30)	0.128(47)
H41	39007(48)	14373(22)	28329(32)	0.178(7)	0.910(12)
H42	49359(83)	13517(40)	44553(52)	0.191(11)	0.704(30)
H43	45146(288)	15376(424)	40785(405)	0.450(246)	0.314(48)
OW5	81646(142)	25961(65)	92491(117)	0.134(23)	0.119(7)
H51	90889(282)	20607(123)	91977(216)	0.134(45)	0.098(11)
H52	87863(581)	31721(154)	90312(424)	0.249(128)	0.119(14)

* Coordinate fixed to define origin

Table 2. Interatomic distances (Å) and angles (°)

Tetrahedra

Si(1)—O(1)	1.594(2)	O(1)—Si(1)—O(4)	109.9(1)
—O(4)	1.633(2)	—O(5)	111.8(1)
—O(5)	1.611(2)	—O(8)	109.9(1)
—O(8)	1.608(1)	O(4)—Si(1)—O(5)	108.1(1)
		—O(8)	106.2(1)
Average	1.612	O(5)—Si(1)—O(8)	110.8(1)
Si(2)—O(2)	1.582(2)	O(2)—Si(2)—O(4)	110.8(1)
—O(4)	1.634(2)	—O(6)	110.5(1)
—O(6)	1.639(1)	—O(7)	110.1(1)
—O(7)	1.618(2)	O(4)—Si(2)—O(6)	107.3(1)
		—O(7)	107.5(1)
Average	1.618	O(6)—Si(2)—O(7)	110.6(1)
Si(3)—O(3)	1.603(2)	O(3)—Si(3)—O(5)	112.3(1)
—O(5)	1.613(2)	—O(6)	111.7(1)
—O(6)	1.632(2)	—O(9)	104.9(1)
—O(9)	1.603(1)	O(5)—Si(3)—O(6)	106.8(1)
		—O(9)	112.9(1)
Average	1.613	O(6)—Si(3)—O(9)	108.3(1)
Si(4)—O(10)	1.616(2)	O(10)—Si(4)—O(11)	106.3(1)
—O(11)	1.610(2)	—O(12)	111.7(1)
—O(12)	1.611(2)	—O(16)	109.5(1)
—O(16)	1.620(2)	O(11)—Si(4)—O(12)	111.7(1)
		—O(16)	109.5(1)
Average	1.614	O(12)—Si(4)—O(16)	108.2(1)
Si(5)—O(8)	1.606(1)	O(8)—Si(5)—O(10)	105.2(1)
—O(10)	1.623(2)	—O(13)	106.0(1)
—O(13)	1.630(2)	—O(14)	114.9(1)
—O(14)	1.577(2)	O(10)—Si(5)—O(13)	106.4(1)
		—O(14)	112.1(1)
Average	1.609	O(13)—Si(5)—O(14)	111.7(1)
Si(6)—O(11)	1.608(2)	O(11)—Si(6)—O(13)	108.8(1)
—O(13)	1.628(2)	—O(15)	108.1(1)
—O(15)	1.598(2)	—O(16)	109.8(1)
—O(16)	1.622(2)	O(13)—Si(6)—O(15)	112.7(1)
		—O(16)	104.2(1)
Average	1.614	O(15)—Si(6)—O(16)	113.1(1)
Al(1)—O(1)	1.724(2)	O(1)—Al(1)—O(2)	106.5(1)
—O(2)	1.709(2)	—O(3)	113.00(6)
—O(3)	1.731(1)	—O(7)	113.30(7)
—O(7)	1.758(2)	O(2)—Al(1)—O(3)	112.98(7)
		—O(7)	112.08(7)
Average	1.731	O(3)—Al(1)—O(7)	99.13(8)
Al(2)—O(9)	1.728(1)	O(9)—Al(2)—O(12)	99.6(1)
—O(12)	1.769(2)	—O(14)	112.7(1)
—O(14)	1.710(2)	—O(15)	108.1(1)
—O(15)	1.735(2)	O(12)—Al(2)—O(14)	111.9(1)
		—O(15)	111.4(1)
Average	1.736	O(14)—Al(2)—O(15)	112.5(1)

Table 2. (Continued)

Si(1)−O(1)−Al(1)	135.82(10)	Si(3)−O(9)−Al(2)	155.76(14)
Si(2)−O(2)−Al(1)	154.26(8)	Si(4)−O(10)−Si(5)	137.24(12)
Si(3)−O(3)−Al(1)	162.38(9)	Si(4)−O(11)−Si(6)	150.08(13)
Si(1)−O(4)−Si(2)	137.19(12)	Si(4)−O(12)−Al(2)	135.17(10)
Si(1)−O(5)−Si(3)	146.51(12)	Si(5)−O(13)−Si(6)	140.95(11)
Si(2)−O(6)−Si(3)	135.79(10)	Si(5)−O(14)−Al(2)	151.08(9)
Si(2)−O(7)−Al(1)	130.76(8)	Si(6)−O(15)−Al(2)	142.15(10)
Si(1)−O(8)−Si(5)	158.92(14)	Si(4)−O(16)−Si(6)	144.24(11)

Ca coordination

Ca−OW(1A)	2.315(13)	Ca−OW(2)	2.502(2)
−OW(3)	2.383(2)	−OW(4)	2.512(3)
−OW(1)	2.464(3)	−O(3)	2.528(2)
−O(12)	2.480(1)	−OW(4A)	2.541(15)
−O(7)	2.498(2)	−O(9)	2.558(2)

Water molecules and hydrogen bonding

A−H⋯B		A⋯B	A−H	H⋯B
Ow(1)	−H(11)⋯O(2)	2.954(2)	0.957(4)	2.164(3)
	−H(11)⋯OW(5)	2.319(11)	0.957(4)	1.944(11)
	−H(12)⋯O(10)	3.525(2)	0.939(4)	2.591(4)[a]
	−H(12)⋯OW(5)	2.319(11)	0.939(4)	2.116(11)
OW(1A)	−H(12)⋯O(10)	3.342(14)	0.839(14)	2.591(4)[a]
	−H(12)⋯OW(5)	2.691(18)	0.839(14)	2.116(11)
	−H(13)⋯O(16)	2.915(14)	1.038(23)	2.019(21)
OW(2)	−H(21)⋯O(6)	3.138(2)	0.949(3)	2.338(3)
	−H(22)⋯O(15)	3.020(2)	0.966(3)	2.054(3)
OW(3)	−H(31)⋯OW(4)	3.055(3)	0.902(5)	2.239(6)
	−H(32)⋯O(11)	3.112(2)	1.032(8)	2.440(8)[a]
	−H(33)⋯O(13)	2.853(2)	0.962(3)	1.907(3)
OW(4)	−H(41)⋯O(4)	2.902(3)	0.947(4)	1.972(3)
	−H(42)⋯O(6)	3.197(3)	0.968(6)	2.359(5)
OW(4A)	−H(41)⋯O(4)	2.878(15)	0.988(15)	1.972(3)
	−H(42)⋯O(6)	3.195(15)	1.124(16)	2.359(5)
	−H(43)⋯O(9)	3.076(14)	0.859(41)	2.708(42)
OW(5)	−H(51)⋯O(1)	2.845(9)	0.984(20)	1.873(17)
	−H(52)⋯O(10)	3.194(9)	0.967(29)	2.355(31)

H(11)−OW(1)−H(12)	108.0(4)
H(12)−OW(1A)−H(13)	68.4(1.6[b]
H(21)−OW(2)−H(22)	106.0(3)
H(31)−OW(3)−H(33)	108.2(5)
H(32)−OW(3)−H(33)	103.7(5)
H(41)−OW(4)−H(42)	105.9(4)
H(41)−OW(4)−H(43)	99.8(4.0)
H(41)−OW(4A)−H(42)	92.5(1.2)[b]
H(41)−OW(4A)−H(43)	78.7(2.8)[b]
H(42)−OW(4A)−H(43)	22.2(3.5)[b]
H(51)−OW(5)−H(52)	106.9(2.4)

[a] Not hydrogen bonded. An arbitrary cut-off at 2.40 Å was applied
[b] Outside the observed range for water molecules in crystalline hydrates
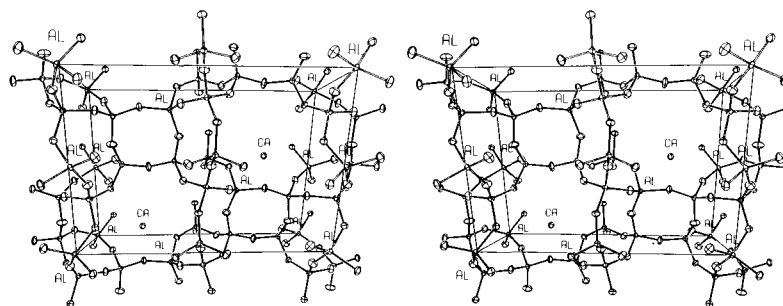
Fig. 1. Stereoview of the yugawaralite framework projected along a. The Al atom sites are labelled. The c axis is vertical

mainly from 4-rings sharing vertices, but some single edges are needed between unshared vertices of the 4-rings. Combination of the two types of linkages produces the 5- and 8-rings. Although 4-, 5- and 8-rings also occur in mordenite and heulandite, the linkages are quite different from those in yugawaralite. Channels parallel to the a and c crystallographic directions generate a two-dimensional system limited by 8-rings. The Ca atom lies at the intersection of two types of channels.

The present sample has complete Si,Al ordering in the tetrahedral sites of the framework as indicated by the refinement of the neutron scattering lengths. Kerr and Williams (1969) also found complete order on the basis of mean tetrahedral Si,Al − O distances in their study of a sample from a different location on Iceland. An analysis of the mean T − O distances of our sample, based on linear interpolation such as those of Jones (1968) or Ribbe and Gibbs (1969), however, would indicate a small Al substitution in the Si sites. This discrepancy with the results of our refinement of the tetrahedral site occupancies (identical to refinement of neutron scattering lengths), shows that mean tetrahedral distances alone are not sufficient for an accurate assessment of the Al content. The T − O distances are also affected by the coordination of the framework oxygens to the cations, by hydrogen bonding to the water molecules, and by the geometrical distortions of the tetrahedra (Baur, 1978; Gibbs, 1982; Alberti and Gottardi, 1984). Although the Al content in the tetrahedral site is without doubt the main factor influencing the mean T − O distance in each tetrahedron, individual distances depend on the complex interaction with first and second neighbour species as well as the degree of orbital hybridization on tetrahedral and oxygen atoms. The degree of mixing between s and p type orbitals on the oxygen atoms has, for instance, been correlated with the negative secant of the T − O − T angle (Coulson, 1961; Newton, 1981). A weak correlation between T − O distance and T − O − T angle has been observed in several aluminosilicates (Gibbs, 1982) and in zeolites (e.g.

Artioli et al., 1984; Kvick et al., 1985). However, data for low albite (Smith et al., 1985), natrolite (Artioli et al., 1984), and scolecite (Kvick et al., 1985) collected around 20 K to minimize the systematic errors from thermal motion show complex relations between distances and angles which require consideration of non-first neighbours or interactions.

Figure 2 illustrates data for yugawaralite and scolecite obtained at low temperatures (Kvick et al., 1985 and the present study). Both zeolites have complete Si,Al order in the framework and have Ca as the extra-framework cation. Oxygens bonded to two Si atoms have longer Si−O distances than those bonded to one Si and one Al with the Ca coordination adding a secondary effect.

The largest distortions from ideal tetrahedral angles are found for the O(3)−Al(1)−O(7) and O(9)−Al(2)−O(12) angles, which are as small as 99.1(1) and 99.6(1)° respectively. Electrostatic interactions associated with edge sharing between the Al/Si and Ca polyhedra explains the closing of the angles. The distorting effect of the Ca coordination on the Si(3) tetrahedron is also evident in the O(3)−Si(3)−O(9) angle of 104.9(1)°. The distortion is here smaller than those observed in the Al tetrahedra because the Si−O distances are shorter and hence the O· · ·O repulsion upon closing of the angle becomes more important. The hydrogen bond interaction with the oxygen atoms result in similar distortions in the tetrahedral geometry as evidenced in the O(13)−Si(6)−O(16) angle of 104.2(1)°. The O(13) oxygen atom is involved in the dominant hydrogen bond in the structure [O(13)· · ·H(33) = 1.907(3) Å].

The cation coordination

The Ca atom is located in one side of the cavity and asymmetrically bonded to four framework oxygens and to four water oxygens (Fig. 3). As expected the framework oxygens bonded to one Si and one Al atom are favored over the less negative oxygens bonded to two Si atoms. The coordination of Ca is somewhat complicated by the multiple water oxygen sites. Water oxygens OW(2) and OW(3) are fully occupied whereas OW(1) and OW(4) show alternative minor sites [OW(1A) and OW(4A)] with an occupancy of less than 20%. These minor sites are also accompanied by a new water oxygen OW(5), which is not coordinated at all to calcium.

The coordination of the Ca ion may be described in terms of two planes; one defined by atoms O(3), O(7), O(9), O(12) and OW(3) and another plane perpendicular (< 89.4°) to it containing atoms OW(1), OW(2), OW(4) and Ca. The details are given in Table 3. The Ca, OW(1) and OW(4) atoms are located above the "pentagon" [0.455(2), 2.502(2), 2.500(2) Å] whereas OW(2) is located below [2.020(2) Å] with the calcium atom virtually in the middle of the triangle OW(1), OW(2), OW(4) with Ca· · ·OW distances of 2.464(3), 2.502(3) and 2.512(3) Å. The calcium is slightly closer to the water
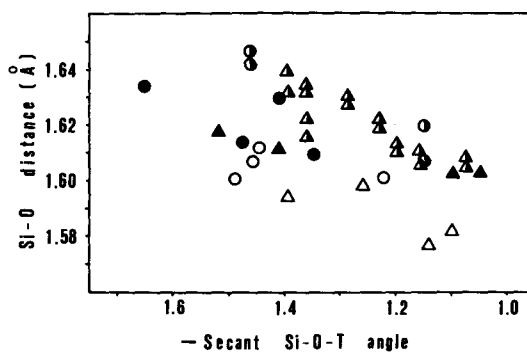
Fig. 2. Si—O vs. -sec Si—O—T correlation for yugawaralite (triangles) and scolecite (circles). Filled symbols refer to oxygen atoms coordinated to the Ca atom; half filled symbols are for oxygen atoms bridging two Si atoms
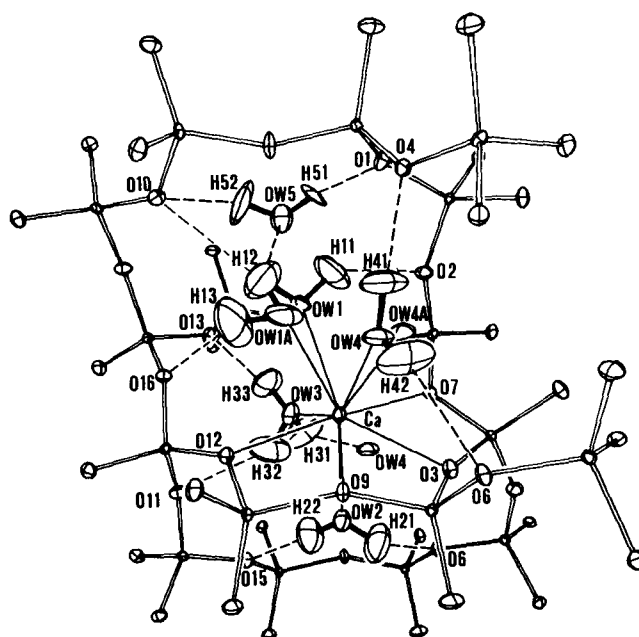

Fig. 3. Cation coordination and hydrogen bonding system. Ellipsoids at 90% probability level. H(43) was excluded to avoid overcrowding. Only the Ca atom, the water molecules, and the framework oxygen acceptors of hydrogen bonds are labelled

oxygen of the "pentagon" [2.383(2) Å] than to the framework oxygens [2.528(2), 2.498(2), 2.558(2), 2.480(1) Å] in agreement with the observations in scolecite (Kvick et al., 1985) where the Ca···OW distances were consistently shorter than the Ca···O distances to the framework.

Table 3. Distances from a least-squares plane defined by atoms O(3), O(7), O(9), O(12) and OW(3). The distance from any point with fractional coordinates x,y,z is given by: Distance $= 4.57535^*x - 1.06699^*y - 9.27067^*z + 4.40437$

Atom	Distance	Atom	Distance
O(3)	$-0.276(2)$ Å	Ca	0.455(2)
O(7)	0.327(2)	OW(1)	2.502(2)
O(9)	0.055(2)	OW(2)	$-2.020(2)$
O(12)	0.155(2)	OW(4)	2.501(2)
OW(3)	$-0.285(2)$	OW(5)	3.984(10)
		OW(1A)	2.389(17)
		OW(4A)	$-2.472(16)$

A similar coordination is obtained when OW(1) and OW(4) are replaced by the OW(1A) and OW(4A) positions; a replacement which only rotates the "trigonal" plane around the Ca$\cdots$OW(2) vector by 20.5°. The OW(4A) atom is well behaved with thermal parameters similar to those of the fully occupied water oxygens (RMS amplitude of displacement 0.13 Å) whereas the oxygen OW(1A) shows twice the displacement (0.22 Å) possibly indicating further statistical disorder in this atom related to the appearance of the new oxygen site OW(5). It should be pointed out, however, that considerable correlation between thermal parameters and the occupancy factor was observed for oxygen OW(1A) making a detailed analysis complicated.

It is evident from the calculated distances that sites OW(1) and OW(1A) as well as sites OW(4) and OW(4A) cannot be simultaneously occupied because of the short O$\cdots$O separation (0.55 and 0.51 Å). Furthermore, sites OW(5) and OW(1) are separated by only 2.319(1) Å, which is considerably shorter than the minimum allowed O$\cdots$O distance of 2.39 Å (Küppers, Kvick and Olovsson, 1981) also ruling out simultaneous occupancy of these sites. We therefore believe that the energetics of the system at 13 K allows a minor simultaneous occurrence of sites OW(5), OW(1A) and OR(4A) in place of the major OW(1) and OW(4) constellation with a ratio of approximately 1 to 4. The reason for this is not immediately obvious but the situation resembles the occurrence of water disorder in edingtonite upon cooling (Kvick and Smith, 1986). Here a second partial Ba site could be refined closer to the framework oxygens at 20 K, and this alternative cation site was accompanied by changes in the water structure. The Ca$\cdots$H(13) and Ca$\cdots$H(43) distancs of 2.83(2) and 2.87(3) Å associated with sites OW(1A) and OW(4A) are considerably shorter than the remaining Ca$\cdots$H distances, which all are larger than 3.00 Å, suggestive of a partial Ca site close to the "pentagon". There are however no clear indications of this in the difference Fourier maps or in the anisotropic thermal parameters of Ca. The $B_{eq} = 0.45(2)$ Å^2 for Ca is however twice

as large as the value 0.24(2) Å² found in scolecite at 20 K (Kvick, Ståhl and Smith, 1985).

The water molecules and the hydrogen bonding

There are seven different water oxygen locations in this structure with only two fully occupied oxygen sites and a multitude of alternative hydrogen sites.

OW(1) lies well inside the cavity, displaced from the center of the 8-ring in the opposite direction with respect to the Ca ion. The geometry of the water molecule is well defined [OW(1)−H(11) = 0.957(4) Å, OW(1)−H(12) = 0.939(4) Å with an H−O−H angle of 108.0(4)°] and it is occupied at the 80% level. The hydrogen bonding is extremely weak with the H(11)···O(2) distance = 2.164(3) Å. The shortest oxygen distance involving H(12) is 2.591(4) Å which is clearly outside the range of what we consider a normal hydrogen bond (H···O smaller than 2.4 Å). The weak hydrogen bonding coupled with a fairly long Ca···OW(1) coordination of 2.464(3) Å evidently gives this water a rather labile position, and two secondary water sites OW(1A) and OW(5) are occurring with occupancies of 18(4) and 11(1)% respectively. The hydrogen atom H(12), with an occupancy of 88(2)%, is 0.84(2) Å away from OW(1A) but there are only diffuse hydrogens in the region where a second hydrogen position is expected. However, a hydrogen position inconsistent with H(12), labelled H(13), may be refined with an occupancy of 16(2)%. The H(13)−OW(1A) distance of 1.04(2) Å is reasonable. The large displacement parameters of OW(1A) indicate that there may be considerable statistical disorder in this oxygen site possibly coupled to a partial occupancy of OW(5). The hydrogen bonding is again weak with the strongest interaction being H(13)···O(16) = 2.02(2) Å; this hydrogen position is affected by a short Ca···H(13) contact. A possible H(12)···OW(5) bond of 2.12(1) Å may contribute to the stability of this configuration. However it is clear that the bonding situation around the alternative OW(1A) site is far from ideal. Water 5, on the other hand, although only occupied at the 12(1)% level, is well behaved with H(51)···OW(5) = 0.98(2) Å; H(52)···OW(5) = 0.97(3) Å with an H−O−H angle of 107(2)° and rather strong hydrogen bonding H(51)···O(1) = 1.87(2) Å; H(52)···O(10) = 2.36(3) Å in addition to the bond accepted from OW(1A). The slightly lower refined occupancy value of H(51) (9.8%) is due to the high correlation during the refinement with the thermal parameters, which also are unrealistically low. The molecule is, to our knowledge, the only water for which both O and H positions have been located in a zeolitic cage not coordinated to the cation. This situation may offer a satisfactory explanation for the low temperature endothermic peak observed in the DTA analysis of yugawaralite (Gottardi and Galli, 1985) which was previously attributed

to absorbed water (Leimer and Slaughter, 1969). The release of the water molecules can be rationalized in terms of a multi-step process: the hydrogen-bonded water molecules are released below 100° and the water molecules strongly coordinated to the Ca atom are released above 250°. The complete understanding of the dehydration process, however, has to await further structure studies at a few more stages of the dehydration.

Water OW(2) is completely characterized by one oxygen and two hydrogen positions. The internal water angle [106.0(3)°] is slightly larger than the value for a molecule in the gas phase (104.52°, Kuchitsu, 1971) and slightly smaller than the mean value of 107.2° tabulated from a survey of crystalline hydrates (Chiari and Ferraris, 1982). The hydrogen bonds are weak with: $H(21)\cdots O(6)$ = 2.338(3) Å and $H(22)\cdots O(15)$ = 2.054(3) Å.

Water OW(3) is strongly coordinated to Ca in the coordination "pentagon" and the oxygen position is therefore well anchored in the structure. One of the hydrogens H(33) has full occupancy with two alternative matching hydrogen sites [H(31) and H(32)] with $\sim 50\%$ occupancy. Both sites give reasonable water geometries with the $H(31)-OW(3)-H(33)$ angle = 108.2(5)° and $H(32)-OW(3)-H(33)$ angle = 103.7(5)°. The OW(3) distances to H(31), H(32) and H(33) are 0.902(5), 1.03(1) and 0.962(3) Å respectively. The only strong hydrogen bond involves atom H(33) which is hydrogen bonded to O(13) with a distance of 1.907(3) Å; H(31) and H(32), in comparison, experience oxygen contacts of 2.24(1) and 2.44(1) Å.

The water site 4 is occupied at the 89(5)% level. A reasonable geometry with a water angle of 105.9(4)° and $H(41)-OW(4)$ = 0.947(4) and $H(42)-OW(4)$ = 0.968(6) Å is observed. The hydrogen occupancies are 91(1) and 70(3)% with hydrogen bonding distances of $H(41)\cdots O(4)$ = 1.972(3) Å and $H(42)\cdots O(6)$ = 2.359(5) Å. The fate of this water molecule appears to be coupled to the situation around OW(1) with the alternative OW(1A) site forcing OW(4) to move to an alternative site, OW(4A), with an occupancy of 13(5)%. An alternative hydrogen site H(43) with an occupancy of 31(5)% is also readily refined. The occupancies for the two oxygens thus account for a full water molecule, and they further suggest that H(43) is attached about 18% to OW(4) and 13% to OW(4A). The reader should note that position H(43) is not well defined and the calculated $H(43)-OW(4)$ distance is unrealistic [0.55(3) Å]. The second hydrogen attached to OW(4A) cannot be located and is probably delocalized in a similar fashion as was discussed for OW(1A). Similar arrangements were observed for oxygen W(2) in brewsterite (Artioli et al., 1985).

Thermal motion

The B_{eq} for the silicon and aluminum atoms vary in the range 0.20(2)—0.26(2) Å², which can be compared to the range of 0.17(1)—0.20(1) Å²

Table 4. Distances between framework oxygen atoms and their nearest neighbors (in Å) with percentage of hydrogen bond

	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Al(1)	Al(2)	Ca	H-bond
O(1)	1.59						1.72			1.87 (10%)
O(2)		1.58					1.71			2.16 (83%)
O(3)			1.60				1.73		2.53	
O(4)	1.63	1.63								1.97 (91%)
O(5)	1.61		1.61							
O(6)		1.64	1.63							2.34 (100%)
										2.36 (70%)
O(7)		1.62					1.76		2.50	
O(8)	1.61				1.61					
O(9)			1.60					1.73	2.56	
O(10)				1.62	1.62					2.36 (12%)
O(11)				1.61		1.61				
O(12)				1.61				1.77	2.48	
O(13)					1.63	1.63				1.91 (100%)
O(14)					1.58			1.71		
O(15)						1.60		1.74		2.05 (100%)
O(16)				1.62		1.62				2.02 (16%)

An arbitrary cut-off at 2.40 Å was applied for hydrogen bonds

found in the 20 K study of scolecite (Kvick, Ståhl and Smith, 1985) and a range of $0.19(1)-0.20(1)$ Å^2 for low-albite at 13 K (Smith, Artioli and Kvick, 1985). This residual motion may be attributed to zero-point vibrations. The B_{eq} for Ca is, however, twice as large as the value found in scolecite [0.45(2) Å^2 vs. 0.24(2) Å^2] indicating that a statistical disorder is present. This results in a higher observed thermal motion for the cation as compared to the "zero-point motion" value found in the ordered scolecite structure.

Conclusions

Comparison of the data for various zeolites shows that the interaction between the framework and extra-framework species is rather complex. Although yugawaralite has an ordered framework, it has a complex set of water positions, some of which represent alternative sites. Based on the existing data for zeolites, it appears that the disorder of water molecules is greater as the degree of bonding to the framework oxygens decreases. As the size of a cavity increases, some water molecules near the center of the cavity can occupy alternative positions in the potential field in contrast to water molecules adjacent to the framework. Disorder of the Al/Si distribution in the framework may also cause positional disorder of water molecules, and particularly complex distributions can be expected in zeolites with large cavities (e.g., faujasite, Baur, 1964).

Table 4 qualitatively illustrates the charge compensation of the framework oxygens in yugawaralite as related to the distances from tetrahedral Si or Al sites, Ca coordination and hydrogen bonding. As found in previous studies (i.e. the fibrous zeolites, brewsterite, bikitaite), the oxygen atoms coordinated to the extra-framework cations do not serve as hydrogen bond acceptors. It also confirms the observation in the scolecite structure that oxygen atoms covalently bonded to two Si atom are reasonable hydrogen bond acceptors [O(4), O(6) and O(13)].

A detailed explanation of the multiple proton and oxygen positions in the presence of an ordered framework awaits a sophisticated analysis of the energy interactions between chemical species.

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