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Refinement of the structure of pectolite, $Ca_2NaHSi_3O_9$

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Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

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Auszug

Die Struktur-von Pektolith wurde auf Grund neuer Zählrohrdiffraktometer-Werte verfeinert. Aus den Verfeinerungsergebnissen und aus der Untersuchung der Ultrarot-Spektren wird auf eine Wasserstoffbindung zwischen den Atomen O(3) und O(4) geschlossen. Schwankungen der Si—O-Abstände werden in Termen von ($d\pi$—$p\pi$)-Bindungen diskutiert.

Abstract

The pectolite structure has been refined by least squares using new counter-diffractometer data. Evidence for hydrogen bonding between O(3) and O(4) is based on the refinement results and examination of infrared spectra. Variations in Si—O distances are discussed in terms of $d\pi$—$p\pi$ bonding between silicon and oxygen.

Introduction

The crystal structure of pectolite, $Ca_2NaHSi_3O_9$, was solved by BUERGER (1956) and subsequently refined by PREWITT and BUERGER (1963) using intensity data obtained from precession photographs. Since it was not possible to reduce R below 0.17 using these data (sets of $hk0$, $h0l$, and $0kl$ reflections) and because of the unusual interatomic distances which resulted from the refinement, intensity data have been recollected and refined by least squares. This is a report of the new refinement.

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Selection of material

A problem which arises when working with pectolite is that it is difficult to obtain an uniform single crystal. The mineral occurs in needles which tend to "feather" when broken. The feathered end of a broken crystal consists of many smaller, somewhat misoriented crystals which cause the major diffraction spots on a Weissenberg film to be streaked parallel to the needle (when the needle axis is the rotation axis). When using a Weissenberg counter diffractometer, this is especially troublesome because the long tails of the diffraction peaks make the background corrections rather difficult.

A large number of pectolite samples from several localities were searched for a crystal which would be small enough to be entirely bathed by the x-ray beam and which would produce negligible streaking in the diffraction photographs. This was not achieved but, instead, a long needle which would extend out of the x-ray beam at all equi-inclination angles, μ_e, was chosen. This crystal* was transparent and bounded by distinct (100) and (001) faces with b as the needle axis. The crystal had the following dimensions:

between (100) and $(\bar{1}00)$	.110 mm
between (001) and $(00\bar{1})$	.087 mm
needle length	3.68 mm.

Even with this crystal, which was photographed with each end of the needle out of the x-ray beam, the Weissenberg photographs showed a slight streaking of the diffraction spots, indicating some misorientation of different regions of the crystal. These were, however, by far the best photographs obtained from any of the pectolite crystals examined.

An interesting result of the search for good single crystals was that many of those examined were twins. When the members of the twin present in equal amounts, b-axis oscillation photographs showed an apparent mirror symmetry normal to b. This is discussed in PREWITT and BUERGER (1963) in a comparison of twinned pectolite and twinned wollastonite.

Apparently there are no published analyses of Bergen Hill pectolite. SCHALLER (1955), however, gives several analyses for pectolite including two for New Jersey pectolites, one from Paterson and the

* U.S. National Museum number 2452. Locality: Erie railroad cut, Bergen Hill, New Jersey (MANCHESTER, 1919).

Table 1

Compositions of two pectolites and the composition calculated from $Ca_2NaHSi_3O_9$ (data from SCHALLER, 1955)

	Paterson, N.J.	Franklin, N.J.	Calculated
CaO	33.20 wt. %	31.15 wt. %	33.74 wt. %
MgO	.12	2.57*	—
FeO	1.00	1.29	—
Na_2O	9.01	7.97	9.32
SiO_2	53.80	52.04	54.23
H_2O	2.94	3.07	2.71
etc.	—	2.12	—
	100.07	100.21	100.00

* Includes 0.26% ZnO.

other from Franklin. Both of these analyses are given in Table 1 along with the stoichiometric composition. It is likely that the Bergen Hill material has a composition more like the Paterson pectolite than the Franklin pectolite.

Unit cell

BUERGER (1956) published unit-cell data on pectolite which were obtained from precession films. An attempt was made in the present study to obtain precision Weissenberg photographs (BUERGER, 1942) from which measurements could be made and then refined with a least-squares program written by BURNHAM (1962*b*). Because of pectolite's needlelike habit, however, the only satisfactory photographs were ones taken with b as the rotation axis, thus giving refined values of only a^*, c^*, and β^*. Since these reciprocal-cell parameters

Table 2. *Pectolite cell parameters*

	BUERGER (1956)	Results of refinement*	Adopted cell
a	7.99 Å	7.9882 ± 0.0001 Å	7.988 Å
b	7.04	7.03996	7.040
c	7.02	7.0247 ± 0.0001	7.025
α	90.52°	90.520°	90.52°
β	95.18°	95.181°	95.18°
γ	102.47°	102.469°	102.47°
V			383.98 Å^3

* Refinement using precision-Weissenberg data (59 observations) and BURNHAM (1962*b*) program LCLSQ III.

compared very favorably with those of BUERGER, the old values for b^*, α^*, and γ^* were combined with the new for a^*, c^*, and β^* to give a slightly different direct cell. The old and new cells are given in Table 2. A test for piezoelectricity was negative, thus supporting the assumed space group, $P\bar{1}$.

Intensity collection

Three-dimensional x-ray intensities were collected with a Weissenberg counter diffractometer using Cu$K\alpha$ radiation. Ni foils at the x-ray tube and at the proportional-counter aperture were used in conjunction with a pulse-height analyzer to discriminate against unwanted radiation. The proportional detector was a standard Philips Xe-filled tube with preamplifier. The largest counting rate observed was about $9 \cdot 10^3$ c.p.s. Background was counted for 50 seconds on each side of a peak, and the total intensity plus background was obtained as the crystal rotated through a given angle, $\Delta\Phi$. The integrated intensity, I, was obtained from

$$I = C - (B_1 + B_2)T/100$$

where C is the total count, B_1 and B_2 are backgrounds, and T is the time required to collect C.

Structure factors were obtained using data reduction programs written by BURNHAM (1962*a*) and PREWITT (1960). This included a prismatic-crystal absorption correction in which path lengths for the zero level were computed for all reflections, and then divided by cos μ_e. In addition, the linear absorption coefficient, μ_l, was replaced by $\mu_l/\cos\ \mu_e$ to compensate for the increased scattering volume for upper levels due to the use of an "infinite" crystal. A total of 1357 structure factors were thus produced.

Refinement

All refinement was carried out using a full-matrix, least-squares refinement program written by PREWITT (1966). Starting coordinates were those given in PREWITT and BUERGER (1963). Form factors for atoms, assumed to be half-ionized, and corrections for the real and imaginary anomalous-scattering factors for Ca, were taken from International Tables (1962). After an initial cycle to adjust the scale factor, the initial R value ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$) was 0.174, which is, incidentally, about the same as was found using the original

Table 3. *Observed and calculated structure factors for pectolite*
Reflections excluded from refinement are marked with an asterisk (*)

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	1	17	15	6	0	5	24	24	-3	1	-7	4	3*	2	1	8	4	5	-7	2	0	21	21
		2	49	48			6	4	4			-6	4	0*	3	1	-8	17	18			1	37	37
		3	43	43	7	0	-6	5	4			-5	4	4			-7	8	8			2	32	32
		4	84	87			-5	9	13			-4	19	18			-6	19	18			3	23	23
		5	26	25			-4	28	29			-3	13	13			-5	2	2*			4	28	28
		6	63	66			-3	48	48			-2	31	30			-4	18	17			5	40	43
		7	29	28			-2	20	20			-1	2	2*			-3	8	6			6	15	16
		8	16	16			-1	7	7			0	42	41			-2	10	9	-6	2	-6	9	9
1	0	-8	27	27			0	10	9			1	11	12			-1	31	30			-5	2	5*
		-7	9	8			1	46	46			2	5	5			0	47	45			-4	27	28
		-6	54	54			2	17	18			3	32	31			1	6	6			-3	43	45
		-5	3	2*			3	33	33			4	26	25			2	42	41			-2	14	14
		-4	27	25			4	5	5			5	3	1*			3	9	8			-1	21	21
		-3	83	102			5	7	7			6	20	20			4	14	13			0	12	11
		-2	72	80	8	0	-5	48	47			7	4	4			5	2	2*			1	25	24
		-1	23	19			-4	10	10			8	20	20			6	8	7			2	9	9
		0	13	13			-3	14	14	-2	1	-8	17	18			7	4	3*			3	44	45
		1	7	4			-2	17	18			-7	3	1*	4	1	-7	22	22			4	7	8
		2	93	100			-1	29	28			-6	16	15			-6	15	15			5	3	1*
		3	8	8			0	19	19			-5	2	1*			-5	4	3			6	6	6
		4	54	54			1	35	35			-4	22	21			-4	27	27	-5	2	-6	4	5
		5	25	25			2	11	11			-3	2	1*			-3	16	16			-5	17	17
		6	19	19			3	22	22			-2	19	17			-2	5	5			-4	45	48
		7	2	1*	9	0	-3	31	32			-1	13	12			-1	27	25			-3	10	9
		8	17	17			-2	21	21			0	20	18			0	36	35			-2	35	36
2	0	-8	35	34			-1	36	35			1	39	37			1	16	14			-1	28	27
		-7	28	28			0	8	8			2	4	5			2	13	12			0	55	57
		-6	43	44			1	17	16			3	29	28			3	18	17			1	31	31
		-5	17	16	-9	1	-2	19	19			4	8	8			4	13	12			2	45	46
		-4	54	55			-1	9	9			5	9	9			5	17	17			3	23	23
		-3	35	33			0	2	2*			6	3	0*			6	9	9			4	4	4
		-2	64	69			1	3	3*			7	5	4			7	10	10			5	47	48
		-1	5	4			2	25	25			8	2	1*	5	1	-7	12	12			6	14	14
		0	45	45			3	10	10	-1	1	-8	20	20			-6	16	15			7	38	38
		1	71	73	-8	1	-4	7	7			-7	11	10			-5	17	15	-4	2	-7	26	26
		2	17	12			-3	4	3*			-6	29	27			-4	34	34			-6	45	47
		3	23	22			-2	14	14			-5	2	2*			-3	8	8			-5	20	19
		4	19	19			-1	2	1*			-4	34	33			-2	21	21			-4	18	18
		5	6	5			0	3	3*			-3	2	1*			-1	20	19			-3	3	2*
		6	57	59			1	1	0*			-2	32	30			0	21	21			-2	57	65
		7	5	4			2	2	1*			-1	10	9			1	19	17			-1	45	48
		8	30	30			3	2	2*			0	9	9			2	14	13			0	22	21
3	0	-8	11	11			4	4	4*			1	15	11			3	21	20			1	22	22
		-7	27	27			5	12	12			2	60	60			4	22	21			2	88	102
		-6	59	62	-7	1	-5	6	6			3	15	14			5	5	5			3	57	61
		-5	54	56			-4	18	18			4	3	2*			6	22	22			4	47	49
		-4	19	19			-3	8	8			5	13	13	6	1	-6	17	17			5	54	55
		-3	5	4			-2	4	4*			6	32	31			-5	17	17			6	24	25
		-2	56	55			-1	3	3*			7	5	5			-4	15	14			7	6	6
		-1	13	14			0	33	32			8	9	8			-3	3	2*	-3	2	-7	11	10
		0	74	77			1	3	3*	0	1	-8	13	13			-2	10	8			-6	20	20
		1	25	24			2	5	4			-7	8	8			-1	5	5			-5	15	15
		2	44	44			3	3	1*			-6	24	23			0	19	18			-4	44	46
		3	55	57			4	22	21			-5	16	15			1	0	1*			-3	34	33
		4	73	80			5	4	3*			-4	9	9			2	4	4			-2	48	50
		5	21	20			6	15	15			-3	26	26			3	4	3*			-1	68	81
		6	27	26	-6	1	-6	9	9			-2	66	67			4	14	14			0	54	58
		7	17	16			-5	3	1*			-1	3	0*			5	11	11			1	5	7
4	0	-8	6	7			-4	22	22			0	4	4*	7	1	-6	15	15			2	43	43
		-7	34	34			-3	6	5			1	3	1*			-5	8	7			3	59	62
		-6	5	4			-2	5	4			2	56	56			-4	8	7			4	12	11
		-5	14	13			-1	10	9			3	15	15			-3	5	5			5	2	2*
		-4	45	45			0	24	24			4	33	32			-2	10	10			6	26	26
		-3	64	68			1	13	13			5	9	9			-1	6	5			7	27	26
		-2	26	24			2	28	28			6	26	26			0	25	25			8	21	21
		-1	44	42			3	1	2*			7	15	15			1	7	6	-2	2	-7	18	18
		0	32	31			4	23	23			8	27	27			2	23	22			-6	63	67
		1	53	52			5	24	23	1	1	-8	6	7			3	3	3*			-5	15	15
		2	12	12			6	24	24			-7	1	2*			4	17	17			-4	101	113
		3	42	42			7	4	4*			-6	19	18	8	1	-4	2	1*			-3	45	45
		4	39	40	-5	1	-6	17	17			-5	10	10			-3	2	1*			-2	11	9
		5	12	11			-5	3	3*			-4	4	4*			-2	10	9			-1	3	2*
		6	18	17			-4	9	8			-3	10	10			-1	10	11			1	48	48
		7	42	41			-3	16	16			-2	28	25			0	5	5			2	35	33
5	0	-7	6	5			-2	14	13			-1	30	27			1	4	4			3	42	42
		-6	19	18			-1	9	9			0	15	13			2	7	7			4	37	36
		-5	66	72			0	15	14			1	11	10			3	4	4			5	19	19
		-4	30	30			1	4	4*			2	11	9	9	1	-2	17	16			6	56	59
		-3	63	68			2	13	12			3	8	7			-1	5	4			7	24	24
		-2	51	51			3	16	15			4	36	34			0	11	12			8	3	3*
		-1	41	41			4	19	18			5	3	2*	-9	2	-2	20	20	-1	2	-8	30	29
		0	42	42			5	12	12			6	10	11			-1	37	37			-7	20	19
		1	101	108			6	6	6			7	3	2*			0	30	30			-6	44	45
		2	72	76			7	24	24			8	12	12			1	33	33			-5	7	7
		3	12	11	-4	1	-7	11	11	2	1	-8	14	14			2	9	8			-4	47	46
		4	28	28			-6	15	14			-7	2	1*			3	52	52			-3	31	30
		5	35	34			-5	7	7			-6	7	6	-8	2	-3	52	53			-2	64	66
		6	41	40			-4	20	20			-5	2	1*			-2	3	3*			-1	11	9
6	0	-7	39	37			-3	13	13			-4	21	19			-1	15	15			0	16	14
		-6	5	7			-2	34	34			-3	37	36			0	2	2*			1	29	26
		-5	48	47			-1	7	6			-2	13	13			1	49	50			2	18	14
		-4	12	12			0	48	47			-1	27	25			2	16	16			3	27	26
		-3	44	43			1	28	27			0	34	31			3	19	19			4	25	25
		-2	8	6			2	14	13			1	2	1*			4	4	4*			5	15	14
		-1	73	75			3	16	15			2	33	30			5	38	37			6	26	25
		0	12	11			4	29	29			3	3	3*	-7	2	-5	56	52			7	13	13
		1	24	23			5	8	7			4	13	12			-4	3	3*			8	25	24
		2	39	40			6	13	12			5	2	1*			-3	4	3*	0	2	-8	27	26
		3	34	32			7	13	13			6	15	15			-2	36	37			-7	18	17
		4	33	33			8	19	19			7	2	2*			-1	74	82			-6	26	26

Table 3. *(Continued)*

h	k	l	F_o	F_c
0	2	-5	16	15
		-4	26	26
		-3	28	26
		-2	21	18
		-1	31	26
		0	15	13
		1	12	11
		2	67	65
		3	33	32
		4	50	50
		5	4	4
		6	43	43
		7	19	19
		8	29	28
1	2	-8	3	3*
		-7	22	23
		-6	59	62
		-5	21	20
		-4	38	39
		-3	38	38
		-2	38	35
		-1	48	46
		1	3	2*
		2	16	15
		3	44	43
		4	105	112
		5	16	16
		6	63	67
		7	20	20
2	2	-8	23	22
		-7	31	31
		-6	25	25
		-5	3	3*
		-4	11	11
		-3	58	62
		-2	46	45
		-1	5	2
		0	59	58
		1	79	81
		2	50	49
		3	37	36
		4	46	47
		5	16	15
		6	18	19
		7	11	11
3	2	-7	9	9
		-6	23	23
		-5	54	57
		-4	46	49
		-3	60	62
		-2	92	103
		-1	24	23
		0	20	19
		1	49	48
		2	65	67
		3	3	2*
		4	18	18
		5	20	20
		6	44	45
		7	24	24
4	2	-7	37	37
		-6	15	15
		-5	49	51
		-4	5	4
		-3	16	17
		-2	48	49
		-1	32	33
		0	56	56
		1	28	28
		2	35	35
		3	7	6
		4	47	48
		5	17	17
		6	5	5
5	2	-6	3	3*
		-5	3	2*
		-4	8	8
		-3	46	47
		-2	8	7
		-1	29	29
		0	12	12
		1	22	21
		2	15	14
		3	47	48
		4	27	28
		5	4	4*
		6	6	6
6	2	-6	12	13
		-5	44	47
		-4	29	29
		-3	27	26
		-2	29	29
		-1	38	38
		0	22	22
		1	77	81
		2	40	40
		3	2	1*
		4	3	2*
		5	57	53
7	2	-5	39	38
		-4	5	5
		-3	17	17
		-2	13	13
		-1	56	57
		0	5	5
		1	19	18
		2	3	4*
		3	53	52
8	2	-3	54	53
		-2	12	11
		-1	35	33
		0	29	29
		1	41	39
		2	20	20
-9	3	-1	4	4
		0	29	29
		1	21	20
		2	6	5
		3	8	7
-8	3	-3	11	11
		-2	8	7
		-1	3	2*
		0	27	26
		1	20	17
		2	39	38
		3	11	10
		4	6	5
-7	3	-4	6	5
		-3	14	14
		-2	13	13
		-1	5	5
		0	36	36
		1	4	3*
		2	5	4
		3	32	32
		4	20	19
		5	2	1*
		6	9	9
-5	3	-6	23	22
		-5	6	6
		-4	44	46
		-3	24	24
		-2	24	23
		-1	6	6
		0	25	24
		1	12	12
		2	17	17
		3	5	5
		4	28	28
		5	11	11
		6	27	26
		7	1	0*
-4	3	-7	12	12
		-6	16	16
		-5	5	4
		-4	25	25
		-3	17	17
		-2	13	12
		-1	18	17
		0	8	7
		1	26	25
		2	10	10
		3	4	4
		4	21	20
		5	15	14
		6	5	5
		7	23	23
-3	3	-7	8	8
		-6	6	6
		-5	4	4*
		-4	8	8
		-3	29	29
		-2	7	6
		-1	3	3*
		0	9	8
		1	13	12
		2	61	60
		3	10	10
		4	18	17
		5	13	13
		6	2	1*
		7	8	8
-2	3	-7	2	1*
		-6	17	16
		-5	15	14
		-4	5	5
		-3	14	14
		-2	46	45
		-1	38	36
-2	3	0	8	8
		1	6	6
		2	47	46
		3	30	29
		4	35	35
		5	18	17
		6	14	13
		7	29	29
-1	3	-7	17	16
		-6	29	29
		-5	21	21
		-4	22	22
		-3	10	9
		-2	37	35
		-1	14	14
		0	5	5
		1	9	8
		2	12	11
		3	31	30
		4	33	33
		5	23	22
		6	9	8
		7	11	11
0	3	-7	11	10
		-6	2	0*
		-5	19	18
		-4	39	39
		-3	35	34
		-2	26	25
		-1	18	16
		0	9	9
		1	43	40
		2	52	51
		3	5	5
		4	2	1*
		5	17	17
		6	39	38
		7	10	10
1	3	-7	21	21
		-6	14	13
		-5	4	4
		-4	20	19
		-3	4	4
		-2	68	68
		-1	13	13
		0	6	6
		1	16	16
		2	28	27
		3	5	4
		4	17	16
		5	9	9
		6	9	9
		7	9	8
2	3	-7	10	10
		-6	3	3*
		-5	22	21
		-4	20	20
		-3	13	12
		-2	23	23
		-1	2	0*
		0	9	9
		1	12	11
		2	29	29
		3	33	33
		4	6	6
		5	4	4*
		6	2	1*
		7	2	1*
3	3	-7	13	13
		-6	14	14
		-5	8	8
		-4	34	34
		-3	6	6
		-2	22	21
		-1	31	29
		0	20	19
		1	9	8
		2	14	14
		3	3	3*
		4	50	52
		5	3	2*
		6	30	30
4	3	-6	17	16
		-5	9	9
		-4	16	16
		-3	22	21
		-2	0	0*
		-1	4	3*
		0	28	27
		1	7	6
		2	32	32
		3	24	24
		4	22	21
		5	10	9
		6	26	26
5	3	-6	1	1*
		-5	0	1*
		-4	9	9
		-3	28	28
		-2	15	16
5	3	-1	4	3*
		0	30	30
		1	4	8
		2	12	12
		3	14	13
		4	2	2*
		5	27	27
6	3	-5	10	10
		-4	8	8
		-3	5	5
		-2	32	32
		-1	34	34
		0	26	26
		1	4	4*
		2	4	3*
		3	11	10
		4	13	13
7	3	-4	13	13
		-3	18	18
		-2	17	17
		-1	11	11
		0	22	22
		1	7	6
		2	4	4*
-9	4	0	11	10
		1	35	33
		2	13	13
-8	4	-3	26	25
		-2	7	7
		-1	26	25
		0	14	14
		1	12	12
		2	9	8
		3	39	38
		4	31	29
-7	4	-4	20	19
		-3	28	27
		-2	15	15
		-1	3	1*
		0	12	11
		1	55	56
		2	5	5
		3	23	23
		4	7	6
		5	36	34
-6	4	-5	43	41
		-4	12	11
		-3	7	6
		-2	58	61
		-1	64	68
		0	9	9
		1	45	45
		2	46	47
		3	46	47
		4	29	29
		5	54	54
		6	16	16
-5	4	-6	5	5
		-5	15	13
		-4	28	26
		-3	41	43
		-2	20	19
		-1	42	42
		0	12	11
		1	27	27
		2	15	14
		3	37	37
		4	11	9
		5	5	4
		6	5	5
-4	4	-6	28	27
		-5	6	6
		-4	62	67
		-3	30	29
		-2	18	17
		-1	9	8
		0	46	47
		1	32	31
		2	57	60
		3	7	7
		4	20	20
		5	29	29
		6	37	37
-3	4	-6	35	34
		-5	17	16
		-4	11	10
		-3	20	19
		-2	44	45
		-1	21	21
		0	17	17
		1	4	4
		2	47	48
		3	35	35
		4	38	38
		5	31	30
-2	4	-7	5	4
		-6	16	15
-2	4	-5	5	4
		-4	22	20
		-3	11	10
		-2	52	53
		-1	18	18
		0	9	8
		1	8	7
		2	69	76
		3	37	36
		4	9	8
		5	14	12
		6	34	33
		7	17	17
-1	4	-7	20	20
		-6	56	56
		-5	8	8
		-4	81	85
		-3	26	25
		-2	35	33
		-1	39	37
		1	38	40
		2	37	37
		3	28	27
		4	76	80
		5	11	10
		6	52	53
		7	24	23
0	4	-7	22	21
		-6	36	34
		-5	5	4
		-4	6	6
		-3	34	34
		-2	74	78
		-1	15	14
		0	13	13
		1	15	15
		2	51	51
		3	13	12
		4	20	19
		5	6	5
		6	11	12
		7	3	2*
1	4	-7	28	26
		-6	27	26
		-5	32	31
		-4	40	40
		-3	40	41
		-2	49	51
		-1	4	4
		0	15	14
		1	20	19
		2	47	47
		3	18	17
		4	13	13
		5	20	20
		6	31	31
2	4	-7	23	22
		-6	39	39
		-5	32	32
		-4	21	21
		-3	3	3*
		-2	63	66
		-1	32	32
		0	50	48
		1	10	10
		2	14	14
		3	25	25
		4	62	65
		5	5	5
		6	29	29
3	4	-6	4	4*
		-5	3	1*
		-4	10	9
		-3	39	41
		-2	16	15
		-1	35	35
		0	11	11
		1	43	42
		2	19	18
		3	48	50
		4	29	28
		5	15	14
		6	1	0*
4	4	-6	11	11
		-5	56	58
		-4	32	33
		-3	49	51
		-2	46	46
		-1	47	46
		0	6	5
		1	67	68
		2	65	65
		3	5	5
		4	12	11
		5	43	41
5	4	-5	41	40
		-4	4	3*
		-3	14	14
		-2	11	11
		-1	61	61

Table 3. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
5	4	0	9	8	-4	5	6	22	22	1	5	5	4	3*	-5	6	-1	30	30	1	6	-2	36	37
		1	6	6	-3	5	-6	9	9				6	19			0	6	5			-1	24	23
		2	14	14			-5	10	10	2	5	-6	13	13			1	36	37			0	27	26
		3	25	24			-4	3	2*			-5	3	3*			2	47	49			1	27	27
		4	19	18			-3	5	5			-4	26	26			3	29	28			2	28	28
6	4	-4	30	30			-2	2	1*			-3	13	13			4	18	18			3	16	15
		-3	45	44			-1	23	23			-2	20	20	-4	6	-5	14	14			4	27	27
		-2	11	11			0	19	19			-1	35	35			-4	28	26	2	6	-5	46	45
		-1	18	17			1	42	42			0	36	36			-3	12	11			-4	19	18
		0	12	13			2	29	28			1	6	5			-2	32	32			-3	34	34
		1	26	26			3	15	14			2	49	52			-1	29	29			-2	47	50
		2	6	5			4	7	7			3	13	13			0	22	21			-1	36	36
		3	29	29			5	17	17			4	4	4			1	14	13			0	5	4
7	4	-2	7	7			6	2	1*			5	10	10			2	35	35			1	31	31
		-1	39	38	-2	5	-6	8	8	3	5	-5	7	7			3	32	33			2	59	62
		0	11	10			-5	1	1*			-4	12	13			4	5	5			3	13	13
-8	5	-2	3	3*			-4	38	38			-3	27	28			5	25	25			4	9	9
		-1	9	9			-3	10	10			-2	2	2*	-3	6	-5	8	8	3	6	-4	25	24
		0	27	27			-2	16	15			-1	17	16			-4	64	63			-3	6	6
		1	18	18			-1	7	6			0	10	10			-3	32	32			-2	25	24
		2	10	10			0	14	15			1	32	32			-2	27	27			-1	30	30
		3	2	2*			1	13	13			2	4	3*			-1	32	33			0	15	15
-7	5	-3	2	1*			2	45	46			3	30	31			0	61	65			1	4	3*
		-2	2	2*			3	25	25			4	3	4*			1	33	33			2	19	18
		-1	2	1*			4	15	15			5	14	15			2	35	36			3	9	9
		0	21	21			5	2	2*	4	5	-5	28	27			3	13	13	4	6	-5	17	18
		1	16	15			6	43	42			-4	20	20			4	33	33			-4	11	11
		2	27	27	-1	5	-6	32	31			-3	5	5			5	14	14			-1	16	16
		3	12	12			-5	1	1*			-2	24	24	-2	6	-5	19	18			0	13	14
		4	21	21			-4	7	6			-1	27	27			-4	4	3*			1	15	15
-6	5	-4	2	2*			-3	26	25			0	16	16			-3	8	8			2	2	1*
		-3	32	33			-2	58	59			1	6	6			-2	37	37	-5	7	0	6	5
		-2	4	4			-1	1	1*			2	4	3*			-1	3	2*	-4	7	-1	15	14
		-1	14	13			0	7	7			3	24	25			0	18	17			0	12	12
		0	0	0*			1	7	7			4	26	25			1	9	10			1	3	2*
		1	15	15			2	45	46	5	5	-4	22	22			2	26	27			2	33	32
		2	14	13			3	6	6			-3	16	16			3	3	3*	-3	7	-2	32	32
		3	17	16			4	35	35			-2	5	5			4	13	14			-1	2	1*
		4	7	6			5	3	3*			-1	9	9			5	16	15			0	21	21
		5	13	12			6	17	17			0	23	22	-1	6	-5	16	16			1	11	11
-5	5	-5	14	14	0	5	-6	24	23			1	4	3*			-4	16	16			2	25	24
		-4	6	6			-5	11	11			2	3	3*			-3	6	5	-2	7	-2	7	6
		-3	16	16			-4	17	16			3	14	14			-2	30	31			-1	19	19
		-2	34	35			-3	10	10	6	5	-2	6	6			-1	14	14			0	12	12
		-1	19	19			-2	6	6			-1	15	15			0	21	20			1	13	13
		0	30	30			-1	35	35			0	11	11			1	7	7			2	5	5
		1	30	30			0	3	1*			1	22	22			2	36	36	-1	7	-3	18	17
		2	26	26			1	13	13	-7	6	-2	2	1*			3	9	9			-2	10	9
		3	15	15			2	8	8			-1	14	13			4	8	7			-1	4	3*
		4	21	21			3	19	18			0	13	13			5	26	26			0	32	31
		5	11	11			4	25	25			1	11	10	0	6	-5	15	15			1	7	7
		6	3	3*			5	4	3*			2	11	11			-4	38	38			2	23	23
-4	5	-6	10	9			6	5	5			3	12	12			-3	8	7	0	7	-2	40	39
		-5	5	5	1	5	-6	16	16	-6	6	-3	14	14			-2	34	36			-1	7	8
		-4	19	18			-5	16	15			-2	18	17			-1	28	28			0	5	3
		-3	25	26			-4	16	15			-1	8	9			0	66	65			1	13	12
		-2	38	40			-3	31	32			0	17	16			1	34	34			2	31	32
		-1	9	9			-2	27	27			1	28	28			2	31	32	1	7	-1	15	14
		0	45	47			-1	21	21			2	24	22			3	32	32			0	10	10
		1	10	10			0	44	44			3	14	14			4	59	59			1	11	11
		2	9	9			1	14	14			4	28	27			5	9	9					
		3	37	37			2	25	25	-5	6	-4	6	6	1	6	-5	18	18					
		4	26	25			3	7	8			-3	15	14			-4	4	3*					
		5	15	14			4	24	24			-2	54	57			-3	33	35					

BUERGER data and the same atom coordinates. In the next two cycles, atom positional coordinates were varied, and a weighting scheme suggested by CRUICKSHANK *et al.* (1961) was incorporated into the program where

$$\sqrt{w} = 1/(a + F_o + cF_o^2)^{\frac{1}{2}}.$$

In this expression, $a = 2F_{\min}$ and $c = 2/F_{\max}$. At the end of the second cycle the R was 0.085.

In the next cycle, temperature factors, in addition to atom coordinates, were varied, resulting in an R of 0.079. There were, however, negative temperature factors for atoms Si(1), Si(2), Si(3), and O(9). Another cycle was run in which unobserved reflections were rejected from the refinement, but included in the R value. The R was reduced

to 0.075, and all temperature factors refined to positive values. A further cycle using all 1357 reflections but with the rejection test, left R at 0.075.

It was noted that for the strongest reflections, the calculated value was much larger than the observed, indicating the need for a secondary-extinction correction. A correction to the observed intensities proposed by ZACHARIASEN (1963) was made using

$$I_c = I_o/(1-tI_o),$$

where t is a very small number determined by comparing the I_o and I_c. The need for this correction was supported by the fact that removing the two strongest reflections (120 and $\bar{2}20$) reduced R to 0.070, and that removing the twenty strongest reduced R to about 0.05.

After the correction for the extinction was made, the refinement was concluded using all reflections and assuming anisotropic temperature factors. This last cycle included H between O(3) and O(4) as described in the section on hydrogen bonding. The final R for all reflections was 0.039.

Table 3 is a list of observed and calculated structure factors for pectolite, Table 4*a* lists the final atom coordinates and equivalent

Table 4*a*. *Final pectolite atom coordinates and isotropic temperature factors**

Atom	x	y	z	B
Ca(1)	.8548	.5936	.1449	.41 Å^2
Ca(2)	.8467	.0839	.1405	.39
Na	.5524	.2596	.3433	1.16
H	.162	.625	.530	2.5
Si(1)	.2185	.4015	.3374	.21
Si(2)	.2150	.9544	.3440	.22
Si(3)	.4505	.7353	.1447	.19
O(1)	.6526	.7871	.1280	.35
O(2)	.3300	.7043	−.0535	.31
O(3)	.1864	.4960	.5395	.34
O(4)	.1783	.8465	.5411	.44
O(5)	.0633	.3860	.1733	.34
O(6)	.0600	.8961	.1768	.38
O(7)	.3992	.5349	.2720	.36
O(8)	.3955	.9092	.2746	.39
O(9)	.2628	.1908	.3851	.32

* Calculated standard errors are 0.0001 for x, y, and z of Ca and Si, 0.0002 for Na, and 0.0004 for O. H was not refined. The B's are equivalent isotropic values (HAMILTON, 1959).

Table 4*b*. *Final pectolite anisotropic temperature factors**

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca(1)	18(1)	13(2)	26(2)	−1(1)	4(1)	−1(1)	.43	.25	.51	−.02	.09	−.02
Ca(2)	16(1)	14(2)	26(2)	0(1)	4(1)	−1(1)	.39	.27	.51	.00	.09	−.02
Na	22(3)	76(4)	73(3)	−4(3)	14(2)	0(3)	.53	1.44	1.43	−.09	.30	.00
Si(1)	10(2)	4(2)	14(2)	−2(1)	−2(1)	−1(2)	.24	.08	.27	−.04	−.04	−.02
Si(2)	10(2)	6(3)	14(2)	−1(1)	−1(1)	−3(2)	.24	.11	.27	−.02	−.02	−.06
Si(3)	3(2)	11(3)	13(2)	−3(1)	0(1)	0(2)	.07	.21	.25	−.06	.00	.00
O(1)	11(4)	13(6)	27(6)	0(4)	6(4)	3(5)	.27	.25	.53	.00	.13	.06
O(2)	13(4)	25(7)	4(5)	−2(4)	−2(4)	−1(4)	.31	.47	.08	−.04	−.04	.02
O(3)	23(4)	14(6)	11(5)	9(4)	−2(4)	−4(4)	.56	.27	.22	.19	−.04	−.08
O(4)	30(5)	16(6)	12(5)	−2(4)	4(4)	−2(5)	.72	.30	.23	−.04	.09	−.04
O(5)	15(4)	18(7)	13(5)	−2(4)	−1(4)	3(5)	.36	.34	.25	−.04	−.02	.06
O(6)	11(4)	20(7)	21(5)	−2(4)	−6(4)	−8(5)	.27	.38	.41	−.04	−.13	−.15
O(7)	7(4)	12(6)	30(5)	−7(4)	0(4)	7(5)	.17	.23	.59	−.15	.00	.13
O(8)	3(4)	16(6)	37(6)	−5(4)	1(4)	−15(5)	.07	.30	.72	−.11	.02	−.29
O(9)	13(4)	6(7)	24(5)	−2(4)	−3(4)	−2(5)	.31	.11	.47	−.04	−.07	−.04

* All β's have been multiplied by 10^4. Standard errors are in parentheses. The B_{ij}'s are analogous to the isotropic B (CRUICKSHANK, 1965).

isotropic temperature factors, and Table 4*b* lists the anisotropic temperature factors in two different but equivalent forms, β's and B's.

Structure

Figure 1 shows the pectolite structure projected along *b*. This diagram can be used to identify the atoms in Fig. 2 which is a projection of a portion of the pectolite structure onto (101). The structure is made up of double columns or bands of edge-sharing Ca octahedra which extend in the *b* direction. Adjoining bands are linked by single silicate chains and irregularly coordinated Na atoms. The silicate chains share only corners with the Ca octahedra, but five edges of the Na polyhedron are shared with the silicate tetrahedra. This is in contrast to the wollastonite structure where the Ca octahedra are found in bands which are three edge-sharing octahedra wide with the Ca(1) and Ca(2) octahedra each sharing one edge with the Si(3) tetrahedron, and the Ca(3) octahedron sharing edges with only the other octahedra.

Figures 3*a* and 3*b* show the sections of the electron density containing the cations. These sections were computed using data from

the last cycle of refinement, and were contoured using a Cal-Comp plotter.

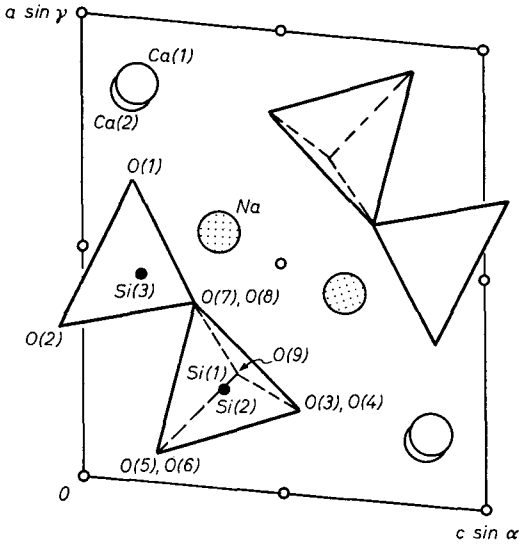

Fig. 1. Pectolite structure projected along b

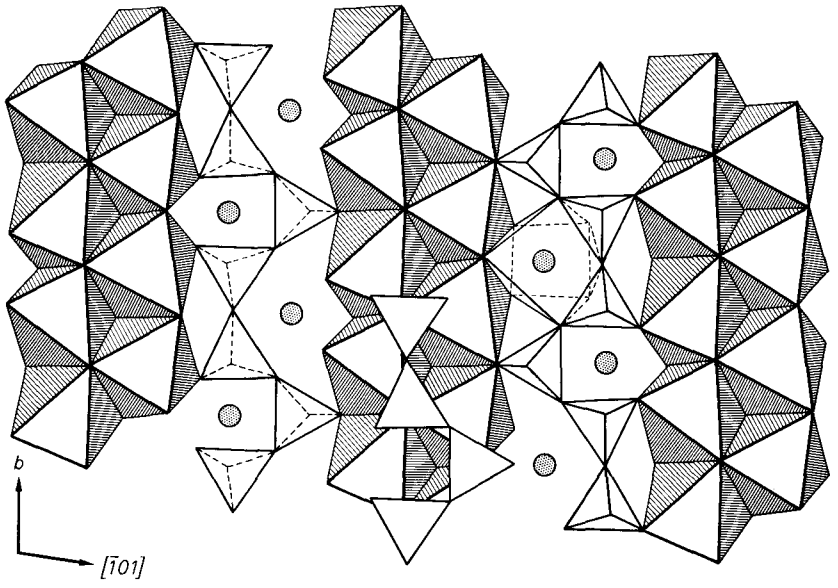

Fig. 2. Projection of a portion of an octahedral layer of the pectolite structure onto (101). The shaded circles represent sodium ions, the octahedra contain calcium ions, and the tetrahedra contain silicon ions

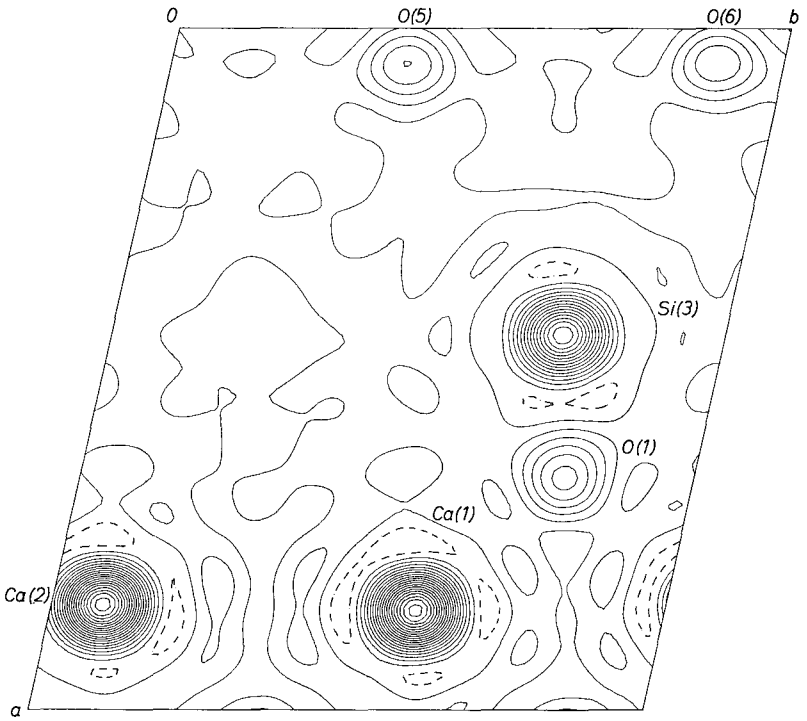

Fig. 3*a*. Electron-density section, $\varrho\,(x, y, .14)$ containing Ca(1), Ca(2), Si(3), O(5), and O(6). The contour interval is $3e/\text{Å}^3$. The $-3e$ contour is dashed

Table 5 is a compilation of the important interatomic distances and interbond angles in pectolite, computed using the coordinates of Table 4. Each silicon is coordinated by four oxygen atoms, the average Si—O distance being 1.630 Å. The range from the smallest (1.592 Å) to the largest (1.676 Å) Si—O distance is 0.084 Å. Ca(1) and Ca(2) are octahedrally coordinated by six oxygens at average distances of 2.368 Å and 2.360 Å, respectively. Na is surrounded by six oxygens at an average distance of 2.443 Å with two more at 2.977 Å and 3.007 Å. If all eight oxygens are considered, the Na polyhedron is intermediate between a square antiprism and a D_{2d} dodecahedron.

Hydrogen bonding

PREWITT and BUERGER (1963) stated that the most probable location for H in the pectolite structure is between O(3) and O(4) which are separated by only 2.482 Å. This is a reasonable assumption

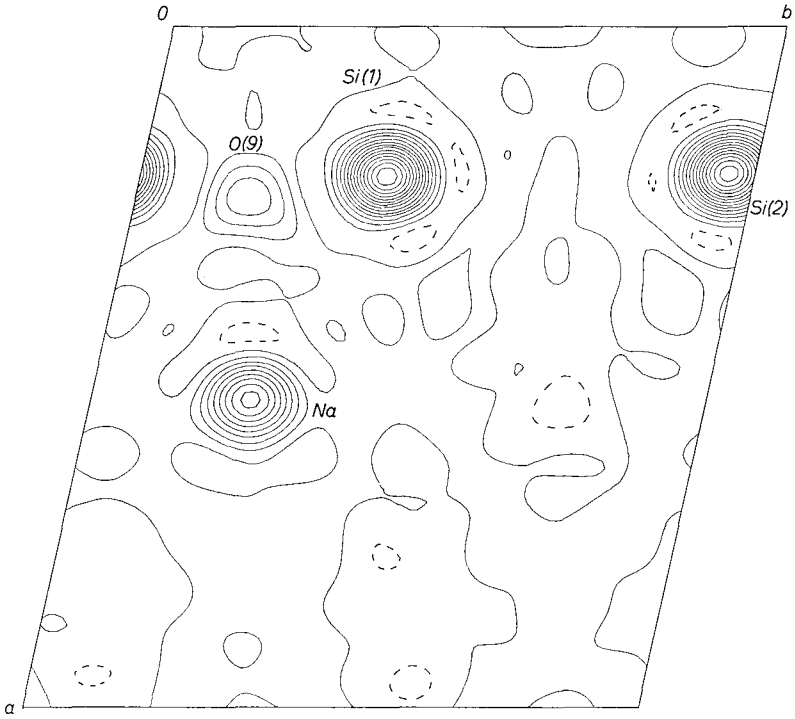

Fig. 3*b*. Electron-density section, $\varrho\,(x, y, .34)$ containing Na, Si(1), Si(2), and O(9). Contours are as in Fig. 3*a*

because, if H is ignored, O(3) and O(4) are "undersaturated" oxygens according to Pauling's electrostatic valence rule. From Table 6 it can be seen that each oxygen is coordinated to only three cations which contribute to a formal change balance of $\frac{2}{6} + \frac{1}{6} + 1 = +1\frac{1}{2}$, leaving a residual charge of $+\frac{1}{2}$ on each oxygen to be accounted for by hydrogen.

In an attempt to confirm the hydrogen location, electron-density and difference-Fourier sections containing O(3) and O(4) were calculated and examined for possible hydrogen peaks. Although the O(3)—O(4) distance suggests a symmetrical hydrogen bond (NAKAMOTO, MARGOSHES and RUNDLE, 1955), the only peak between O(3) and O(4) on the difference map occurs closer to O(3) and slightly to one side of the line joining O(3) and O(4). The distances and angles are 0.97 Å for O(3)—H, 1.54 Å for O(4)—H and 163° for O(3)—H—O(4). Even though this seems reasonable, it should be noted that this peak

Table 5. *Interatomic distances and interbond angles**

Ca(1)	O(1)	2.323 Å
	O(2)	2.336
	O(3)	2.343
	O(5)	2.383
	O(5′)	2.438
	O(6)	2.385
	O(av)	2.368
Ca(2)	O(1)	2.313
	O(2)	2.315
	O(4)	2.321
	O(5)	2.429
	O(6)	2.370
	O(6′)	2.409
	O(av)	2.360
Na	O(2)	2.311
	O(3)	2.471
	O(4)	2.498
	O(7)	2.536
	O(7′)	3.007
	O(8)	2.534
	O(8′)	2.977
	O(9)	2.305
	O(av)	2.443 [excluding O(7′) and O(8′)]
Si(1)	O(3)	1.627
	O(5)	1.600
	O(7)	1.648
	O(9)	1.629
	O(av)	1.626
Si(2)	O(4)	1.605
	O(6)	1.609
	O(8)	1.656
	O(9)	1.642
	O(av)	1.628
Si(3)	O(1)	1.592
	O(2)	1.604
	O(3)	1.673
	O(8)	1.676
	O(av)	1.636
H	O(3)	.970
	O(4)	1.537
	Na	2.341

Table 5. *(Continued)*

Around Si(1)		
O(3)	O(5)	2.714 Å
	O(7)	2.623
	O(9)	2.610
O(5)	O(7)	2.686
	O(9)	2.683
O(7)	O(9)	2.596
Around Si(2)		
O(4)	O(6)	2.699
	O(8)	2.642
	O(9)	2.647
O(6)	O(8)	2.687
	O(9)	2.647
O(8)	O(9)	2.585
Around Si(3)		
O(1)	O(2)	2.711
	O(7)	2.669
	O(8)	2.673
O(2)	O(7)	2.658
	O(8)	2.658
O(7)	O(8)	2.642
Other distances		
O(3)	O(4)	2.482
	O(4′)	4.559
O(5)	O(6)	3.596
O(5)	O(6′)	3.444
O(2)	O(5)	3.273
O(2)	O(6)	3.308
O(1)	O(5)	3.624
	O(6)	3.687
Ca(1)	Ca(2)	3.575
	Ca(2′)	3.466
	Na	3.394
Ca(2)	Na	3.304

Table 5. *(Continued)*

Na	Na	4.292 Å
Si(1)	Si(2)	3.142
	Si(3)	3.069
Si(2)	Si(3)	3.093
Si(1)—O(9)—Si(2)		147.8°
Si(1)—O(7)—Si(3)		135.0°
Si(2)—O(8)—Si(3)		136.4°
O(3)—H—O(4)		163.2°

* Calculated errors are 0.003 Å for Ca—O, Na—O, and Si—O, 0.004 Å for O—O and Na—Na, and 0.001 Å for Ca—Ca and Si—Si distances.

Table 6. *Oxygen coordination in pectolite*

O(1)	Ca(1)	2.323 Å	O(6)	Ca(1)	2.385 Å
	Ca(2)	2.313		Ca(2)	2.370
	Si(3)	1.592		Ca(2′)	2.409
				Si(2)	1.609
O(2)	Ca(1)	2.336			
	Ca(2)	2.315	O(7)	Na	2.536
	Na	2.311		Na′	3.007
	Si(3)	1.604		Si(1)	1.648
				Si(3)	1.673
O(3)	Ca(1)	2.343			
	Na	2.471	O(8)	Na	2.534
	H	.970		Na	2.977
	Si(1)	1.627		Si(2)	1.656
				Si(3)	1.676
O(4)	Ca(2)	2.321			
	Na	2.498	O(9)	Na	2.305
	H	1.537		Si(1)	1.629
	Si(2)	1.605		Si(2)	1.642
O(5)	Ca(1)	2.383			
	Ca(1)	2.438			
	Ca(2)	2.429			
	Si(1)	1.600			

is not much above the general background, and must be regarded with caution.

After it became apparent that the x-ray results were inconclusive, infrared spectra were recorded, assuming from the small oxygen—

oxygen distance that an absorption band due to OH stretching would occur at about 1700 cm^{-1} (NAKAMOTO *et al.*, 1955). No evidence for this was found, however. Recently, RYALL and THREADGOLD (1966) published infrared spectra for several pyroxenoids, including pectolite. They confirmed that there is no absorption band in the expected region, but pointed out a rather strong band at 1395 cm^{-1}, and a weak one at 1610 cm^{-1}. Re-examination of the author's infrared spectra confirms the presence of the bands reported by RYALL and THREADGOLD. They attributed the former to an OH bending mode, and the latter to absorbed water. It appears, therefore, that although the infrared data do not confirm the presence of a symmetrical O—H—O bond, it is probable that hydrogen is associated with O(3) and O(4) and that the infrared evidence is consistent with the x-ray results.

Discussion

It is interesting to examine the pectolite structure, keeping in mind CRUICKSHANK's (1961) discussion of d—p π-bonding in compounds containing tetrahedrally coordinated silicon, phosphorus, sulfur, and chlorine. In this discussion CRUICKSHANK proposed that π overlap between d_{z^2} and $d_{x^2-y^2}$ orbitals of the central atom, and p orbitals of the ligands could explain the variations in bond lengths observed in many of these compounds. CRUICKSHANK (1961) computed π-bond orders which might be expected for a chain or ring of tetrahedra, and from these predicted bridge and non-bridge M—O distances for the S_3O_9 ring and the SiO_3^{-2} chain. MCDONALD and CRUICKSHANK (1967*a*, 1967*b*) have convincingly applied the d—p π bonding argument to S_3O_9, and found that the experimental results correspond closely to the theory. However, the agreement for Na_2SiO_3 is not as satisfactory. It is apparent that other considerations must be taken into account for the latter compound and for pectolite as well.

There are two differences between these silicates and S_3O_9 which should be noted. The first is that, although the oxygens are approximately in a closest-packed arrangement, the average O—O distance in the silicates is about 0.2 Å greater than in S_3O_9. This means that the angle [T—O—T] between tetrahedral sites (T) is always larger in the silicates. For example, in a metasilicate chain based on closest packing of oxygen spheres of 1.32 Å radius, and a resulting T—O distance of 1.617 Å, the T—T distance between neighboring tetrahedra is 3.048 Å, and the T—O—T angle is 141°. LIEBAU (1961) found that

the average Si—O—Si angle is about 140° in silicates, and about 120° in sulfates.

MCDONALD and CRUICKSHANK (1967*b*) found an average S—O—S angle in S_3O_9 of 121°. The second difference is that in the silicates, cations other than Si also influence the Si—O bond lengths.

Using the π-bond orders calculated for S_3O_9 with S—O—S angles of 120°, CRUICKSHANK (1961) predicted bridge Si—O distances of 1.70 Å and non-bridge distances of 1.56 Å for a metasilicate chain or ring with a Si—O—Si angle of 120°. In a similar way the bond orders can be calculated for a chain in which the Si—O—Si angles are 180°. These bond orders are $\frac{3}{7}$ and $\frac{4}{7}$, corresponding to 1.65 Å and 1.58 Å for bridge and nonbridge distances, respectively. Extrapolating versus the cosine of the angle to 140°, gives 1.67 Å and 1.57 Å. MCDONALD and CRUICKSHANK (1967*a*) find mean distances of 1.67 Å and 1.59 Å for Na_2SiO_3, and the averages for pectolite are 1.65 Å and 1.61 Å. MCDONALD and CRUICKSHANK remark that the dimensions of the hypothetical isolated chain cannot be realized in these structures, but the evidence is that π bonding is important.

The effect of other cations on the Si—O distances is difficult to assess quantitatively but, in general, one would think that a cation close to a bridge oxygen might be expected to increase the bridge Si—O distances, and any covalent bonding or excess coulombic attraction between a non-bridge oxygen and other cation may cause increased Si—O distances. However, in Na_2SiO_3 no definite effect can be seen, even though the bridge oxygen is only 2.404 Å away from Na. Pectolite is more complicated because of the presence of hydrogen. Table 6 gives the coordination of each oxygen in pectolite and also the distances to the coordinating cations. The non-bridge oxygens are O(1) through O(6), and the bridge ones, O(7) through O(9). O(2), O(5), and O(6) are normal non-bridge oxygens, being coordinated by three cations other than silicon. O(1) is unusual in that it is surrounded by only two close cations, Ca(1) and Ca(2), plus Si(3). Here, however, the O(1)—Si(3) and O(1)—Ca(2) are the smallest distances of their kind in the structure. O(3) and O(4) are presumably involved with H, and O(3)—Si(1) is longer than the other non-bridge distances because H is closer to O(3) than to O(4). O(7) and O(8) are normal bridge oxygens with an average O—Si distance of 1.663, which is close to the predicted value. Although there is a sodium ion about 2.54 Å from each of these oxygens, it apparently has little effect on the O—Si distances. However, for O(9), the Na at 2.305 Å and

the relatively larger Si(1)—O(9)—Si(2) angle of 147.8° apparently cause the mean O(9)—Si distances to be shorter than expected, 1.636 Å.

It would seem, therefore, that if these individual differences are taken into account, the variations in observed interatomic distances in the pectolite structure can be examined on a reasonable basis. Furthermore, the simple π-bonding theory does appear to explain the variations in Si—O distances, and can be retained until a more quantitative approach is made.

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