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A Refinement of the Crystal Structure of Datolite, $CaBSiO_4(OH)$

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Abstract

The structure of datolite has been refined ($R = 0.059$) using least-squares methods and 1297 three-dimensional counter-collected intensities in order to locate the hydrogen atom and provide more precise structural parameters, thereby alleviating some of the ambiguities of previous structural studies. The datolite structure is based on sheets of four- and eight-membered rings of alternating SiO_4 and $BO_3(OH)$ tetrahedra with the sheets bonded together by calcium atoms. The T–O(br) bond lengths of the SiO_4 and the $BO_3(OH)$ tetrahedra are 1.648(2), 1.651(2), 1.661(2) Å and 1.475(3), 1.486(3), 1.464(3) Å, respectively, while the T–O(nbr) bond lengths are 1.570(2) and 1.496(3) Å. The hydrogen atom is located at a distance of 0.75(5) Å from O(5) in the approximate position predicted on the basis of infrared (Sahl, 1966) and nuclear magnetic resonance (Sugitani, Watanabe, and Nagashima, 1972) studies. The SiO_4 and $BO_3(OH)$ tetrahedra are more distorted than those of Pavlov and Belov (1959) but less distorted than those of Pant and Cruickshank (1967). The parameters $\Delta = \langle \text{Si–O(br)} \rangle - \langle \text{Si–O(nbr)} \rangle$, mean Si–O(br) bond length, and Si–O–B angle fit the data presented by Brown and Gibbs (1970) for a model that includes covalent bonding. An extended Hückel molecular orbital calculation for the SiO_4 tetrahedron suggests that Mulliken Si–O bond overlap populations, n(Si–O), may be used to order Si–O bond length variations in silicates where all oxygen atoms are not charge balanced and where the neighboring cations and anions are ignored.

Introduction

The structure of datolite was first determined and refined using film data and Fourier syntheses by Ito and Mori (1953). They found it to be based on sheets of four- and eight-membered rings of alternating SiO_4 and $BO_3(OH)$ tetrahedra with the sheets bonded together by calcium atoms. In the sheets the bridging oxygens, O(br), are bonded to one Si, one B, and one or two Ca atoms; whereas the non-bridging oxygens, O(nbr), are bonded either to one Si and two Ca or to one B, one H, and two Ca. Ito and Mori's values of $\langle \text{Si–O(nbr)} \rangle = 1.52$ Å and $\langle \text{Si–O(br)} \rangle = 1.66$ Å revealed a significant irregularity in the SiO_4 group. Similar irregularities were observed in the $BO_3(OH)$ group where the three B-O(br) bonds averaged 1.45 Å, while the B-OH(nbr) bond was 1.56 Å. Later, Pavlov and Belov (1959) using projection data reported the SiO_4 and $BO_3(OH)$ groups to be much more regular. In an effort to resolve the apparent discrepancy between the results of Ito and Mori (1953) and Pavlov and Belov (1959) and to obtain more precise values for the Si–O and the B–O distances, Pant and Cruickshank (1967) reinvestigated the structure of datolite. Using the film data of Ito and Mori (1953), they refined the structure using least-squares methods. This refinement resulted in a reduction of R from 0.22 (Ito and Mori, 1953) to 0.12 with a concomitant reduction in the estimated standard deviations of the Si–O bond lengths from 0.03 Å to 0.01 Å. Whereas their refinement resulted in a significant decrease in the difference between the average Si–O(nbr) and Si–O(br) bond lengths, $\langle \text{Si–O(nbr)} \rangle = 1.56$ Å and $\langle \text{Si–O(br)} \rangle = 1.67$ Å, the boron and the silicon tetrahedra were still quite irregular. Using the Pauling-Zachariasen method of balancing valences, Pant and Cruickshank (1967) were able to rationalize not only the B–O and the Si–O bond length variations but also the large differences in the Ca–O bond distances. The observed variations in the Si–O bond lengths were also found to be consistent with the predictions of Cruickshank's (1961) d–p π-bonding model.

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TABLE 1. Crystallographic Data for Datolite, Space Group $P2_1/c$*

	Ito and Mori (1953)	This study
a	4.84(1)Å	4.832(4)Å
b	7.60(1)	7.608(4)
c	9.62(1)	9.636(8)
β	90.15°	90.40(7)°
	Z = 4	

* Estimated standard deviations are given in parentheses and refer to the last decimal place

The structure of datolite was re-examined in the present study using precise three-dimensional counter-collected data with the two following objectives in mind: (1) to locate the hydrogen atom whose position in the structure had not been determined previously by X-ray methods, (2) to obtain precise structural parameters for later comparison with other precise data [danburite, Phillips, Ribbe, and Gibbs (1971); howlite, Phillips, Foit, and Gibbs (in preparation); and reedmergnerite, Appleman and Clark (1965)] to examine the effects of tetrahedral boron on the Si–O bond in Si–O–B linkages.

Experimental

Crystallographic Data

The crystal used in our study was from Westfield, Massachusetts, and was obtained from the C. A. Michael Collection at Virginia Polytechnic Institute and State University. Precession and Weissenberg X-ray photographs indicated space group $P2_1/c$ which is consistent with that previously reported by Ito and Mori (1953). The lattice parameters (Table 1) were determined from multiple measurements made with a four-circle X-ray goniostat and are in good agreement with those of Ito and Mori (1953).

Intensity data

The fragment used for the data collection was nearly equant and less than 0.1 mm in maximum dimension. Two complete data sets, each consisting of approximately 1600 intensities (Sin $\theta/\lambda < 0.77$), were gathered using an automated four circle X-ray goniostat, Nb filtered radiation, and a scintillation counter. Sporadic electronic malfunction during collection of the first data set necessitated the collection of an identical second set. Both sets were corrected for Lorentz and polarization effects, but absorption effects were neglected because of the fragment's small size and small linear absorption coefficient (~19

TABLE 2. Final Refined Atom Parameters for Datolite

						x10^5				
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B[a]
Ca	.99176(8)	.10618(5)	.33611(4)	332(14)	166(6)	87(4)	-23(6)	19(5)	-7(3)	.334(9)Å
Si	.46882(10)	.26626(7)	.08440(5)	248(18)	102(7)	58(5)	33(9)	9(7)	-7(4)	.22(1)
B	.5683(4)	.4107(3)	.3415(2)	283(60)	148(25)	107(16)	-8(32)	19(26)	25(17)	.32(3)
O(1)	.2401(3)	.4008(2)	.0376(2)	611(48)	278(20)	156(12)	108(26)	-13(20)	-2(13)	.59(2)
O(2)	.6694(3)	.3010(2)	.4575(1)	488(46)	267(19)	107(12)	72(25)	20(19)	38(12)	.49(2)
O(3)	.6755(3)	.3346(2)	.2104(1)	423(46)	284(20)	92(11)	59(25)	-8(18)	-50(12)	.46(2)
O(4)	.3152(3)	.0876(2)	.1460(2)	602(49)	137(18)	187(13)	6(24)	111(20)	8(12)	.52(2)
O(5)	.2588(3)	.4137(2)	.3363(2)	387(47)	298(20)	156(13)	87(25)	35(19)	4(13)	.53(2)
H	.20(1)	.444(7)	.405(5)	835[b]	337	210	0	3	0	.78(92)

[a] isotropic temperature factors from last cycle of refinement before changing to anisotropic temperature factors.

[b] the anisotropic thermal parameters for hydrogen represent a conversion from isotropic to anisotropic with no subsequent refinement.

cm^{-1} for MoKα radiation). The refinement was carried out using the data of the second set minus: (1) all F_0 for which the difference between the two sets was greater than 10 percent and (2) all F_o whose values were less than four standard deviations of the measurement. This left 1297 data for the refinement.

Refinement

The refinement was initiated using the positional parameters of Pant and Cruickshank (1967) and ORFLS, a Fortran IV full-matrix least-squares program written by Busing, Martin, and Levy (1962). The form factor tables were constructed from the data of Cromer and Waber (1965) for neutral atoms. Unit weighting of the data was found to be adequate in that it gave nearly constant values of $w\ |\Delta F|^2$ for ten equal sized groups of increasing F_o. Therefore, $w\ |\Delta F|^2$ was essentially independent of F_o consistent with the criteria for a good weighting scheme. During the initial stages of refinement, 115 reflections (mostly low angle and intense) apparently affected by secondary extinction were removed.

Several cycles of refinement varying positional and anisotropic thermal parameters and scale factor, followed by a calculation of root mean square (*rms*) components of thermal displacement along the principal axes, revealed a geometrical similarity of thermal ellipsoids except for O(5). One *rms* displacement for O(5) was markedly larger than the corresponding displacement for the other oxygen atoms. This was assumed to be due to H–O bonding in that direction. Direction cosines were then calculated and the hydrogen atom was placed in that direction at a distance of one Angstrom from the O(5) position. This position is very close to that predicted for hydrogen on the basis of both infrared (Sahl, 1966) and nuclear magnetic resonance (Sugitani *et al*, 1972) studies. Additional refinement varying only the hydrogen positional parameters resulted in a 0.002 reduction in the residual.

The refinement was completed by simultaneously varying all positional and all anisotropic thermal parameters (except hydrogen whose isotropic temperature factor was held at 0.78). The final residuals are 0.036 (1182 data) and 0.059 (1297 data). The refined positional and thermal parameters and the structure factors are listed in Tables 2 and 5, respectively. The dimensions and orientations of the thermal ellipsoids and the bond distances (Tables 3 and 4) were calculated using the Fortran function and error program written by Busing, Martin, and Levy (1964).

Discussion

Description of the Structure

The tetrahedral sheets in datolite (Fig. 1) are bonded together by calcium atoms each of which is coordinated to six oxygen atoms and two hydroxyl groups at the corners of a distorted tetragonal antiprism. As pointed out by Pant and Cruickshank (1967), the calcium atoms lie almost in the (100) planes with an approximate disposition of $x = \pm 0.29$ about the origin. The hydrogen atom with $x = 0.20$ is situated near the outer surface of the tetrahedral sheet at a distance of about 0.75 Å from O(5), at distances ranging from 2.56 to 3.08 Å from its remaining four nearest oxygen neighbors, and at a distance of 1.89 Å from its nearest cation neighbor, boron. Based on a table presented by Zachariasen (1963) relating H–O bond strength to bond length, the bond strength (ζ) for the H–O(5) bond should very nearly equal one.

SiO_4 and $BO_3(OH)$ groups

Our refinement has yielded SiO_4 and $BO_3(OH)$ tetrahedra which are less distorted than those of

TABLE 3. Magnitude and Orientation of the Principal Axes of the Thermal Ellipsoids in Datolite

Atom, axis		rms displacement Å	Angle (°) with respect to:		
			+a	+b	+c
Ca,	r_1	0.059(1)	144(8)	98(7)	55(10)
	r_2	0.064(1)	115(10)	122(6)	137(10)
	r_3	0.072(1)	114(4)	33(6)	111(5)
Si,	r_1	0.047(2)	128(8)	52(7)	61(12)
	r_2	0.054(2)	113(13)	74(13)	150(12)
	r_3	0.059(2)	47(8)	43(7)	94(12)
B,	r_1	0.056(7)	31(39)	68(34)	111(22)
	r_2	0.063(6)	60(40)	139(28)	65(24)
	r_3	0.075(5)	84(15)	57(18)	34(17)
O(1),	r_1	0.075(4)	141(6)	53(7)	98(15)
	r_2	0.086(4)	87(14)	100(13)	170(13)
	r_3	0.099(3)	51(6)	39(7)	97(11)
O(2),	r_1	0.067(4)	83(31)	115(13)	26(22)
	r_2	0.072(4)	156(12)	72(16)	74(32)
	r_3	0.095(3)	67(7)	31(6)	70(6)
O(3),	r_1	0.060(5)	100(21)	67(6)	25(13)
	r_2	0.069(4)	163(13)	80(10)	104(20)
	r_3	0.097(3)	76(6)	25(5)	110(5)
O(4),	r_1	0.063(4)	89(17)	4(16)	94(12)
	r_2	0.073(4)	36(5)	93(20)	126(5)
	r_3	0.103(3)	54(5)	87(4)	36(5)
O(5),	r_1	0.062(4)	21(5)	108(5)	102(7)
	r_2	0.086(4)	97(8)	75(13)	164(11)
	r_3	0.097(3)	70(5)	23(9)	79(13)

Pant and Cruickshank (1967) but significantly more distorted than those of Pavlov and Belov (1959). The mean Si–O bond length is 1.633 Å with ⟨Si–O(nbr)⟩ and ⟨Si–O(br)⟩ bond lengths equal to 1.570 Å and 1.653 Å, respectively (Table 4). However, the greatest decrease in distortion was noted for the $BO_3(OH)$ group where ⟨B–O(nbr)⟩ = 1.496 Å and ⟨B–O(br)⟩ = 1.475 Å. The bond lengths in the boron tetrahedron deviate less than 0.016 Å from the mean value of 1.480 Å. This decrease in the distortion of the SiO_4 and the $BO_3(OH)$ tetrahedra is also reflected in the O–*T*–O angles. The differences between the maximum and minimum O–Si–O and O–B–O angles are 9.8 and 5.0°, respectively (our work), 14.8 and 6.6° (Pant and Cruickshank, 1967).

Pant and Cruickshank (1967) remark that the differences between the Si–O(br) and the Si–O(nbr) bond lengths should be relatively large compared to other silicates because of the small value of the mean Si–O(br)–B angle (~124°). Comparing datolite with Na_2SiO_3 and αNa_2SiO_3, they show that there is an apparent correlation between the *T*–O–*T* angle and the difference in length between the Si–O(br) and Si–O(nbr) bonds. More recently, Brown and Gibbs (1970) presented a curve showing the variation of Δ = ⟨Si–O(br)⟩ − ⟨Si–O(nbr)⟩ as a function of the Si–O–Si angle for a large number of silicates having T_2O_6, T_2O_5, and T_2O_7 frameworks (T = Si, Al). Despite the fact that in datolite these are Si–O–B bond angles, there appears to be a good fit to their data. Likewise, the mean Si–O(br) bond length fits their general curve relating the variation of the Si–O(br) bond length to the Si–O–Si angle.

As the Si–O bond length variations in datolite appear to be consistent with certain aspects of a model that includes covalent bonding, an extended Hückel molecular orbital calculation was undertaken on the silicate ion to learn whether Mulliken Si–O bond overlap populations, *n*(Si–O), could be used to order the observed Si–O bond lengths in an ion where all the oxygen atoms are not balanced in the Pauling sense. In the calculation, all the Si–O bond lengths were clamped at a constant value of 1.63 Å, the O–Si–O angles were fixed at their observed values and all neighboring cations and anions were ignored (see Gibbs *et al*, 1972, for further details). The *n*(Si–O) values obtained in the calculation are plotted *vs* the observed Si–O bond lengths in Figure 2. The trend is as expected, with the short Si–O(1) bond being involved with the largest bond overlap population and the larger Si–O(2), Si–O(3) and

TABLE 4. Interatomic Distances and Angles in Datolite

Atoms	Distance Å	Atoms	Angles°
Si - O(1)	1.570(2)	O(1) - Si - O(2)'	113.95(8)
Si - O(2)'	1.648(2)	O(1) - Si - O(3)	115.26(8)
Si - O(3)	1.651(2)	O(1) - Si - O(4)	108.69(8)
Si - O(4)	1.661(2)	O(2)'- Si - O(3)	106.74(8)
		O(2)'- Si - O(4)	106.15(8)
Mean Si - O	1.633	O(3) - Si - O(4)	105.34(8)
O(1) - O(2)'	2.698(2)	Mean O - Si - O	109.36
O(1) - O(3)	2.721(2)		
O(1) - O(4)	2.626(2)		
O(2)'- O(3)	2.647(2)		
O(2)'- O(4)	2.645(2)		
O(3) - O(4)	2.633(2)		
Mean O - O	2.662		
B - O(2)	1.475(3)	O(2) - B - O(3)	107.9(2)
B - O(3)	1.486(3)	O(2) - B - O(4)'	109.5(2)
B - O(4)	1.464(3)	O(2) - B - O(5)	111.1(2)
B - O(5)	1.496(3)	O(3) - B - O(4)'	106.9(1)
		O(3) - B - O(5)	109.4(2)
Mean B - O	1.480	O(4)'- B - O(5)	111.9(2)
O(2) - O(3)	2.395(2)	Mean O - B - O	109.5
O(2) - O(4)'	2.399(2)		
O(2) - O(5)	2.450(2)		
O(3) - O(4)'	2.370(2)		
O(3) - O(5)	2.433(2)		
O(4) - O(5)	2.452(2)		
Mean O - O	2.417		
Ca - O(1)'	2.276(2)	Si - O(2)'- B'	123.0(1)
Ca - O(1)''	2.280(2)	Si - O(3) - B	122.4(1)
Ca - O(2)	2.453(2)	Si - O(4) - B''	127.5(1)
Ca - O(3)	2.607(2)		
Ca - O(3)'	2.658(2)	Mean Si - O - B	124.3
Ca - O(4)''	2.420(2)		
Ca - O(5)'	2.672(2)		
Ca - O(5)''	2.518(2)		
Mean Ca - O	2.486		
H - O(5)	0.75(5)		

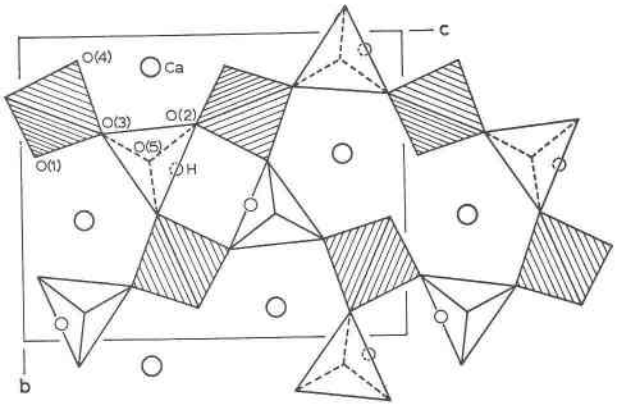

FIG. 1. The structure of datolite projected down [100] showing the four- and eight-membered rings of alternating SiO_4 (shaded) and $BO_3(OH)$ tetrahedra (unshaded).

TABLE 5. Observed and Calculated Structure Factors for Datolite (*k*, *l*, F_{obs}, F_{calc})

H = 0			
0	-12	108.4	110.9
0	-10	92.8	96.1
0	-8	117.4	125.6
0	-6	132.0	146.8
0	-4	140.8	177.2
0	6	133.2	146.8
0	8	121.0	125.6
0	10	96.4	96.1
0	12	109.1	110.9
1	-12	18.9	14.1
1	-11	25.9	24.7
1	-8	167.4	190.8
1	-7	40.9	36.4
1	-6	18.8	18.3
1	-5	67.8	62.3
1	-4	123.4	140.5
1	-3	16.4	14.0
1	3	17.4	14.0
1	4	119.9	140.5
1	5	68.1	67.3
1	6	17.2	18.3
1	7	37.8	36.4
1	8	162.7	190.8
1	9	27.9	26.3
1	11	26.1	24.7
2	-14	20.3	20.3
2	-13	43.4	42.0
2	-11	82.7	85.1
2	-10	74.9	74.0
2	-9	25.8	24.1
2	-8	47.4	47.1
2	-7	12.1	7.1
2	-6	152.4	170.9
2	-5	166.2	216.5
2	-4	46.0	43.7
2	-3	33.4	32.4
2	2	103.0	114.2
2	3	32.7	32.4
2	4	48.2	43.7
2	5	164.4	216.5
2	6	149.1	170.9
2	7	11.8	7.1
2	8	46.3	47.1
2	9	25.6	24.1
2	10	74.3	74.0
2	11	83.4	85.1
2	13	41.8	42.0
2	14	21.1	20.3
3	-14	127.3	132.4
3	-13	40.0	38.2
3	-11	35.3	33.0
3	-10	154.1	170.3
3	-7	27.1	27.4
3	-6	61.6	62.5
3	-5	39.4	36.1
3	-4	118.5	129.8
3	-3	110.7	120.4
3	-1	45.6	47.7
3	1	45.8	47.7
3	2	149.6	215.4
3	3	112.7	120.4
3	4	117.5	129.8
3	5	37.4	36.1
3	6	62.5	62.5
3	7	28.4	27.4
3	10	155.1	170.3
3	11	34.6	32.9
3	13	37.8	38.2
3	14	127.2	132.4
4	-14	28.6	26.8
4	-11	13.1	14.3
4	-10	107.1	107.8
4	-9	22.4	22.2
4	-7	12.7	10.4
4	-6	176.0	235.5
4	-4	40.5	39.2
4	-3	37.6	35.1
4	-1	105.7	113.1
4	0	146.0	184.1
4	0	147.4	184.1
4	1	106.6	113.1
4	2	125.7	141.0
4	3	37.2	35.3
4	4	40.9	39.2
4	6	165.7	235.5
4	7	13.6	10.4
4	9	21.1	22.2
4	10	104.6	107.8
4	11	15.1	14.3
4	14	28.5	26.8
5	-13	38.3	35.7
5	-11	24.1	21.9
5	-10	54.9	56.1
5	-8	24.0	23.7
5	-7	42.2	39.1
5	-6	37.8	35.1
5	-5	73.4	77.1
5	-4	84.4	87.2
5	-3	39.2	42.0
5	-2	68.4	69.7
5	2	72.4	69.7
5	3	39.4	42.0
5	4	84.5	87.2
5	5	75.0	77.1
5	6	34.3	35.1
5	7	40.9	39.1
5	8	26.6	23.7
5	9	82.4	83.[illegible]
5	10	54.5	56.
5	11	24.9	21.9
5	13	41.9	35.7
6	-12	115.2	119.0
6	-11	68.1	66.4
6	-10	70.0	68.7
6	-8	38.1	36.[illegible]
6	-7	43.1	37.[illegible]
6	-6	62.4	67.4
6	-5	33.5	34.9
6	-3	64.3	67.7
6	-2	13.7	12.7
6	-1	94.6	103.8
6	0	171.9	227.5
6	0	174.6	227.5
6	1	98.2	103.8
6	2	18.1	12.7
6	3	67.8	67.7
6	4	125.4	140.9
6	5	34.1	34.9
6	6	63.8	67.4
6	8	41.4	36.1
6	10	70.5	68.7
6	11	66.5	66.4
6	12	119.3	119.0
7	-11	47.1	47.2
7	-10	47.3	45.4
7	-9	29.5	28.0
7	-8	78.9	81.8
7	-7	52.3	52.6
7	-6	18.2	17.1
7	-5	60.2	62.3
7	-4	155.1	193.9
7	-3	50.1	53.4
7	-2	36.8	35.1
7	2	36.8	35.1
7	3	50.7	53.4
7	4	166.7	193.9
7	5	61.3	62.3
7	6	19.7	17.1
7	7	50.6	52.6
7	8	81.5	81.8
7	9	29.1	28.0
7	10	45.9	45.4
7	11	47.3	47.2
8	-9	26.9	24.8
8	-8	27.7	26.4
8	-7	30.4	29.3
8	-4	52.4	50.5
8	-3	80.5	80.9
8	-1	39.2	36.8
8	0	57.0	57.5
8	0	60.8	57.5
8	1	40.3	36.8
8	3	77.5	80.9
8	4	49.8	50.5
8	5	93.0	98.5
8	7	28.8	29.3
8	8	30.7	26.4
8	9	27.4	24.3
8	10	17.4	7.7
9	-8	66.2	68.8
9	-5	29.5	24.6
9	-3	46.0	44.0
9	-2	71.6	68.4
9	-1	81.9	83.3
9	1	82.5	83.3
9	2	68.0	68.4
9	3	42.1	44.0
9	5	25.2	24.6
9	7	19.6	14.9
10	-7	56.7	57.5
10	-5	44.1	45.4
10	-4	37.0	34.6
10	-3	58.1	58.1
10	-2	21.8	21.1
10	-1	27.0	22.2
10	0	102.1	102.8
10	0	100.5	102.8
10	1	24.2	22.2
10	2	22.5	21.1
10	3	58.2	58.1
10	4	37.2	34.6
10	5	47.1	45.4
10	6	114.6	119.6
10	7	58.2	57.5
11	-5	51.2	50.9
11	-4	36.1	34.0
11	-3	15.5	11.7
11	-2	78.1	79.4
11	-1	38.5	33.7
11	1	38.7	33.7
11	2	74.6	79.4
11	3	14.0	11.7
11	4	35.1	34.0
11	5	51.1	50.9
H = 1			
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0	-12	17.3	17.7
0	-10	57.6	56.8
0	-8	84.3	87.7
0	-6	173.0	219.1
0	-4	135.7	151.5
0	4	158.4	195.5
0	6	157.6	183.4
0	8	70.6	72.9
0	10	94.2	94.1
0	12	35.4	34.5
0	14	48.0	48.5
1	-14	82.6	81.1
1	-13	80.8	78.7
1	-12	33.7	32.6
1	-10	107.6	110.5
1	-9	103.5	104.2
1	-8	26.0	25.1
1	-7	129.5	136.7
1	-6	108.1	116.5
1	-5	80.8	78.2
1	-4	110.3	112.4
1	-3	124.4	137.8
1	3	160.6	208.5
1	4	48.6	47.0
1	5	33.6	33.7
1	6	37.8	38.2
1	7	64.6	62.6
1	8	56.9	56.8
1	9	105.1	108.5
1	10	83.6	83.1
1	12	44.7	44.2
1	13	18.6	16.7
1	14	81.9	83.2
2	-13	18.2	16.6
2	-12	52.5	49.9
2	-11	99.5	97.9
2	-10	56.5	54.1
2	-9	16.9	16.0
2	-8	61.1	62.6
2	-7	76.1	74.8
2	-6	90.0	86.8
2	-5	121.0	132.7
2	-4	98.0	97.7
2	-3	169.9	228.8
2	-2	44.2	41.1
2	0	151.4	191.7
2	2	79.5	78.9
2	4	21.8	15.4
2	5	74.9	75.0
2	6	71.0	70.1
2	7	122.7	131.1
2	8	52.5	51.2
2	11	70.7	69.1
2	12	62.6	62.9
2	13	97.2	97.5
3	-13	27.9	27.5
3	-12	44.6	45.8
3	-11	33.5	31.3
3	-10	56.2	57.4
3	-9	57.0	57.8
3	-8	134.9	147.5
3	-7	48.0	45.1
3	-6	65.5	65.9
3	-5	9.4	4.6
3	-4	153.2	182.9
3	-3	12.5	13.2
3	-2	84.0	80.7
3	-1	34.0	31.4
3	0	148.0	182.6
3	1	92.7	89.7
3	2	10.2	8.5
3	3	57.4	54.8
3	4	140.8	182.9
3	5	67.1	64.8
3	6	73.1	72.6
3	7	79.8	82.0
3	8	140.4	154.7
3	9	62.8	62.6
3	10	63.8	62.7
3	13	23.8	21.3
3	14	25.5	22.7
4	-12	101.9	103.2
4	-11	62.4	60.7
4	-11	41.3	39.4
4	-10	9.3	8.5
4	-9	76.0	76.3
4	-8	23.9	19.0
4	-6	10.0	5.3
4	-5	69.8	66.9
4	-4	76.6	74.2
4	-1	46.0	41.7
4	0	156.1	199.8
4	1	73.6	70.1
4	2	15.1	15.1
4	3	78.6	80.1
4	4	108.2	113.2
4	5	116.0	122.9
4	6	18.0	16.1
4	7	90.1	92.2
4	8	104.7	110.6
4	9	16.9	14.8
4	10	32.2	31.5
4	11	44.6	42.4
4	12	106.4	111.9
4	13	45.2	43.0
5	-13	88.9	90.5
5	-12	13.5	7.5
5	-11	67.2	67.3
5	-10	23.4	23.9
5	-9	70.5	70.9
5	-8	78.4	78.7
5	-7	110.9	117.0
5	-6	14.7	10.6
5	-5	78.1	81.4
5	-4	87.7	88.4
5	-3	142.8	154.7
5	-2	13.7	11.0
5	0	87.4	88.2
5	0	83.7	88.2
5	1	79.4	77.7
5	2	71.5	70.0
5	4	105.7	109.4
5	5	44.9	46.1
5	6	17.1	17.2
5	7	25.4	22.8
5	8	52.1	50.7
5	9	104.1	103.4
5	10	40.9	40.4
5	11	32.3	31.5
5	13	81.1	80.1
6	-12	30.9	27.5
6	-11	41.4	41.8
6	-9	49.4	48.3
6	-8	18.4	15.4
6	-7	72.0	73.5
6	-5	98.6	102.2
6	-4	32.7	31.5
6	-3	48.1	48.1
6	-2	22.2	18.1
6	-1	27.3	24.2
6	1	71.8	70.3
6	2	105.6	109.4
6	3	60.3	62.8
6	4	26.9	27.0
6	5	105.4	108.9
6	6	77.1	77.0
6	7	61.7	60.7
6	10	60.8	58.2
6	11	43.3	42.5
7	-10	96.5	99.8
7	-9	44.0	46.1
7	-8	27.4	23.0
7	-7	44.1	44.0
7	-6	11.4	9.7
7	-5	58.4	56.0
7	-3	34.7	35.4
7	-2	135.5	149.0
7	0	95.7	100.6
7	0	95.9	100.6
7	1	33.1	30.5
7	2	115.4	117.1
7	4	22.5	23.1
7	5	48.7	48.0
7	6	21.2	21.4
7	7	44.5	45.1
7	8	58.4	56.8
7	10	65.8	68.3
7	11	45.6	44.4
8	-10	62.1	62.1
8	-8	25.1	22.6
8	-7	14.2	13.4
8	-6	90.3	93.9
8	-5	32.7	31.0
8	-4	17.4	14.8
8	-3	103.9	111.6
8	-2	17.5	16.6
8	-1	109.6	110.4
8	0	28.8	28.5
8	0	26.6	28.5
8	1	64.7	63.7
8	2	53.1	54.9
8	3	16.4	13.5
8	4	13.4	10.3
8	5	56.7	55.9
8	6	89.4	91.1
8	7	88.1	88.9
8	8	18.7	13.9
8	9	38.2	36.0
8	10	42.1	40.9
9	-9	77.0	76.7
9	-8	43.4	40.0
9	-7	83.3	82.8
9	-6	20.3	21.1
9	-5	93.3	98.8
9	-4	67.2	67.8
9	-3	82.5	84.9
9	-2	43.5	42.2
9	-1	37.0	33.0
9	0	26.2	22.1
9	0	23.5	22.1
9	1	17.7	17.2
9	3	87.4	86.6
9	4	32.9	30.6
9	5	59.1	61.6
9	6	44.4	43.2
9	7	61.7	60.7
9	8	23.7	22.5
9	9	56.0	55.2
10	-6	59.1	54.9
10	-4	33.1	30.4
10	-3	26.0	22.7
10	-1	58.4	59.2
10	0	79.3	78.4
10	0	78.6	78.4
10	1	18.2	17.6
10	2	50.7	47.7
10	3	77.8	80.6
10	4	51.4	51.6
11	-4	50.1	51.5
11	-3	51.5	53.0
11	-2	17.1	15.6
11	-1	57.1	58.1
11	1	80.9	79.8
11	2	39.2	39.1
11	3	42.7	42.5
11	4	81.7	80.6
H = 2			
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0	-4	180.9	233.1
0	-2	129.5	134.4
0	2	38.7	37.5
0	4	54.5	54.1
0	6	37.2	37.2
0	8	15.3	15.2
0	10	11.7	6.0
0	12	136.7	143.6
0	14	27.6	25.0
1	-14	14.0	11.3
1	-13	59.4	55.4
1	-12	73.8	73.4
1	-11	26.8	25.7
1	-10	14.8	17.3
1	-9	72.5	68.8
1	-8	103.7	104.5
1	-7	113.9	118.8
1	-6	29.3	27.4
1	-4	92.0	93.0
1	-3	166.8	154.5
1	-2	15.7	12.1
1	-1	151.2	168.8
1	0	41.0	34.7
1	0	39.0	34.7
1	2	22.5	19.4
1	3	172.8	215.6
1	4	192.7	249.2
1	5	48.6	45.6
1	6	14.1	10.1
1	7	55.2	53.4
1	8	121.3	126.7
1	9	108.8	112.3
1	10	44.0	42.1
1	11	48.6	45.9
1	12	37.9	35.2
1	13	76.8	72.7
2	-13	51.7	47.7
2	-12	33.9	36.1
2	-11	63.8	62.7
2	-10	59.1	57.6
2	-9	64.6	63.4
2	-7	133.2	143.2
2	-6	106.7	107.8
2	-5	44.6	40.0
2	-4	137.5	146.8
2	-3	47.3	42.5
2	-2	41.7	38.7
2	0	84.5	82.6
2	0	83.8	82.6
2	1	156.4	189.7
2	2	87.8	86.4
2	3	50.1	45.0
2	4	29.6	26.5
2	5	81.5	82.4
2	6	68.8	65.5
2	7	139.1	156.9
2	8	25.2	23.4
2	10	18.7	15.8
2	11	35.3	35.4
2	12	56.9	55.5
2	13	49.4	49.0
2	14	28.0	27.3
3	-13	16.9	11.9
3	-11	43.8	42.9
3	-10	43.8	41.6
3	-9	46.6	43.0
3	-8	44.6	43.2
3	-7	61.7	60.5
3	-6	41.2	35.3
3	-4	26.3	24.9
3	-3	57.0	51.5
3	-1	112.7	114.2
3	0	23.9	18.6
3	0	20.3	18.6
3	2	176.1	213.5
3	3	27.5	24.3
3	4	27.3	27.1
3	5	44.8	45.8
3	6	63.6	60.7
3	7	11.0	12.7
3	8	69.4	67.3
3	9	63.8	63.2
3	10	104.5	106.8
3	11	14.3	10.1
3	12	44.4	43.6
3	13	49.5	48.3
4	-13	49.6	48.5
4	-12	43.3	40.7
4	-10	80.8	78.2
4	-9	43.4	42.4
4	-8	32.0	29.9
4	-7	40.7	40.7
4	-6	152.2	175.2
4	-5	65.2	64.2
4	-4	10.3	8.4
4	-3	83.5	82.8
4	-2	68.8	63.8
4	-1	100.6	101.8
4	0	42.0	41.1
4	0	41.3	41.1
4	2	122.6	126.3
4	3	10.8	10.7
4	4	51.4	51.1
4	6	104.0	106.9
4	7	24.3	20.7
4	8	36.7	36.2
4	10	48.8	48.4
4	11	39.7	37.1
4	12	25.5	21.1
4	13	65.0	63.4
5	-12	12.1	3.4
5	-11	16.4	15.9
5	-10	31.3	30.8
5	-9	72.6	70.8
5	-8	62.0	59.2
5	-7	92.3	94.1
5	-5	18.1	14.5
5	-4	18.5	16.2
5	-3	155.8	176.0
5	-2	87.3	84.5
5	-1	26.6	25.8
5	0	62.9	62.8
5	0	62.8	62.8
5	1	31.1	30.0
5	2	97.8	99.1
5	3	180.5	212.7
5	4	29.6	26.4
5	5	122.1	130.8
5	6	41.1	38.4
5	7	103.5	111.8
5	8	33.9	32.2
5	9	72.8	72.7
5	10	72.8	71.5
5	11	54.5	54.4
6	-12	85.6	85.2
6	-11	65.5	65.4
6	-10	30.7	28.6
6	-9	28.6	27.8
6	-8	26.5	21.6
6	-7	15.1	14.0
6	-6	17.6	17.3
6	-5	59.3	55.4
6	-4	27.9	24.0
6	-3	69.2	68.8
6	-2	72.8	75.6
6	0	91.5	90.4
6	0	91.6	90.4
6	1	53.0	51.8
6	2	30.7	34.8
6	3	21.4	19.0
6	4	65.3	62.2
6	5	32.9	30.4
6	6	30.3	28.2
6	7	58.6	58.2
6	9	20.9	18.8
6	10	19.8	15.7
6	11	48.7	48.8
6	12	51.5	51.7
7	-10	16.1	15.4
7	-9	27.2	28.3
7	-8	141.4	156.8
7	-6	13.8	12.9
7	-5	41.2	40.4
7	-4	73.2	73.1
7	-3	29.2	24.9
7	-2	56.6	54.7
7	-1	63.7	63.4
7	0	66.2	65.1
7	0	64.7	65.1
7	1	59.0	58.2
7	2	54.4	52.4
7	3	46.1	43.9
7	4	88.7	88.2
7	5	15.4	11.0
7	7	50.1	47.4
7	8	121.4	125.8
7	9	49.5	48.2
7	11	29.0	29.0
8	-8	55.5	55.4
8	-7	118.9	124.7
8	-6	21.6	18.4
8	-5	59.2	59.2
8	-4	54.2	52.5
8	-3	16.5	13.8
8	0	113.7	114.5
8	0	112.8	114.5
8	1	54.1	55.0
8	3	28.5	28.1
8	4	48.0	47.4
8	5	40.8	45.8
8	7	62.0	62.4
8	8	69.7	72.5
8	9	50.4	48.7
8	10	24.4	22.7
9	-8	15.9	16.1
9	-7	20.3	21.7
9	-6	29.9	29.6
9	-5	21.8	20.0
9	-4	22.3	20.4
9	-3	94.2	94.1
9	-2	79.8	76.2
9	-1	62.4	60.4
9	0	23.8	21.7
9	0	22.5	21.9
9	1	77.5	78.7
9	2	33.0	30.0
9	3	95.2	94.7
9	5	23.6	19.5
9	7	18.8	17.7
10	-6	63.4	61.5
10	-5	46.5	43.2
10	-4	13.7	15.6
10	-2	80.4	76.3
10	-1	26.6	25.5
10	2	57.4	55.1
10	3	49.9	47.0
10	4	37.4	34.7
10	5	57.3	53.4
10	6	80.2	82.5
11	-3	34.3	30.8
11	-2	87.7	89.7
11	-1	18.0	16.5
11	1	50.9	50.1
11	2	36.7	36.0
11	3	73.5	72.4
H = 3			
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0	-6	145.9	164.8
0	-4	76.1	76.9
0	-2	31.3	29.1
0	0	161.4	193.3
0	0	161.5	193.3
0	2	171.7	223.1
0	4	30.4	30.5
0	8	189.5	227.4
0	10	22.8	20.9
1	-13	15.2	20.5
1	-11	39.4	39.0
1	-10	37.5	34.4
1	-9	68.7	67.2
1	-8	26.8	24.4
1	-7	22.1	21.9
1	-6	81.7	81.0
1	-5	60.7	58.9
1	-4	74.0	73.3
1	-3	113.8	117.9
1	-2	143.1	152.7
1	-1	22.1	17.4
1	0	25.8	23.0
1	0	25.6	23.0
1	1	43.9	40.3
1	2	103.2	105.0
1	3	80.4	78.7
1	4	80.5	80.6
1	5	61.0	59.9
1	6	93.7	96.0
1	7	62.4	61.3
1	8	42.4	42.7
1	9	25.6	22.5
1	10	128.2	135.1
1	11	25.3	22.1
1	12	13.5	9.5
1	13	46.8	41.8
2	-13	99.5	98.5
2	-12	77.9	79.9
2	-11	87.9	87.4
2	-10	24.9	25.1
2	-9	23.2	20.2
2	-8	35.6	34.3
2	-7	74.5	74.5
2	-6	39.4	39.6
2	-5	142.8	153.5
2	-4	149.4	161.6
2	-3	31.1	31.0
2	-2	24.3	22.6
2	-1	103.8	105.4
2	0	72.4	65.5
2	0	73.0	69.5
2	1	103.5	107.0
2	2	34.7	32.3
2	3	119.8	129.5
2	4	25.7	23.7
2	5	125.3	133.9
2	6	20.6	19.4
2	7	42.3	39.8
2	8	62.6	60.5
2	9	31.4	31.1
2	11	114.3	116.1
2	12	87.5	88.1
2	13	28.1	28.9
3	-13	28.1	24.2
3	-12	47.7	46.5
3	-10	14.6	10.8
3	-9	23.7	20.5
3	-8	128.0	131.0
3	-7	14.4	9.6
3	-6	25.2	27.5
3	-5	61.7	58.6
3	-4	85.2	82.9
3	-3	85.8	89.4
3	-2	32.0	31.1
3	1	37.4	37.1
3	2	11.4	9.0
3	3	98.8	99.8
3	4	171.2	195.2
3	5	63.1	63.1
3	6	26.1	26.7
3	7	27.1	27.2
3	8	64.2	63.1
3	10	56.9	55.2
3	12	48.4	46.1
4	-12	82.9	84.8
4	-11	17.0	17.7
4	-10	23.8	19.2
4	-9	26.1	25.6
4	-7	116.7	117.4
4	-6	20.2	19.3
4	-5	24.4	25.1
4	-3	64.9	64.0
4	-2	62.3	63.1
4	-1	81.4	81.1
4	1	99.8	99.9
4	2	34.3	35.0
4	3	43.8	41.6
4	5	52.8	51.3
4	6	54.8	54.2
4	7	34.8	33.6
4	8	85.3	85.7
4	9	64.9	64.6
4	12	101.2	103.3
5	-12	25.8	27.1
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5	-10	13.1	7.4
5	-9	93.3	90.8
5	-8	90.4	90.5
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5	-6	23.0	21.7
5	-5	16.9	10.4
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5	-2	65.4	61.9
5	-1	53.1	49.4
5	0	19.5	13.9
5	0	15.6	13.9
5	1	116.3	124.1
5	3	18.1	12.8
5	4	59.2	55.9
5	5	29.1	26.0
5	6	73.6	73.4
5	7	44.7	41.7
5	8	68.7	66.7
5	9	83.1	85.5
5	10	38.2	35.1
5	11	31.9	32.4
6	-11	49.2	47.5
6	-10	120.7	125.2
6	-9	61.8	60.2
6	-8	20.2	16.3
6	-7	101.9	102.1
6	-6	89.1	90.4
6	-5	46.1	43.7
6	-4	64.4	65.2
6	-3	16.1	16.4
6	-1	20.9	19.2
6	1	88.6	89.0
6	2	101.8	104.0
6	4	27.0	27.6
6	5	67.7	68.2
6	6	127.8	135.4
6	7	72.3	70.3
6	8	67.7	66.6
6	8	21.1	20.5
6	9	41.8	43.3
6	11	29.3	28.0
7	-10	28.7	28.6
7	-9	18.1	19.4
7	-6	59.0	57.3
7	-5	43.8	42.1
7	-4	53.2	51.7
7	-3	30.2	28.9
7	-2	114.5	118.0
7	-1	72.5	74.6
7	0	43.0	40.3
7	0	41.5	40.3
7	1	52.1	49.9
7	2	86.4	86.2
7	3	15.8	11.9
7	4	47.1	47.1
7	6	69.5	70.4
7	7	66.2	64.1
7	8	27.9	27.0
7	10	108.2	112.7
8	-9	29.7	28.4
8	-8	13.0	15.0
8	-7	38.4	35.3
8	-6	64.8	64.6
8	-5	83.1	83.7
8	-2	29.1	26.7
8	-1	118.5	125.6
8	0	24.4	22.0
8	0	24.3	22.0
8	1	89.3	87.8
8	2	66.6	62.9
8	3	67.4	69.4
8	4	36.4	33.7
8	5	39.5	36.0
8	6	75.0	74.0
8	7	25.5	22.4
8	8	27.1	23.6
9	-7	58.0	59.7
9	-6	15.1	11.1
9	-5	35.1	35.7
9	-4	15.9	12.5
9	-3	45.5	43.0
9	-2	16.2	15.2
9	0	71.3	69.0
9	0	69.1	69.0
9	1	19.7	20.0
9	2	15.8	12.0
9	3	73.3	76.7
9	4	43.3	43.0
9	5	47.4	48.7
9	6	48.5	44.2
9	7	92.6	97.2
10	-5	20.2	17.0
10	-4	95.3	95.7
10	-3	52.8	52.0
10	-1	50.4	48.7
10	0	98.9	98.5
10	0	97.6	98.5
10	1	41.2	37.8
10	5	38.8	36.3
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0	-6	50.6	48.4
0	-4	111.4	116.0
0	-2	39.5	38.5
0	0	177.4	213.4
0	0	177.8	213.4
0	2	18.2	17.3
0	4	78.1	77.8
0	6	86.1	86.4
0	8	136.9	144.0
0	10	76.4	72.4
0	12	113.7	119.8
1	-12	19.1	20.6
1	-11	25.4	21.9
1	-10	47.0	46.7
1	-9	66.6	64.2
1	-8	121.8	123.0
1	-7	44.0	40.9
1	-6	41.9	39.4
1	-5	10.7	6.8
1	-4	146.9	158.9
1	-3	52.7	48.0
1	-2	28.8	26.2
1	-1	58.8	54.7
1	0	105.9	107.6
1	0	103.0	107.6
1	1	77.0	78.2
1	2	47.6	48.6
1	3	27.8	23.2
1	4	125.0	130.6
1	5	57.8	54.6
1	6	83.9	85.3
1	7	18.3	18.1
1	8	27.0	26.0
1	9	57.2	57.0
1	10	15.8	11.3
1	11	33.0	30.6
2	-12	29.2	25.7
2	-11	54.5	51.8
2	-10	73.0	73.9
2	-9	23.3	22.6
2	-8	61.0	59.2
2	-7	24.9	23.6
2	-6	65.8	65.7
2	-5	105.7	105.8
2	-4	38.0	35.5
2	-3	69.8	66.5
2	-2	22.8	20.9
2	-1	17.8	14.5
2	1	110.0	111.5
2	2	84.2	83.8
2	3	113.8	118.6
2	5	59.0	57.9
2	6	94.1	95.9
2	7	62.2	62.1
2	8	63.4	62.3
2	9	17.6	15.1
2	11	49.5	49.1
2	12	25.5	22.3
3	-12	16.4	9.2
3	-11	13.4	9.5
3	-10	109.4	112.3
3	-9	31.7	30.6
3	-8	29.5	26.6
3	-6	57.8	55.3
3	-5	46.9	44.7
3	-4	112.4	116.4
3	-3	37.5	34.6
3	-2	157.0	171.5
3	0	95.4	98.8
3	0	97.4	98.8
3	1	87.7	88.7
3	1	20.7	17.8
3	2	117.6	121.1
3	4	12.9	11.9
3	5	45.1	42.0
3	7	22.8	19.9
3	8	45.6	45.5
3	9	54.5	54.8
3	10	93.1	93.2
3	11	33.7	31.7
4	-10	114.3	116.4
4	-9	32.9	27.9
4	-8	38.4	38.3
4	-7	74.2	73.6
4	-6	99.4	99.8
4	-5	48.5	45.5
4	-3	25.0	23.5
4	0	70.6	71.0
4	0	70.3	71.0
4	1	49.6	46.7
4	2	93.6	93.2
4	4	45.7	45.5
4	5	26.0	23.6
4	6	149.7	159.6
4	7	43.6	43.9
4	9	76.1	74.2
4	10	39.9	36.8
4	11	60.6	61.5
5	-9	79.3	79.6
5	-8	38.4	37.4
5	-7	81.7	79.0
5	-6	50.2	50.6
5	-5	73.0	71.9
5	-4	10.7	6.0
5	-3	40.0	39.5
5	-2	95.7	94.9
5	-1	73.7	70.5
5	1	15.9	14.4
5	3	81.8	83.4
5	4	45.8	43.5
5	5	42.9	41.9
5	6	60.9	58.7
5	7	29.2	28.8
5	8	19.7	18.1
5	9	39.0	37.2
5	10	43.4	45.0
6	-8	33.8	33.0
6	-7	14.4	10.0
6	-6	37.6	34.7
6	-5	89.2	92.3
6	-4	101.1	103.9
6	-3	24.9	22.3
6	-2	16.9	20.0
6	-1	52.0	50.9
6	0	132.6	140.1
6	0	136.6	140.1
6	1	74.9	73.0
6	2	17.4	11.9
6	4	19.1	17.3
6	5	25.0	24.8
6	6	34.6	31.8
6	7	42.4	38.4
6	8	50.0	52.3
6	9	55.9	50.9
7	-8	98.0	100.6
7	-7	17.6	19.5
7	-6	12.2	8.5
7	-5	40.3	41.7
7	-4	85.7	86.0
7	-3	31.9	32.0
7	-1	29.2	26.6
7	1	44.0	42.3
7	2	67.3	68.4
7	3	67.0	64.9
7	4	117.5	119.6
7	6	54.7	53.1
7	7	41.0	38.2
7	8	74.7	74.0
8	-5	31.4	32.7
8	-4	76.4	75.9
8	-2	22.2	19.1
8	-1	25.8	26.1
8	0	77.6	76.9
8	1	58.7	58.5
8	2	22.4	21.7
8	3	65.2	66.4
8	4	25.4	23.6
8	5	88.1	85.4
8	6	18.0	16.2
8	7	61.4	61.9
9	-4	66.7	63.9
9	-3	97.2	99.5
9	-2	25.8	25.4
9	-1	84.8	84.2
9	0	40.1	39.1
9	0	39.2	38.1
9	1	60.6	61.1
9	2	55.0	53.3
9	3	13.3	13.4
9	4	22.1	18.8
9	5	39.4	36.2
H = 5			
0	-11	81.8	85.2
0	-8	57.1	53.9
0	-6	120.9	125.4
0	-2	17.3	19.2
0	2	112.6	108.9
0	4	54.5	56.0
0	6	68.0	69.3
0	8	36.2	34.3
1	-10	32.2	29.9
1	-9	57.8	57.7
1	-8	35.4	35.5
1	-7	97.4	99.3
1	-6	82.1	82.2
1	-5	22.9	20.6
1	-4	43.7	40.7
1	-3	52.9	52.0
1	-2	140.5	144.5
1	-1	101.5	103.0
1	0	93.0	95.4
1	1	53.1	55.4
1	2	48.4	45.2
1	3	87.6	89.5
1	4	50.4	50.6
1	5	30.6	26.0
1	6	44.9	48.0
1	7	21.5	17.9
1	8	38.6	36.7
1	9	80.6	78.8
1	10	74.7	74.5
2	-10	44.7	41.0
2	-8	28.1	29.1
2	-7	34.5	32.6
2	-5	49.1	49.9
2	-4	33.6	31.0
2	-3	13.7	13.8
2	-2	35.5	31.9
2	-1	90.4	91.5
2	0	75.2	73.6
2	0	76.2	73.6
2	1	65.2	64.6
2	2	63.4	62.2
2	3	28.1	24.8
2	5	38.2	37.3
2	6	33.0	36.7
2	7	79.6	80.9
2	8	87.7	89.1
2	9	43.9	41.1
2	10	32.9	30.5
3	-10	30.4	30.1
3	-9	56.6	53.2
3	-8	118.9	120.4
3	-7	59.9	58.0
3	-5	33.4	34.1
3	-4	54.8	53.0
3	-2	54.4	52.1
3	-1	60.7	58.5
3	0	68.3	66.9
3	0	68.2	66.9
3	1	21.8	21.7
3	2	71.8	71.7
3	3	35.5	33.9
3	4	141.0	148.9
3	5	12.9	9.9
3	6	51.4	51.8
3	7	27.1	19.2
3	8	81.9	82.1
3	9	37.7	37.5
3	10	16.2	14.6
4	-9	13.4	11.7
4	-8	16.8	14.5
4	-7	39.6	38.6
4	-6	62.7	61.7
4	-5	73.4	75.6
4	-4	87.8	87.9
4	-3	22.1	18.0
4	-2	23.9	22.0
4	0	100.2	98.9
4	0	98.1	98.9
4	2	21.1	19.4
4	3	61.5	59.3
4	5	46.9	45.7
4	6	12.8	4.1
4	8	89.1	91.4
4	9	18.5	15.5
5	-9	22.8	26.4
5	-8	34.7	33.6
5	-7	72.6	70.9
5	-6	51.3	48.2
5	-5	22.5	22.0
5	-4	16.7	15.6
5	-3	111.1	112.2
5	-2	45.2	41.7
5	-1	73.1	70.7
5	0	40.3	38.9
5	0	38.5	38.9
5	1	49.6	49.2
5	2	16.8	16.6
5	3	81.4	79.9
5	4	75.3	74.8
5	5	60.1	60.0
5	6	19.5	17.9
5	9	84.6	84.7
6	-8	26.1	23.8
6	-7	41.8	44.9
6	-6	66.4	64.8
6	-5	44.8	43.8
6	-4	68.1	68.9
6	-1	26.0	26.7
6	0	31.6	31.4
6	0	30.8	31.4
6	1	39.3	39.6
6	2	70.6	69.9
6	3	58.5	57.3
6	4	48.4	48.6
6	5	87.1	85.5
6	6	51.3	52.4
6	7	28.1	28.1
7	-6	67.3	68.9
7	-5	39.8	41.2
7	-4	39.3	41.2
7	-3	37.6	33.0
7	-2	123.0	129.9
7	-1	25.3	22.3
7	1	22.8	21.2
7	2	50.5	49.2
7	3	57.6	57.0
7	4	34.3	32.2
7	6	21.6	22.0
8	-4	22.6	17.1
8	-3	49.7	46.4
8	-2	18.9	19.8
8	-1	59.3	57.5
8	0	43.5	41.6
8	0	43.1	41.6
8	4	31.3	33.6
H = 6			
0	-8	19.1	15.8
0	-6	46.3	46.7
0	-4	97.5	98.2
0	-2	65.4	65.7
0	0	103.3	105.6
0	0	102.2	105.6
0	4	25.7	24.1
0	8	76.2	79.1
1	-8	86.7	88.0
1	-7	54.1	53.9
1	-6	44.4	46.5
1	-4	47.0	43.9
1	-3	96.5	95.4
1	-2	16.4	12.2
1	-1	52.8	51.2
1	0	64.9	64.7
1	0	63.0	64.7
1	2	24.5	23.0
1	3	98.0	98.9
1	4	49.2	48.0
1	5	57.9	56.7
1	6	15.2	16.8
1	8	50.2	49.6
2	-7	75.2	74.4
2	-6	32.7	30.2
2	-5	101.4	100.3
2	-4	38.3	35.2
2	-3	40.0	36.1
2	-1	72.5	71.6
2	0	45.8	43.7
2	0	45.5	43.7
2	1	89.8	90.6
2	2	70.9	69.9
2	4	55.5	56.5
2	5	103.3	107.0
2	6	26.6	25.3
2	7	77.0	78.2
2	8	51.6	50.9
3	-7	21.7	20.6
3	-6	59.0	58.4
3	-3	75.0	74.5
3	-2	79.8	78.8
3	-1	15.5	17.5
3	0	27.4	25.1
3	0	24.7	25.1
3	1	12.0	1.8
3	3	45.9	42.1
3	5	31.5	30.0
3	6	77.2	78.0
3	7	20.4	19.6
4	-7	57.0	52.4
4	-6	74.0	74.1
4	-5	50.3	50.9
4	-3	35.9	33.4
4	-1	106.1	105.5
4	0	28.6	26.7
4	0	27.6	26.7
4	1	65.8	63.3
4	2	109.4	111.3
4	3	14.6	15.4
4	4	51.2	51.6
4	6	51.0	52.8
4	7	72.2	69.5
5	-6	60.9	59.4
5	-5	21.8	20.1
5	-4	13.7	14.2
5	-3	45.6	44.0
5	-2	53.6	51.5
5	-1	72.4	71.4
5	0	48.3	48.2
5	0	47.9	48.2
5	2	17.2	15.0
5	3	104.8	107.6
5	4	22.0	21.0
5	5	51.6	52.6
5	6	15.4	18.1
6	-4	70.6	69.8
6	-3	53.4	50.4
6	-2	39.8	38.4
6	-1	77.7	78.8
6	0	16.9	10.5
6	0	16.6	10.5
6	1	40.6	40.6
6	2	26.2	25.1
7	0	56.5	56.0
7	0	56.3	56.0
H = 7			
0	-4	45.0	43.3
0	-2	32.9	34.0
0	0	65.0	66.1
0	0	62.6	66.1
0	2	135.2	142.2
0	4	66.9	67.8
1	-5	13.9	9.7
1	-4	72.3	72.3
1	-3	38.0	38.0
1	-2	76.0	77.6
1	1	30.8	27.9
1	2	27.3	25.1
1	3	28.2	28.5
1	5	19.4	21.7
2	-4	89.1	90.8
2	-3	38.1	37.1
2	-1	38.9	36.9
2	0	43.0	41.1
2	0	42.4	41.1
2	1	63.1	59.9
2	3	17.5	15.7
2	4	52.1	53.7
3	-2	51.8	51.2
3	0	72.7	74.2
3	0	74.3	74.2
3	1	21.0	17.4
3	2	70.8	72.3
3	3	37.8	35.5
4	-1	32.4	28.8
4	0	70.8	73.1
4	0	71.4	73.1
4	1	48.4	47.2

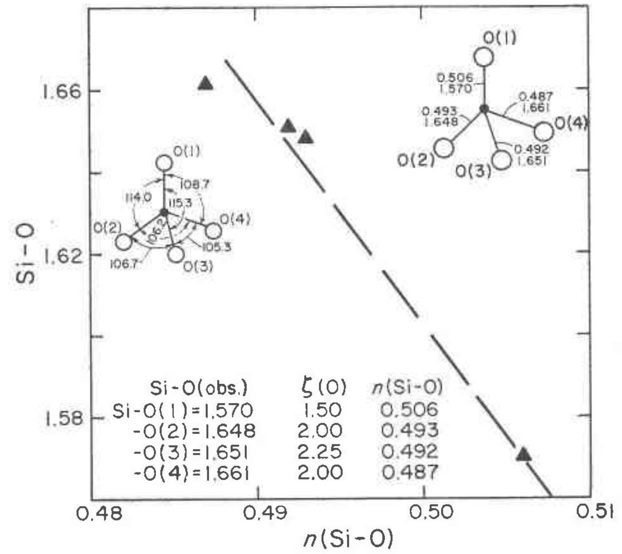

FIG. 2. A plot of Si–O bond lengths *vs* Mulliken Si–O bond overlap populations, n(Si–O) for datolite. Si–O distances, electrostatic bond strength ζ(O), and n(Si–O) are tabulated in the lower portion of the figure.

Si–O(4) bonds being involved with the smallest ones. These results suggest that n(Si–O) calculations may be used to order the Si–O bond length variations in silicates where all the oxygen atoms are not charge balanced and where the neighboring cations and anions are ignored. However, the Si–O bond length variations in datolite can be ordered equally well (Fig. 2) by the sum of the electrostatic bond strengths received by oxygen, ζ(O) (Smith, 1954; Baur, 1961, 1970). Therefore, it appears that n(Si–O) and ζ(O) are reflecting similar aspects of the Si–O bond (see Gibbs *et al*, 1972).

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References

APPLEMAN, D. E., AND J. R. CLARK (1965) Crystal structure of reedmergnerite, a boron albite, and its relation to feldspar crystal chemistry. *Amer. Mineral.* **50,** 1827–1850.

BAUR, W. H. (1961) Verzerrte Koordinationspolyeder in heteropolaren Kristallstrukturen und die elektrostatische Valenzregel von Pauling. *Naturwissenschaften,* **48,** 549–550.

——— (1970) Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Amer. Crystallogr. Ass.* **6,** 129–155.

BROWN, G. E., AND G. V. GIBBS (1970) Stereochemistry and ordering in the tetrahedral portion of silicates. *Amer. Mineral.* **55,** 1587–1607.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) A Fortran crystallographic least squares program. *U. S. Nat. Tech. Inform. Serv.,* ORNL-TM-**305.**

———, ———, AND ——— (1964) A Fortran crystallographic function and error program. *U. S. Nat. Tech. Inform. Serv.,* ORNL-TM-**306.**

CROMER, D. T., AND J. T. WABER (1965) Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18,** 104–109.

CRUICKSHANK, D. W. J. (1961) The role of 3*d* orbitals in π bonds between a) silicon, phosphorus, sulfur, or chlorine and b) oxygen or nitrogen. *J. Chem. Soc.* **1961,** 5486–5504.

——— (1965) Errors in least-squares methods. *In,* J. S. Rollett, Ed., *Computing Methods in Crystallography,* Pergamon Press Ltd., Oxford.

GIBBS, G. V., M. M. HAMIL, S. J. LOUISNATHAN, L. S. BARTELL, AND H. YOW (1972) Correlations between Si–O bond length, Si–O–Si angle, and bond overlap populations calculated using extended Hückel molecular orbital theory. *Amer. Mineral.* **57,** 1578–1613.

ITO, T., AND H. MORI (1953) The crystal structure of datolite. *Acta Crystallogr.* **6,** 24–32.

PANT, A. K., AND D. W. J. CRUICKSHANK (1967) A reconsideration of the structure of datolite, $CaBSiO_4(OH)$. *Z. Kristallogr.* **125,** 286–297.

PAVLOV, P. V., AND N. V. BELOV (1959) The structures of herderite, datolite, and gadolinite determined by direct methods. *Kristallografia,* **4,** 324–340 (in Russian); *Sov. Phy.-Crystallogr.* **4,** 300–314 (1960).

PHILLIPS, M. W., P. H. RIBBE, AND G. V. GIBBS (1971) Refinement of the crystal structure of danburite (abstr.) *Geol. Soc. of Amer. Abstr. Prorgams,* **3,** 338.

SAHL, K. (1966) Messung des Ultrarot-Pleochroismus von Mineralen. V. Der pleochroismus der OH Streckfrequenz in Datolit. *N. Jahrb. Mineral. Monatsch.,* pp. 45–49.

SMITH, J. V. (1954) A review of the Al–O and Si–O distances. *Acta. Crystallogr.* **7,** 479–481.

SUGITANI, Y., M. WATANABE, AND K. NAGASHIMA (1972) The positions of the hydrogen atoms in datolite as determined by nuclear magnetic resonance. *Acta Crystallogr.* **B28,** 326–327.

ZACHARIASEN, W. H. (1963) The crystal structure of monoclinic metaboric acid. *Acta Crystallogr.* **16,** 385–389.

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