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The Crystal Structure of Ancylite, $(RE)_x(Ca,Sr)_{2-x}(CO_3)_2(OH)_x(2-x)H_2O$

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Abstract

The crystal structure of ancylite $(La,Ce)_{1.38}(Sr,Ca)_{0.62}(CO_3)_2(OH)_{1.38}\cdot 0.62H_2O$, $a = 5.03$, $b = 8.53$, $c = 7.29$ Å, space group *Pmcn*, $Z = 2$, has been determined by Patterson and Fourier methods, using 502 intensities measured with an automatic diffractometer. The least squares refinement led to a final discrepancy index $R = 0.059$.

The crystal structure of ancylite can be ideally derived from that of the orthorhombic carbonates with the introduction of hydroxyl groups lying on the mirror planes and bonded to the heavy cations. These have a ten-fold coordination (average M-O distance 2.61 Å). The relationships between the aragonite-ancylite series and the vaterite-bastnaesite series are discussed.

Introduction

Ancylite is a carbonate whose general chemical formula is: $(RE)_x(Sr,Ca)_{2-x}(CO_3)_2(OH)_x \cdot (2-x)H_2O$. The mineral is found in pegmatites of alkaline rocks and in carbonatites. The two sub-species, strontian ancylite and calcian ancylite, are defined on the basis of the Sr/Ca ratio in the chemical formula. The rare earths are represented mainly by La and Ce.

Sawyer, Caro, and Eyring (1973) synthesized the compound $RE(OH)CO_3$, which represents the limiting composition of ancylite if $x = 2$; this compound is isostructural with ancylite.

The crystal used for this structural study comes from the pegmatites of the nepheline syenite at Mont St. Hilaire, Quebec, Canada (Chao *et al,* 1967).

Chemical Analysis

The available amount of ancylite was so small that wet chemical analysis was not possible. A preliminary non-dispersive X-ray spectrometer analysis revealed only La, Ce, Sr, and Ca. Five grains of ancylite were analyzed for these elements by electron microprobe. The sample current was 1 mA and the accelerating potential was 15 kV. Synthetic anorthite, synthetic anorthite containing 10 mole percent $SrAl_2Si_2O_8$, and synthetic La and Ce glasses served as standards. The raw data were corrected by the Bence-Albee method (Table 1). A thermogravimetric analysis has been made with a MOM Derivatograph on 0.2 g of ancylite in order to determine water and carbon dioxide by weight loss. The weight loss from 25° to 1100°C was 28.4 wt percent while the average sum of the heavy element oxides, determined with the microprobe, was 65.5 percent. Thus the electron probe data for the heavy elements were corrected to yield a total sum of 100 percent. As it was impossible to determine from the thermogravimetric curve the weight losses due respectively to H_2O and CO_2, the total weight loss has been assigned as 20 percent to water and as 80 percent to carbon dioxide. The results of the analyses are given in Table 1. The chemical formula derived from the corrected data is in good agreement with the results of the structure analysis and with the experimental density measured by flotation in Clerici's solution (Table 2).

Experimental

The lattice parameters were determined with a Philips PW1100 single crystal automatic diffractometer (Table 2). The X-ray diffraction data were collected from a crystal fragment whose dimensions were: 0.16 × 0.10 × 0.08 mm using Mo$K\alpha$ radiation monochromatized by a flat graphite crystal. The intensities of the reflections of four octants of the reciprocal sphere were measured up to $2\theta = 60°$ by the θ-2θ scan mode with a symmetrical scan range of 1.6° in 2θ from the calculated scattering angle. The scan rate was 0.08°/sec. Three standard reflections, monitored at three-hour intervals, showed no variation in intensity greater than 3 percent.

Processing of the data was carried out in the manner described by Davies and Gatehouse (1973) to yield values of F_o and σF_o. The F_o of the four octants of the reciprocal sphere were averaged in order to have a set of 502 independent reflections, 498 of which have $F_o > \sigma F_o$ and have been used in subsequent calculations. No absorption nor extinction corrections were applied.

TABLE 1. Chemical Data of Ancylite

Oxides	Weight percent *	Weight percent **	Atomic proportions ***		
La_2O_3	21.90	23.96	La	0.57	2.04
Ce_2O_3	30.74	33.63	Ce	0.84	
SrO	9.92	10.85	Sr	0.41	
CaO	2.92	3.19	Ca	0.22	
CO_2	28.36	22.12	C	2.01	
H_2O		6.24	H	2.45	
Total	65.48	100.00			

* Electron microprobe analysis (average of 5 grains) by R. Rinaldi, Dept. of Geophysical Sciences, University of Chicago.
** Recalculated taking into account the total weight loss of 28.36 %.
*** Number of atoms on the basis of 8 oxygen atoms per formula unit.

Crystal Structure Analysis

The crystal structure of ancylite has been determined by Patterson and Fourier methods in the space group *Pmcn*[1] for which the systematic absences are: *h0l* when $l = 2n+1$, *0kl* when $k+l = 2n+1$.

The least squares isotropic refinement, carried out on the structure amplitudes with a locally modified version of the program ORFLS (Busing, Martin, and Levy, 1962), reduced the conventional *R* index from 0.125 to 0.082. Three successive least squares cycles, performed with anisotropic thermal parameters, led to a final *R* index of 0.059 for the 498 observed reflections.

Since in space group *Pmcn* there is no equipoint with a multiplicity lower than four, which is the number of heavy atoms occurring in the unit cell, it has been assumed that the distribution of the divalent and trivalent cations was disordered. Therefore the scattering curve of the cation *M* has been computed taking into account the results of the chemical analysis and using the scattering curves of Hanson *et al* (1964). The multipliers of the atoms *M* and O(3) were allowed to vary during the isotropic refinement, but they did not show any change greater than one standard deviation.

The final atomic parameters are given in Tables 3 and 4; bond distances and angles are listed in Table 5. The observed and calculated structure factors are compared in Table 6.

[1] The non-standard *Pmcn* space group was used instead of *Pnma* in order to compare directly the crystal structure of ancylite with those of the orthorhombic carbonates which are described in the *Pmcn* space group. The coordinates of the equivalent positions in this space group are: $\pm|x, y, z;\ 1/2-x, 1/2-y, 1/2+z;\ 1/2+x, -y, -z;\ -x, 1/2+y, 1/2-z|$.

TABLE 2. Unit Cell Data of Ancylite and Strontianite*

	Ancylite	Strontianite
a	5.03(1) Å	5.090(2) Å
b	8.53(1)	8.358(2)
c	7.29(1)	5.997(4)
Chemical formula	$La_{0.56}Ce_{0.82}Sr_{0.40}Ca_{0.22}(CO_3)_2(OH)_{1.38}\cdot 0.62H_2O$	$SrCO_3$
Sp. group	Pmcn	Pmcn
Z	2	4
$D_{obs.}$	4.1	--
$D_{calc.}$	4.15	--

*Estimated standard deviations are given in parentheses.

TABLE 3. Positional Parameters and Temperature Factors *(Standard Deviations in Parentheses)*

Atom	Positional parameters x/a	y/b	z/c	B_H(Å^2)*
M = (La,Ce,Sr,Ca)	1/4	0.3399(1)	0.6476(1)	0.80
C	3/4	.1905(14)	.8099(18)	0.79
O(1)	3/4	.3181(12)	.7210(16)	1.81
O(2)	0.5297(14)	.1218(8)	.8520(10)	1.55
O(3) = (OH,H_2O)	1/4	.4135(14)	.9749(14)	2.43

Atom	Anisotropic temperature factors ($\times 10^4$) β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M	83(3)	25(1)	39(1)	0	0	-2(1)
C	83(41)	11(12)	56(20)	0	0	11(13)
O(1)	160(39)	52(13)	108(20)	0	0	37(14)
O(2)	123(25)	55(9)	85(12)	-17(13)	8(15)	6(8)
O(3)	318(52)	93(16)	63(16)	0	0	38(14)

*Equivalent isotropic temperature factors after Hamilton (1959).

TABLE 4. Analysis of the Anisotropic Thermal Parameters in Ancylite*

Atom	r.m.s.	U_ia	U_ib	U_ic		r.m.s.	U_ia	U_ib	U_ic
M	0.095(2)	90	30	80	O(2)	0.11(1)	33	60	77
	0.103(2)	0	90	90		0.15(1)	57	48	60
	0.103(1)	90	70	20		0.16(1)	84	57	34
C	0.06(4)	90	27	73	O(3)	0.10(2)	90	63	27
	0.10(2)	0	90	90		0.20(2)	90	27	63
	0.13(2)	90	73	17		0.20(2)	0	90	90
O(1)	0.11(2)	90	33	56					
	0.14(2)	0	90	90					
	0.19(2)	90	56	34					

* Root mean square thermal vibration along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoid.

TABLE 5. Interatomic Distances and Principal Bond Angles*

Atoms			Atoms		
M - O(1)	"	2.579(2) Å	C - O(1)		1.268(9) Å
O(2)	"	2.595(7)	O(2)	"	1.291(8)
O(2')	"	2.648(7)			
O(2")	"	2.768(7)	Average		1.283
O(3)		2.468(11)			
O(3')		2.502(10)	O(3) - O(3')		2.939(13)
			O(1) - C - O(2)"		120.8°(5)
Average		2.615	O(2) - C - O(2')		118.3°(8)

* Estimated standard deviations are given in parentheses. Bond distances and angles preceded by the sign " occur twice.

TABLE 6. Observed and Calculated Structure Factors

h	k	F_{obs}	F_{calc}
		$l = 0$	
2	0	156.0	-166.3
4	0	139.1	143.1
6	0	75.1	-76.1
1	1	106.4	-110.1
3	1	98.4	99.9
5	1	54.7	-54.3
7	1	47.5	45.8
0	2	87.4	-91.3
2	2	73.3	75.9
4	2	48.9	-50.3
6	2	34.9	33.6
1	3	45.1	-44.9
3	3	40.5	41.9
5	3	11.7	-9.7
0	4	138.8	-140.2
2	4	57.7	60.2
4	4	71.4	-73.8
6	4	36.2	37.4
1	5	93.7	98.9
3	5	84.6	-90.8
5	5	56.1	58.5
0	6	108.6	113.2
2	6	99.1	-107.0
4	6	75.8	81.9
6	6	56.5	-58.0
1	7	49.3	-52.1
3	7	35.7	37.6
5	7	39.3	-40.1
0	8	18.5	-19.0
2	8	40.1	42.1
4	8	15.9	-16.4
1	9	30.4	-34.5
3	9	30.2	33.1
0	10	45.2	-48.1
2	10	44.8	48.2
1	11	61.0	68.5
0	12*	4.1	46.3
		$l = 1$	
0	1	62.8	63.0
1	1	74.7	-76.6
2	1	20.2	-17.7
3	1	41.8	42.4
4	1	35.5	34.1
5	1	41.7	-42.1
6	1	20.2	-18.8
7	1	19.8	19.3
0	2	94.5	-91.3
1	2	54.7	-53.9
2	2	135.5	138.0
3	2	59.6	59.4
4	2	62.4	-63.7
5	2	32.7	-32.2
6	2	54.1	52.5
0	3	118.9	-117.1
1	3	108.9	113.7
2	3	69.3	71.6
3	3	77.6	-79.4
4	3	64.0	-65.2
5	3	64.8	67.3
6	3	38.5	38.8
0	4	93.2	93.5
1	4	67.1	68.5
2	4	74.7	-77.3
3	4	49.4	-50.5
4	4	56.8	57.3
5	4	35.7	35.8
6	4	38.6	-38.3
0	5	28.6	28.0
1	5	23.2	-22.3
2	5	42.7	-44.4
3	5	28.3	28.9
4	5	19.5	18.8
5	5	14.0	-12.4
6	5	17.1	-16.1
0	6	10.3	4.2
1	6	18.9	16.8
2	6	33.1	-34.9
3	6	21.3	-20.7
4	6	10.8	9.5
5	6	10.2	7.2
6	6	15.8	-14.9
0	7	53.1	54.8
1	7	53.3	-56.0
2	7	36.8	-37.9
3	7	41.0	43.5
4	7	35.6	36.3
5	7	36.5	-37.3
0	8	70.6	-75.3
1	8	56.2	-58.4
2	8	61.3	66.3
3	8	44.9	47.8
4	8	51.2	-54.6
5	8	35.7	-36.9
0	9	40.3	-41.3
1	9	52.4	55.3
2	9	46.6	48.1
3	9	49.1	-52.8
4	9	31.0	-32.5
0	10	42.7	43.5
1	10	21.8	22.2
2	10	26.3	-27.2
3	10	16.3	-16.6
0	11*	4.1	-0.1
1	11	5.8	-3.8
2	11	7.1	-4.7
		$l = 2$	
0	0	69.6	-74.0
1	0	145.0	-156.2
2	0	37.5	38.3
3	0	90.6	97.6
4	0	38.3	-38.3
5	0	84.0	-89.0
6	0	23.7	22.2
0	1	89.6	-92.7
1	1	15.1	-5.3
2	1	122.8	129.9
3	1	13.4	-8.3
4	1	63.9	-67.7
5	1	11.0	6.5
6	1	54.7	54.8
0	2	54.5	50.2
1	2	65.1	64.7
2	2	39.9	-39.3
3	2	49.1	-49.9
4	2	23.2	22.8
5	2	32.9	33.7
6	2	15.2	-13.7
0	3	21.2	15.7
1	3	13.6	-5.3
2	3	32.6	31.5
3	3	9.9	-2.5
4	3	8.8	-1.7
5	3	7.7	-0.1
6	3	12.6	10.1
0	4	32.0	26.5
1	4	79.6	80.0
2	4	16.2	-9.4
3	4	49.7	-50.4
4	4	19.2	16.8
5	4	52.2	52.8
6	4	12.2	-8.8
0	5	92.7	94.5
1	5	29.5	-26.5
2	5	107.3	-111.4
3	5	26.0	23.6
4	5	67.3	69.4
5	5	17.7	-15.0
6	5	55.4	-55.4
0	6	49.6	-49.9
1	6	98.1	-101.1
2	6	43.6	44.9
3	6	82.4	86.4
4	6	31.3	-31.3
5	6	60.9	-61.4
0	7	75.5	-78.6
1	7	14.1	11.3
2	7	46.8	49.4
3	7	10.2	-7.5
4	7	51.1	-51.9
5	7	9.7	8.4
0	8	12.8	10.1
1	8	16.6	15.2
2	8	16.3	-15.9
3	8	20.2	-20.5
4	8	9.4	8.2
5	8	9.0	6.6
0	9	23.8	-24.8
1	9	20.0	18.8
2	9	32.0	33.8
3	9	18.0	-16.0
4	9	18.5	-19.8
0	10	17.8	12.0
1	10	49.0	52.2
2	10	17.7	-12.3
3	10	43.9	-47.1
0	11	62.8	67.7
1	11	19.6	-18.5
2	11	46.4	-52.9
		$l = 3$	
0	1	120.5	-125.3
1	1	42.0	-40.4
2	1	57.2	61.5
3	1	24.7	24.0
4	1	58.5	-63.0
5	1	20.7	-19.9
6	1	31.8	33.1
0	2	35.1	-31.7
1	2	108.4	109.3
2	2	48.1	47.6
3	2	95.4	-100.0
4	2	26.2	-24.6
5	2	49.9	53.6
6	2	21.2	20.7
0	3	159.5	160.6
1	3	58.4	55.9
2	3	104.5	-107.0
3	3	39.8	-39.1
4	3	93.7	96.9
5	3	31.2	30.4
6	3	56.0	-59.0
0	4	24.0	21.6
1	4	65.2	-62.8
2	4	22.1	-20.4
3	4	54.2	53.2
4	4	19.6	18.1
5	4	43.4	-43.3
6	4	14.6	-14.2
0	5	22.6	-20.5
1	5	13.2	-10.1
2	5	46.2	46.9
3	5	13.6	11.8
4	5	20.7	-21.3
5	5	7.8	-4.8
6	5	23.5	22.1
0	6	13.9	5.9
1	6	29.0	-28.5
2	6	19.1	-15.9
3	6	32.2	32.4
4	6	10.2	5.3
5	6	13.4	-12.8
0	7	63.4	-62.1
1	7	25.4	-23.4
2	7	42.1	43.0
3	7	21.5	18.6
4	7	44.8	-45.4
5	7	19.1	-16.6
0	8	27.3	-24.9
1	8	68.9	73.6
2	8	23.1	23.1
3	8	58.4	-62.1
4	8	20.0	-19.3
0	9	55.9	60.2
1	9	24.3	25.0
2	9	66.9	-69.7
3	9	23.6	-23.5
4	9	43.9	47.8
0	10	15.3	15.1
1	10	35.1	-36.5
2	10	8.8	-9.1
3	10	26.2	27.3
0	11	10.3	-8.1
1	11*	4.1	-2.9
		$l = 4$	
0	0	105.2	-112.1
1	0	77.7	80.3
2	0	56.7	59.1
3	0	52.4	-55.1
4	0	66.4	-72.6
5	0	43.3	47.7
6	0	39.5	43.5
0	1	50.8	52.5
1	1	85.3	90.3
2	1	60.3	-64.4
3	1	74.6	-80.9
4	1	32.9	35.8
5	1	45.9	49.0
6	1	27.8	-28.0
0	2	43.1	43.5
1	2	26.8	-25.2
2	2	38.2	-39.7
3	2	23.2	22.3
4	2	27.6	29.4
5	2	17.2	-16.7
6	2	19.2	-20.2
0	3	10.4	4.9
1	3	10.8	-2.5
2	3	23.4	-21.4
3	3	12.6	-9.0
4	3	8.7	4.8
5	3	6.4	-1.0
6	3	6.9	-7.1
0	4	73.2	72.3
1	4	43.9	-42.5
2	4	35.2	-34.7
3	4	29.5	28.5
4	4	45.7	46.8
5	4	27.4	-27.3
6	4	25.4	-25.9
0	5	45.1	-45.6
1	5	85.9	-87.7
2	5	52.4	52.4
3	5	74.4	77.3
4	5	34.5	-34.5
5	5	49.2	-50.5
0	6	77.1	-76.3
1	6	44.9	44.6
2	6	71.5	71.9
3	6	39.6	-40.5
4	6	54.9	-55.9
5	6	30.9	30.1
0	7	34.2	34.8
1	7	58.0	58.4
2	7	21.9	-21.8
3	7	43.4	-44.0
4	7	25.4	24.3
5	7	40.3	39.6
0	8	9.7	-2.8
1	8	11.2	-9.6
2	8	16.4	-13.8
3	8	13.4	11.7
4	8	7.9	1.2
0	9	12.4	10.9
1	9	21.9	21.7
2	9	16.1	-15.1
3	9	21.4	-20.8
0	10	44.4	44.3
1	10	25.1	-22.8
2	10	41.8	-43.1
0	11	35.5	-35.4
		$l = 5$	
0	1	14.1	-7.2
1	1	57.2	59.1
2	1	12.3	4.3
3	1	38.8	-41.4
4	1	8.8	-2.9
5	1	38.6	41.3
6	1	6.4	1.4
0	2	61.3	63.5
1	2	26.1	24.1
2	2	90.6	-96.2
3	2	20.3	-18.6
4	2	50.6	55.5
5	2	13.6	10.8
6	2	47.5	-49.5
0	3	13.2	-4.7
1	3	108.1	-111.0
2	3	13.4	5.3
3	3	82.3	86.0
4	3	10.7	-2.1
5	3	68.6	-71.4
0	4	75.4	-76.5
1	4	14.8	-12.6
2	4	65.3	67.4
3	4	12.5	11.0
4	4	52.4	-54.1
5	4	10.4	-8.4
0	5	15.9	14.5
1	5	38.0	36.4
2	5	12.6	-11.7
3	5	36.7	-36.7
4	5	10.1	8.1
5	5	18.3	17.8
0	6	10.9	-9.4
1	6	10.9	5.9
2	6	31.8	31.7
3	6	9.0	-3.9
4	6	11.7	-10.8
5	6	6.5	3.7
0	7	14.6	-6.4
1	7	60.1	59.5
2	7	13.5	4.8
3	7	46.4	-47.6
4	7	10.7	-5.3
0	8	73.1	74.9
1	8	12.4	2.8
2	8	64.3	-66.9
3	8	10.8	-3.0
0	9	9.4	1.9
1	9	62.1	-62.5
2	9	8.7	-2.0
3	9	57.1	58.7
0	10	38.4	-38.2
1	10	7.9	-8.4
		$l = 6$	
0	0	90.9	95.5
1	0	70.5	76.7
2	0	58.1	-63.3
3	0	51.2	-55.8
4	0	59.1	64.0
5	0	43.1	47.5
0	1	47.0	49.6
1	1	59.0	-62.4
2	1	56.0	-58.9
3	1	53.5	56.5
4	1	36.3	38.4
5	1	33.9	-35.7
0	2	29.2	-29.0
1	2	24.0	-24.9
2	2	28.1	28.2
3	2	20.4	21.5
4	2	22.2	-22.6
5	2	15.6	-15.7
0	3	11.4	7.7
1	3	13.5	-12.8
2	3	19.8	-18.7
3	3	15.1	14.9
4	3	7.2	5.7
5	3	5.3	-4.3
0	4	53.4	-52.7
1	4	43.0	-43.0
2	4	29.9	30.0
3	4	30.7	30.9
4	4	36.0	-35.9
5	4	29.6	-29.4
0	5	45.5	-45.3
1	5	58.2	57.3
2	5	51.3	51.8
3	5	51.7	-52.3
4	5	36.0	-36.0
0	6	52.9	52.2
1	6	45.5	45.8
2	6	51.0	-51.1
3	6	39.8	-40.6
4	6	40.9	41.1
0	7	33.8	33.7
1	7	36.7	-37.6
2	7	23.2	-23.7
3	7	28.7	29.0
0	8	8.5	-7.4
1	8	10.6	-6.9
2	8	18.1	17.7
3	8	11.5	8.9
0	9	12.0	9.6
1	9	16.7	-15.8
2	9	15.7	-14.2
		$l = 7$	
0	1	48.1	48.8
1	1	18.4	-17.5
2	1	28.7	-29.4
3	1	14.5	12.9
4	1	33.7	34.7
5	1	11.6	-10.2
0	2	17.0	-14.0
1	2	69.9	-75.3
2	2	19.6	17.5
3	2	68.0	72.0
4	2	13.2	-9.6
5	2	41.8	-45.7
1	3	77.1	-81.7
2	3	25.6	23.3
3	3	58.3	62.4
4	3	21.2	-19.2
5	3	56.8	-59.5
0	4	8.6	4.0
1	4	64.4	68.8
2	4	5.8	-3.2
3	4	53.5	-57.6
4	4	6.4	4.0
0	5	14.0	11.0
1	5	7.2	-5.4
2	5	24.8	-23.2
3	5	6.4	6.4
4	5	11.4	10.4
0	6	9.5	4.8
1	6	12.9	12.2
2	6	11.0	-7.9
3	6	15.6	-15.7
0	7	52.9	54.8
1	7	12.2	-5.7
2	7	40.0	-42.6
3	7	11.1	5.1
0	8	13.7	-9.1
1	8	58.1	-58.6
2	8	12.2	7.6
		$l = 8$	
0	0	33.4	34.3
1	0	64.2	-68.3
2	0	23.8	-24.3
3	0	50.7	54.3
4	0	23.5	23.8
0	1	43.7	-45.6
1	1	30.0	-30.4
2	1	51.4	54.1
3	1	27.1	28.1
4	1	35.0	-37.2
0	2	10.6	-8.5
1	2	32.0	33.1
2	2	9.3	7.9
3	2	27.9	-28.5
4	2	9.0	-6.7
0	3	4.4	2.4
1	3	7.2	-2.8
2	3	10.4	9.6
3	3	8.0	4.0
4	3	4.4	-1.0
0	4	25.5	-23.8
1	4	36.0	37.9
2	4	18.4	16.1
3	4	28.4	-29.0
0	5	51.2	52.3
1	5	26.8	24.3
2	5	55.6	-56.8
3	5	24.5	-23.0
0	6	23.3	22.4
1	6	57.8	-58.8
2	6	22.0	-20.9
0	7	42.1	-41.2
1	7	18.7	-19.4
		$l = 9$	
0	1	19.0	-19.0
1	1	32.9	-33.8
2	1	12.4	12.6
3	1	24.6	25.9
0	2	48.8	-51.7
1	2	27.8	28.6
2	2	57.0	59.7
3	2	26.4	-26.8
0	3	30.3	28.7
1	3	48.8	51.9
2	3	24.7	-23.0
0	4	39.9	41.4
1	4	23.8	-23.2
2	4	37.6	-38.6
0	5*	4.1	-5.2
1	5	10.4	-8.6
		$l = 10$	
0	0	58.1	-59.0
1	0	8.4	-0.8
0	1	11.0	-8.5
1	1	46.2	49.1
0	2	20.8	21.2
1	2	4.5	2.0

* Reflections marked by an asterisk were considered as unobserved.

Description and Discussion of the Structure

The crystal structure of ancylite can be compared to that of the orthorhombic carbonates aragonite, strontianite and witherite. Ancylite shares with these minerals the space group *Pmcn* and the dimensions of its *a* and *b* cell edges are very close to the corresponding ones in strontianite (Table 2).

It will be useful to recall shortly the main structural features of the orthorhombic carbonates (de Villiers, 1971; Dal Negro and Ungaretti, 1971) before describing the crystal structure of ancylite. The crystal structure of the aragonite carbonate family can be described as a close packing of spheres. The triangular carbonate groups are normal to the *c* cell edge and are grouped in pairs in which one triangle is superposed on the other one after a rotation of 60°. Actually there is not a perfect close packing since the carbon atoms of one pair of CO_3^{2-} groups are not exactly superposed, but are shifted off about 0.1 Å in the *b* direction and the CO_3^{2-} triangles are not perfectly parallel to the *ab* plane, but are tilted off about 2°. The carbonate ions are connected to one another by the divalent cations which have a nine-fold coordination. Comparison of the structures of ancylite and aragonite (Fig. 1) shows that in ancylite the heavy cations, the carbon atoms, and one oxygen of the carbonate group are located on the mirror planes and the positional relationships among these atoms are similar to those existing among the corresponding atoms in aragonite.

The crystal structure of ancylite can ideally be derived from that of the orthorhombic carbonates by introducing in the latter a hydroxyl group (or a water molecule) lying on the mirror plane and bonded to the heavy cations. The introduction of the OH groups in the compact aragonite structure results in the relative shifts of the two superposed carbonate ions and in the angle of tilt between the CO_3^{2-} triangles and the *ab* plane. The former increases from 0.1 Å to 1.0 Å and affects mainly the *b* cell parameter; the latter increases from 2° to 30° and affects the *c* cell parameter (Table 2).

The suggestion of Dexpert, Lemaitre-Blaise, and Caro (1972) that the ancylite-type hydroxy-carbonate is related to the aragonite-type carbonates in the same manner as the bastnaesite fluorocarbonate $(RE)FCO_3$ is related to the vaterite type of calcium carbonate (Mayer, 1969) is correct on the basis of what has been written above. However, there are difficulties in this analogy. The introduction of the F anion in the vaterite structure affects only the *c* direction; in this way vaterite-type layers (normal to *c*) can occur together with bastnaesite-type layers as in parisite ($2CeFCO_3 \cdot CaCO_3$), roentgenite ($3CeFCO_3 \cdot 2CaCO_3$) and synchisite ($CeFCO_3 \cdot CaCO_3$) (Donnay and Donnay, 1953). The syntaxy phenomena, which are frequent among these minerals, can also be explained in the same manner. On the other hand, the modifications produced in the aragonite-type structure by the presence of the OH groups affect both *b* and *c* cell parameters in such a way as to make the co-existence

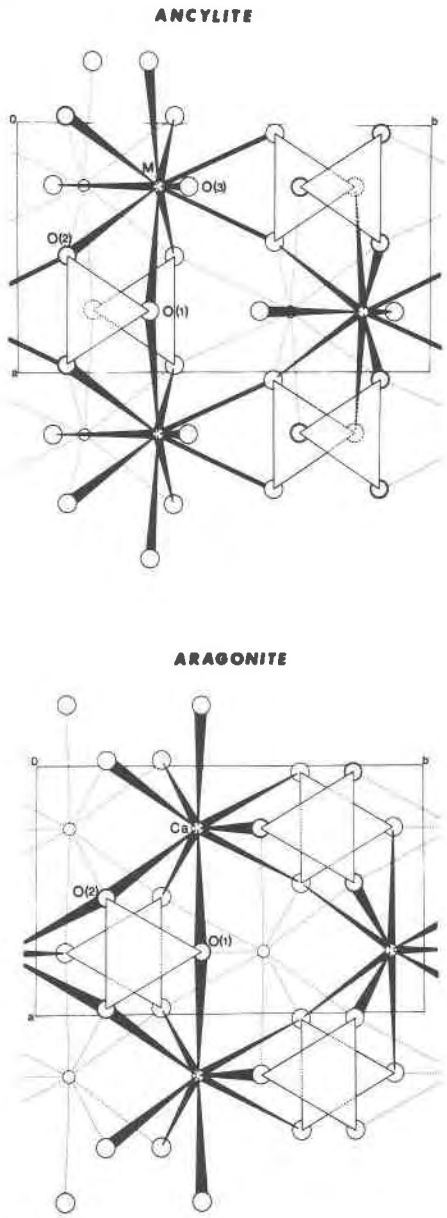

FIG. 1. The crystal structures of ancylite and aragonite viewed along [001].

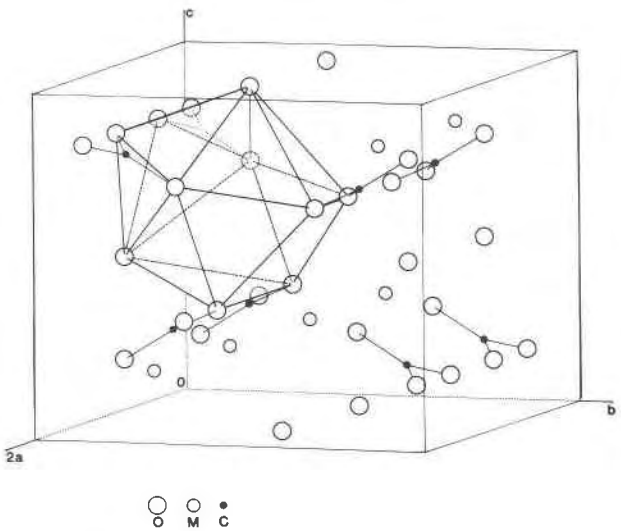

FIG. 2. Clinographic projection of the coordination polyhedron of the cation *M*.

of aragonite-type layers with ancylite-type layers impossible. Thus no family of minerals similar to that mentioned above for the vaterite-bastnaesite series can exist for the aragonite-ancylite series.

In ancylite the cation *M* is bonded to eight oxygen atoms belonging to carbonate ions and to two hydroxyls or water molecules (Figs. 1 and 2). The *M*-O distances (Table 5) range from 2.58 to 2.77 Å for the oxygen atoms, while the *M*-O distances involving the hydroxyls are shorter, being 2.46 and 2.50 Å. The mean *M*-O bond distance, 2.61 Å, is very close to the mean Sr-O bond length in strontianite (2.64 Å). The C-O bond distances are consistent with the values found in the literature.

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