CRYSTAL STRUCTURE OF SCAWTITE

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Scawtite — $Ca_7(Si_6O_{18})(CO_3)\cdot 2H_2O$, which is the third member of calcium carbonate and silicate mineral, is rare in nature[1]. Several mineralogical researches on scawtite have been carried out[2—4]. Pluth and Smith[1] have studied its crystal structure by means of a single-crystal X-ray diffraction photographer and a four-circle single-crystal X-ray diffractometer. They found out that the space group of scawtite is *I2/m* or *Im*, probably. Hence the space group is undetermined. The related problems whether CO_3 is ordered or disordered and how Ca atoms are coordinated have not been solved either.

Using a single crystal, $0.15\times0.2\times0.4$ mm^3 in size, selected from the specimen from Zoulou iron deposit, Suixi County, Anhui Province, the diffraction data of scawtite were collected with a SYNTEX R3 four-circle single-crystal X-ray diffractometer, with Mo$K\alpha$ radiation filtered with a graphite monochromator, under the condition of 55 kV and 30 mA. Based on C-centered lattice and θ-2θ scanning type, in the range of 2θ: 2— 65°, 2012 reflections were collected, among which there were 42 standard and 2 rejected. 11 reflections were chosen for ψ-scanning. After absorption correction, the maximum $R_{trans.}=0.812$ and the minimum $R_{trans.}=0.702$. 1939 independent observable reflections were obtained. The unit cell parameters of scawtite were determined (Table 1). $Z=2$, $D_c=2.76$ g/cm^3.

Table 1

The Unit Cell Parameters and the Space Group of Scawtite (Numbers in Parentheses in Tables 1—4 Indicate the Standard Deviations)

Type		This Note	Ref. [1]	Ref. [4]
Unit cell parameters	a (Å)	10.0394 (0.0019)	10.118 (0.003)	10.1206
	b (Å)	15.1935 (0.0017)	15.187 (0.004)	15.2058
	c (Å)	6.6344 (0.0012)	6.626 (0.001)	6.6345
	β	115.645 (0.013)°	100°40 (1)′	100°37′
Space group		*Cm*	*I2/m* or *Im*	*I2/m*

The diffraction intensities were reduced to absolute intensities when corrections have been completed. The coordinates of heavy atoms were worked out with Direct Method and the coordinates of other non-hydrogen atoms were solved through Fourier synthesis. So the initial

structure model was obtained. Three kinds of space groups *C2*, *Cm* and *C2/m* were used during Block-matrix Least Squares refinement. It is evident that *Cm* is the most suitable as the space group of scawtite. The raw positions of H atoms were calculated out through Difference Fourier after the anisotropic thermal refinement came to converge. Because the relationship between H and the neighboring O was unreasonable, the standard structure model of H_2O molecule was used to calculate the position of H. Finally, $R=0.0219$. Tables 2—4 show the results of the structure determination and refinement.

Table 2

Atomic Coordinates ($\times10^4$) and Thermal Constants ($\times10^3$ Å^2) of Non-hydrogen Atom

No.	x	y	z	U	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C	0	0	0	13(1)	8(1)	23(2)	8(1)	0	2(1)	0
Ca1	9971(1)	0	4714(2)	9(1)	8(1)	7(1)	11(1)	0	2(1)	0
Ca2	1970(1)	1356(1)	4(1)	10(1)	13(1)	7(1)	8(1)	−0(1)	2(1)	−1(1)
Ca3	9908(1)	2509(1)	4863(2)	8(1)	8(1)	7(1)	7(1)	−0(1)	2(1)	−0(1)
Ca4	7731(1)	1447(1)	9757(1)	9(1)	9(1)	8(1)	8(1)	0(1)	2(1)	1(1)
Si1	7187(1)	1040(1)	4209(2)	5(1)	5(1)	6(1)	5(1)	0(1)	1(1)	1(1)
Si2	4889(1)	1765(1)	9845(2)	6(1)	5(1)	8(1)	5(1)	−0(1)	2(1)	0(1)
Si3	2650(1)	1042(1)	5548(2)	6(1)	6(1)	6(1)	6(1)	−0(1)	3(1)	−1(1)
O1	8491(2)	1233(2)	3785(4)	10(1)	8(1)	10(1)	13(1)	2(1)	5(1)	0(1)
O2	7268(3)	0	5009(4)	12(1)	20(1)	6(1)	10(1)	0	6(1)	0
O3	5921(2)	1087(2)	1720(4)	13(1)	11(1)	14(1)	8(1)	2(1)	−3(1)	5(1)
O4	6896(2)	1616(1)	5955(3)	11(1)	15(1)	10(1)	9(1)	−0(1)	6(1)	3(1)
O5	5750(2)	2349(2)	8899(4)	11(1)	11(1)	13(1)	11(1)	−1(1)	6(1)	−2(1)
O6	3974(2)	2274(2)	793(4)	10(1)	11(1)	11(1)	13(1)	0(1)	8(1)	2(1)
O7	3986(3)	1046(2)	7953(4)	13(1)	13(1)	11(1)	10(1)	−0(1)	−1(1)	−2(1)
O8	2925(2)	1614(1)	3796(3)	12(1)	16(1)	12(1)	8(1)	1(1)	4(1)	−5(1)
O9	1392(2)	1270(2)	6063(4)	10(1)	8(1)	10(1)	13(1)	−1(1)	5(1)	−0(1)
O10	2448(3)	0	4689(4)	10(1)	16(1)	6(1)	7(1)	0	3(1)	0
O11	9760(4)	722(3)	673(6)	73(2)	40(2)	96(3)	47(2)	−47(2)	−15(2)	48(2)
O12	601(3)	0	8750(5)	27(1)	14(1)	57(3)	11(1)	0	6(1)	0
O13	3451(4)	0	1331(7)	17(1)	19(2)	14(1)	23(2)	0	13(1)	0
O14	6566(4)	0	8528(6)	15(1)	18(2)	13(1)	15(1)	0	9(1)	0

Table 3

Atomic Coordinates ($\times10^4$) and Isotropic Thermal Constant ($\times10^3$ Å^2) of H

No.	x	y	z	U
H13a	2860(53)	0(810)	2049(102)	81(32)
H13b	4337(26)	0(810)	2541(76)	63(27)
H14a	6503(52)	0(810)	7039(34)	35(19)
H14b	5649(17)	0(810)	8321(85)	33(19)

In conclusion, the space group of scawtite is *Cm*. The fact that Pluth and Smith have not determined the space group reflects the quality of their experimental data and the accuracy of structure. The exchange of the body-centered and the base-centered unit cells is easy, but

Table 4
Bond Length and Bond Angle of Scawtite

Bond	Bond Length (Å)	Bond Angle (°)						
		O1	O1′	O9	O9′	O10	O11	O11′
Ca1-O1	2.384(0.002)							
-O1′	2.385(0.002)	103.5(0.1)						
-O9	2.402(0.002)	74.3(0.1)	172.4(0.1)					
-O9′	2.402(0.002)	172.4(0.1)	74.3(0.1)	106.9(0.1)				
-O10	2.742(0.004)	124.9(0.1)	124.9(0.1)	60.7(0.1)	60.7(0.1)			
-O11	2.812(0.004)	71.5(0.1)	107.2(0.1)	79.2(0.1)	116.1(0.1)	70.4(0.1)		
-O11′	2.812(0.004)	107.2(0.1)	71.5(0.1)	116.1(0.1)	79.2(0.1)	70.4(0.1)	45.9(2)	
-O12	2.458(0.004)	97.0(0.1)	97.0(0.1)	76.3(0.1)	76.3(0.1)	101.2(0.1)	155.0(0.1)	155.0(0.1)
		O5	O6	O8	O9	O12		
Ca2-O5	2.317(0.003)							
-O6	2.473(0.003)	86.1(0.1)						
-O8	2.302(0.002)	97.5(0.1)	74.2(0.1)					
-O9	2.412(0.003)	81.8(0.1)	93.0(0.1)	167.0(0.1)				
-O12	2.476(0.002)	114.4(0.1)	154.3(0.1)	115.7(0.1)	75.8(0.1)			
-O13	2.539(0.002)	176.1(0.1)	90.1(0.1)	80.7(0.1)	99.2(0.1)	69.5(0.1)		
		O1	O4	O5	O6	O8		
Ca3-O1	2.398(0.002)							
-O4	2.394(0.002)	159.0(0.1)						
-O5	2.435(0.002)	106.8(0.1)	75.8(0.1)					
-O6	2.460(0.003)	82.6(0.1)	98.7(0.1)	167.0(0.1)				
-O8	2.394(0.002)	88.1(0.1)	112.4(0.1)	98.1(0.1)	72.9(0.1)			
-O9	2.394(0.002)	74.2(0.1)	86.0(0.1)	79.8(0.1)	111.8(0.1)	160.5(0.1)		
		O1	O4	O5	O6	O11		
Ca4-O1	2.451(0.003)							
-O4	2.295(0.002)	176.6(0.1)						
-O5	2.431(0.003)	100.3(0.1)	77.7(0.1)					
-O6	2.305(0.002)	84.7(0.1)	97.9(0.1)	87.3(0.1)				
-O11	2.328(0.004)	79.4(0.1)	102.9(0.1)	173.8(0.1)	86.5(0.1)			
-O14	2.498(0.002)	97.1(0.1)	80.5(0.1)	97.8(0.1)	174.1(0.1)	88.3(0.1)		
		O1	O2	O3				
Si1-O1	1.608(0.003)							
-O2	1.657(0.001)	107.5(0.2)						
-O3	1.639(0.002)	104.7(0.2)	105.5(0.1)					
-O4	1.592(0.003)	120.3(0.1)	106.9(0.2)	110.9(0.1)				
		O3	O5	O6				
Si2-O3	1.638(0.002)							
-O5	1.612(0.003)	108.0(0.1)						
-O6	1.602(0.003)	110.8(0.2)	117.7(0.1)					
-O7	1.637(0.002)	98.9(0.1)	109.6(0.2)	110.2(0.1)				
		O7	O8	O9				
Si3-O7	1.638(0.002)							
-O8	1.582(0.003)	109.6(0.1)						
-O9	1.605(0.003)	106.8(0.1)	119.8(0.1)					
-O10	1.665(0.001)	105.5(0.1)	108.1(0.1)	106.1(0.2)				
		O11	O11′					
C -O11	1.255(0.005)							
-O11′	1.255(0.005)	121.9(0.4)						
-O12	1.266(0.004)	118.9(0.2)	118.9(0.2)					
		O						
H -O	0.960(0.601)							
-O′	0.960(0.601)	104.5(9.1)						

Cm is more often used. CO_3 group of the structure, which is a triangle geometrically, is ordered (Fig. 1), which is verified clearly by the electron density map. SiO_4 tetrahedra link to each other and construct a 6-cell circle Si_6O_{18}. There are 4 kinds of coordination polyhedra

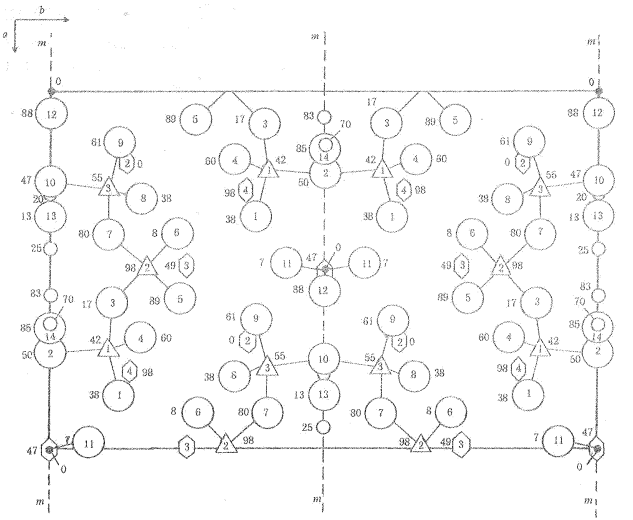

Fig. 1. Projection of a crystal cell down the *c*-axis onto (001). O, H, C, Si and Ca atoms are represented by large circles, small circles, dots, triangles and hexagons respectively. Labels of atoms are indicated inside the symbols and the heights of atoms along the *c*-axis are shown near the symbols (in percentage).

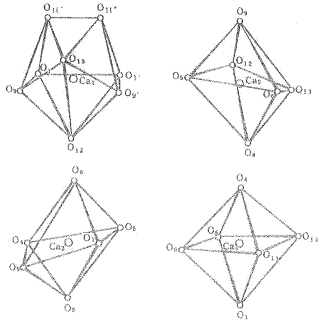

Fig. 2. Coordination polyhedra of Ca atoms.

of Ca (Fig. 2), which link complicatedly, ledge to ledge, and form structural layers, between which there is CO_3, Si_6O_{18} and H_2O. The distortion degrees of the coordination polyhedra of Ca are different. Bond valence analysis indicates that perhaps there is hydrogen bond in the structure of scawtite and that the hydrogen bond is also affected by the neighboring coordination polyhedra (to see another note in preparation).

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