Sclarite, a new mineral from Franklin, New Jersey, with essential octahedrally and tetrahedrally coordinated zinc: Description and structure refinement

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Abstract

Sclarite, ideally $(Zn,Mg,Mn)_4Zn_3(CO_3)_2(OH)_{10}$, is a new mineral species from the Franklin mine, New Jersey. It occurs as 1.5-mm clusters of clear, colorless crystals associated with leucophoenicite, gageite, zincite, and willemite. The mineral has a vitreous luster and white streak. It is brittle with no apparent cleavage and has a Mohs hardness of 3–4. Sclarite is biaxial positive with $\alpha = 1.648(1)$, $\beta = 1.664(1)$, $\gamma = 1.702(2)$, $2V_{meas} = 63.4(6)°$, $2V_{calc} = 67°$, with strong dispersion $r \gg v$. It is monoclinic, space group $A2/a$, with $a = 16.110(7)$, $b = 5.432(1)$, $c = 15.041(10)$ Å, $\beta = 95.490(4)°$, and $Z = 4$. The strongest X-ray powder-diffraction lines are [d(Å), I, hkl] 7.50(10)(002), 3.75(4)($\bar{3}$11,004), 3.63(5)($\bar{1}$13,311), 3.53(4)(113,$\bar{2}$04), 3.398(2)(402), 2.934(2)(313), 2.621(5)($\bar{1}$15), 2.500(4)($\bar{5}$13,006). An electron-microprobe analysis gave FeO 0.1, MgO 6.7, MnO 4.2, ZnO 62.0, CO_2 12.67 (calc.), H_2O 12.97 (calc.), total 98.6 wt%; $D_{obs} = 3.51(5)$ and $D_{calc} = 3.547$ g/cm³. The structure has been refined to $R = 0.069$. It is isostructural with loseyite, with Zn atoms occupying both the octahedral and tetrahedral sites. The mineral is named after Professor Charles B. Sclar of Lehigh University.

Introduction

During the course of a systematic examination of late-stage carbonates from Franklin, New Jersey, we found a mineral with properties and X-ray data very close to those of loseyite, yet distinctly different. Detailed investigation has revealed that it is the Zn analogue of loseyite, and a rare example of a mineral with both octahedrally and tetrahedrally coordinated essential Zn.

We have named this new species *sclarite* in honor of Professor Charles B. Sclar, Professor of Geology at Lehigh University, in recognition of his contributions to mineralogy, petrology, and ore genesis. It is especially fitting that this is a Franklin mineral, in light of Dr. Sclar's long-standing interest in the genesis of this deposit; much of the recent sophisticated work on the Sterling Hill primary ores has been done under his supervision. The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. The holotype and only specimen is in the collection of the Smithsonian Institution under catalogue no. NMNH B13671, and a portion of the holotype is in the National Museum of Natural Sciences, Ottawa, under catalogue no. 53777.

Physical and optical properties

Sclarite occurs as 1.5-mm clusters in which the individual crystals (0.2 mm) form a slightly divergent array, which on the whole resembles a very coarse-surfaced spherule. Sclarite crystals are platy on {001}, elongate parallel to [010], and have a minor {100} side pinacoid.

Sclarite is colorless and transparent in single crystals; aggregates appear grayish white and turbid. The luster is vitreous, and the streak is white; neither cleavage nor parting was observed; the Mohs hardness is 3–4, and the mineral is moderately brittle. The density, measured using heavy-liquid techniques, is 3.51(5) g/cm³, compared with the calculated value of 3.547 g/cm³. Optically, sclarite is biaxial, positive, $2V_{meas} = 63.4(6)°$, $2V_{calc} = 67°$, $\alpha = 1.648(1)$, $\beta = 1.664(1)$, and $\gamma = 1.702(2)$, as determined in Na light. Dispersion is strong, $r \gg v$, and the orientation is $Y = \mathbf{b}$ and $X \wedge \mathbf{c} = +49°$ (in β obtuse). There is no discernible fluorescence in either long- or short-wave ultraviolet.

Chemical composition

Sclarite was chemically analyzed with an ARL-SEMQ electron microprobe, using an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. A wavelength-dispersive microprobe scan indicated the absence of elements with atomic number greater than 9, other than those reported here, and this finding is supported by the strong relation to loseyite, which contains only these detectable elements. The standards used for microprobe analysis were hornblende (Fe, Mg), manganite (Mn), and zincite (Zn). C (carbonate) and water (hydroxyl) could not be directly determined owing to extreme paucity of material. However, their presence is suggested by the close relation to loseyite and has been demonstrated by crystal-structure analysis. The single

TABLE 1. X-ray powder-diffraction data for sclarite

I_{est}	d_{meas} (Å)	d_{calc}* (Å)	hkl
10	7.50	7.49	002
2	5.23	5.23	202
2	4.82	4.82	111
4	3.75	3.75	$\bar{3}$11
		3.74	004
5	3.63	3.64	$\bar{1}$13
		3.63	311
4	3.53	3.53	113
		3.52	$\bar{2}$04
2	3.398	3.401	402
<1	3.277	3.274	204
<1	3.209	3.204	$\bar{4}$11
2	2.934	2.933	313
<1	2.807	2.809	$\bar{4}$13
<1	2.711	2.716	020
<1	2.671	2.673	600
5	2.621	2.623	$\bar{1}$15
<1	2.552	2.553	022
4	2.500	2.505	$\bar{5}$13
		2.495	006
1	2.440	2.444	602
		2.436	$\bar{3}$15
2	2.334	2.336	513
3	2.281	2.284	$\bar{4}$15
		2.281	$\bar{6}$04
		2.280	315
<1	2.216	2.216	$\bar{4}$06
<1	2.203	2.198	024
2	2.150	2.151	$\bar{2}$24
2	2.119	2.122	422
		2.116	711
<1	2.082	2.083	604
1	1.998	2.004	800
		1.994	324
<1	1.888	1.892	802
		1.885	713
<1	1.882	1.883	424
		1.877	$\bar{6}$22
<1	1.839	1.842	804
		1.837	026
1	1.817	1.819	$\bar{2}$26
<1	1.790	1.789	$\bar{1}$31
<1	1.764	1.764	226
<1	1.744		
<1	1.712		
<1	1.697		
<1	1.688		
<1	1.659		
<1	1.607		
<1	1.597		
<1	1.566		
<1	1.549		
<1	1.522		
<1	1.494		
<1	1.481		
<1	1.468		
<1	1.447		
<1	1.442		
<1	1.421		
<1	1.384		
<1	1.378		
<1	1.359		
<1	1.328		
<1	1.312		
<1	1.275		
<1	1.269		
<1	1.258		

* Calculated from cell parameters refined from powder-diffraction data: $a = 16.110(7)$, $b = 5.432(1)$, $c = 15.041(10)$ Å.

carbonate group in the structure was readily determined by the nearly ideal trigonal-planar coordination and short C-O bond lengths. Bond-valence calculations (see Discussion section) clearly indicate a proton bonded to five of the oxygen atoms. Accordingly, CO_2 and H_2O were calculated from the known crystal structure. The resultant analysis yields FeO 0.1, MgO 6.7, MnO 4.2, ZnO 62.0, CO_2 [12.67], H_2O [12.97], total = 98.6 wt%. The empirical formula, calculated on the basis of seven tetrahedral and octahedral cations, is $Zn_{5.39}Mg_{1.18}Mn_{0.42}$-$Fe_{0.01}(CO_3)_2(OH)_{10}$. The ideal formula is $(Zn,Mg,Mn)_4Zn_3$-$(CO_3)_2(OH)_{10}$ with $Z = 4$.

OCCURRENCE

Sclarite occurs on but one known specimen from the Franklin mine, Franklin, Sussex County, New Jersey. It has not been found at the genetically related deposit at Sterling Hill. Our detailed search for sclarite has failed to find additional specimens. This may be due in part to local specimen-collecting biases. Throughout the history of the Franklin and Sterling Hill deposits, most of the collecting has been casual and nonscientific, and collections have a strong residual bias in favor of attractive mineral specimens. The holotype sclarite specimen is decidedly unattractive; it was probably retained by observant collectors for the presence of the rare mineral gageite.

Sclarite occurs on a calcite-free specimen of granular willemite-franklinite ore, which has minor zincite present and exhibits minor shearing. The exposed surface, possibly part of a hydrothermal vein, has been severely altered; the specimen to the naked eye looks quite weathered, but this is a false impression. The exposed ore surface is coated unevenly with sparse leucophoenicite and dense, abundant, microcrystalline, fibrous coatings of gageite and sparse secondary zincite. Upon these minerals are 1-mm spherules of light pink to grayish pink rhodochrosite, additional gageite, and chlorophoenicite; these are coated, in turn, and unevenly, with very sparse sclarite, which is intimately associated with secondary zincite and an unnamed, soft, white, zinc-magnesium carbonate mineral described by Dunn (1986). Willemite is present throughout this secondary assemblage, occurring as a fine dust-like dispersal of microcrystallites.

Although sclarite is currently a one-locality mineral, we note that Kanaki (1972) reported loseyite associated with hydrozincite as a post-mine mineral on mine timbers at Bleiberg, Carinthia, Austria (Niedermayr, 1986). Because these minerals occurred together, because hydrozincite is commonly of near-end-member composition, and because the diffraction maxima of loseyite and sclarite are very similar, such hydrozincite-associated loseyites should be examined compositionally. Other occurrences of loseyite or sclarite may repose undiscovered among hydrozincite specimens at other localities. The determined compositions of sclarite and loseyite indicate some variability among the cations, but the paucity of data precludes speculation about the extent of such solid solution.

TABLE 2. Positional and anisotropic thermal parameters ($\times 100$, Å²) for sclarite

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	0.4097(1)	0.2546(3)	0.2796(1)	1.91(8)	0.79(7)	1.18(7)	−0.02(6)	0.55(5)	0.06(6)
Zn(2)	0.1851(1)	0.2697(3)	0.1980(1)	1.85(8)	0.86(7)	0.94(7)	0.02(6)	0.68(5)	0.11(5)
Zn(3)	0.0386(1)	0.2460(2)	0.3615(1)	1.81(6)	0.82(5)	0.66(5)	−0.05(5)	0.53(4)	0.00(5)
Zn(4)	¼	0.2855(4)	0	2.35(9)	1.49(9)	0.59(7)	0	0.55(6)	0
C	0.3757(7)	0.4185(21)	0.4770(7)	1.5(5)	1.3(5)	0.7(4)	−0.3(4)	0.6(4)	−0.3(4)
O(1)	0.0740(5)	0.2491(16)	0.4933(5)	3.1(4)	1.4(4)	0.5(3)	−0.8(4)	0.3(3)	0.1(3)
O(2)	0.4759(5)	0.0945(14)	0.1752(5)	2.3(4)	0.7(3)	0.9(3)	0.0(3)	0.5(3)	0.0(3)
O(3)	0.1197(5)	0.0812(14)	0.2901(5)	1.8(4)	1.0(3)	0.4(3)	−0.1(3)	0.5(3)	−0.2(3)
O(4)	0.0675(5)	0.4341(14)	0.1445(5)	2.1(4)	0.9(3)	0.4(3)	−0.3(3)	0.3(3)	−0.2(3)
O(5)	0.2442(5)	0.4702(15)	0.1064(5)	2.2(4)	1.3(4)	0.4(3)	0.0(3)	0.7(3)	0.2(3)
O(6)	0.3457(6)	0.0704(18)	0.0314(5)	3.3(5)	2.6(5)	1.0(4)	1.3(4)	0.5(3)	−0.5(3)
O(7)	0.3518(5)	0.4306(15)	0.3924(5)	2.1(4)	1.4(4)	0.5(3)	0.0(3)	0.3(3)	0.1(3)
O(8)	0.2990(5)	0.0848(14)	0.2238(5)	1.7(4)	0.9(3)	0.7(3)	−0.1(3)	0.5(3)	0.2(3)
H(26)	0.440	0.160	0.126	4.0					
H(35)	0.164	0.060	0.342	4.0					
H(41)	0.070	0.472	0.078	4.0					
H(57)	0.285	0.112	0.410	4.0					
H(86)	0.313	0.048	0.162	4.0					

Note: Esd's are in parentheses.

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Precession studies show sclarite to be monoclinic with possible space group choices $A2/a$ and Aa. Results of the crystal-structure refinement, presented below, confirm the same centrosymmetric $A2/a$ space group determined for the isostructural mineral loseyite (Hill, 1981). Unit-cell parameters were refined from X-ray powder-diffraction data obtained with a 114.6-mm-diameter Gandolfi camera with $CuK\alpha$ radiation (Table 1). The refined unit-cell parameters are $a = 16.110(7)$, $b = 5.432(1)$, $c = 15.041(10)$ Å, and $\beta = 95.490(4)°$, with $V = 1310.2(8)$ Å³ and $Z = 4$.

For the intensity-data collection, a reasonably equant plate ($0.16 \times 0.22 \times 0.14$ mm) was chosen and mounted perpendicular to (001). Intensity data were collected at CANMET, Ottawa, on an Enraf Nonius CAD-4 single-crystal diffractometer operated at 50 kV and 26 mA with graphite-monochromated $MoK\alpha$ radiation. Data collection and structure refinement were done by the NRCVAX package of computer programs (Gabe et al., 1985). A set of 48 reflections permuted four ways, $\pm h$ at $\pm 2\theta$ (i.e., 192 reflections), was used to refine the cell parameters: $a = 16.054(2)$, $b = 5.4131(5)$, $c = 15.031(3)$ Å, and $\beta = 95.33(1)°$. Three asymmetric units of data were collected to $2\theta = 60°$ assuming an A-centered lattice. The intensities were corrected for Lorentz and polarization effects and a Gaussian absorption correction ($\mu_l = 106$ cm⁻¹) was applied; transmission factors ranged between 0.13 and 0.29. Of the 5703 measured intensities, 1899 are independent and 1583 of these are observed [$I > 2.5\sigma(I)$]. It is significant that the 3 standard reflections decreased in intensity by 8% over the 8-d duration of the experiment.

For the structure refinement of sclarite, the atomic coordinates in loseyite (Hill, 1981) were used. The H atomic positions were not refined as they are those calculated by Hill (1981) on the basis of donor-acceptor distances of the respective oxygen atoms. The five H atoms were each

assigned an isotropic temperature factor of $U = 0.04$ Å². Refinement of positional parameters, isotropic thermal parameters, and the occupancy factors of Zn and Mg in the four metal sites gave a residual index $R = 0.091$. The occupancy factors of the four metal sites (denoted Zn) split into two very distinct groups. Those for sites Zn(3) and Zn(4) are both within 3 esd's of that expected for a site fully occupied by Zn. Sites Zn(1) and Zn(2) are within 1 esd of having equivalent scattering powers, and for both sites the proportions of Zn and Mg agree well (within 1 esd) with the chemical analysis. Refinement of all positional and anisotropic thermal parameters, except those of the H atoms, converged to an R value of 0.069 and $R_w = 0.081$ for all reflections. Weighting schemes did not improve the R value. Final atomic and thermal-vibration parameters are given in Table 2. Selected interatomic distances and angles are given in Table 3. The observed and calculated structure factors have been deposited.[1]

DISCUSSION

Although the best crystal available was used for the structure refinement of sclarite, the quality of the data limited the convergence to $R = 0.069$. Decrepitation of the crystal would influence the accuracy of the data, but it should be noted that the error of the y atomic coordinate is generally 3 times that of the x and z coordinates. The same disparity was also evident in the isostructural mineral loseyite (Hill, 1981).

Bond-valence sums calculated using the parameters of Brown (1981) are Zn(1) 1.93, Zn(2) 1.91, Zn(3) 1.84, Zn(4) 2.12, C 3.99, O(1) 1.80, O(2) 1.12, O(3) 1.16, O(4) 1.11, O(5) 0.95, O(6) 1.82, O(7) 1.71, and O(8) 1.04 v.u. These values clearly indicate the presence of hydroxyl at the

TABLE 3. Selected interatomic distances (Å) and angles (°) for sclarite

Zn(1) octahedron				Zn(2) octahedron			
Zn(1)-O(2)	2.156(8)	O(2)-O(2)'	85.1(3)	Zn(2)-O(3)	2.081(7)	O(3)-O(4)	88.4(3)
-O(2)'	2.066(8)	-O(3)	94.5(3)	-O(4)	2.172(8)	-O(7)	83.4(3)
-O(3)	2.087(8)	-O(4)	89.4(3)	-O(5)	2.054(7)	-O(8)	97.4(3)
-O(4)	2.090(8)	-O(8)	89.4(3)	-O(7)	2.328(8)	-O(8)'	94.0(3)
-O(7)	2.223(8)	O(2)'-O(3)	89.0(3)	-O(8)	2.089(8)	O(4)-O(5)	88.6(3)
-O(8)	2.104(8)	-O(4)	92.5(3)	-O(8)'	2.073(8)	-O(7)	86.6(3)
Average	2.121	-O(7)	90.1(3)	Average	2.133	-O(8)	86.0(3)
		O(3)-O(7)	85.9(3)			O(5)-O(7)	97.7(3)
		-O(8)	91.5(3)			-O(8)	85.8(3)
		O(4)-O(7)	90.2(3)			-O(8)'	84.6(3)
		-O(8)	87.3(3)			O(7)-O(8)	84.3(3)
		O(7)-O(8)	95.4(3)			O(8)-O(8)'	103.3(3)

Zn(3) tetrahedron				Zn(4) tetrahedron			
Zn(3)-O(1)	2.009(7)	O(1)-O(2)	106.4(3)	Zn(4)-O(5) ×2	1.896(8)	O(5)-O(5)'	116.3(3)
-O(2)	1.973(8)	-O(3)	113.5(3)	-O(6) ×2	1.951(9)	-O(6) ×2	102.1(3)
-O(3)	1.975(8)	-O(4)	102.4(3)	Average	1.923	-O(6)' ×2	114.8(4)
-O(4)	1.957(8)	O(2)-O(3)	110.3(3)			O(6)-O(6)'	106.7(4)
Average	1.978	-O(4)	112.6(3)				
		O(3)-O(4)	111.4(3)				

				Carbonate group			
				C-O(1)	1.274(14)	O(1)-O(6)	120.0(9)
				-O(6)	1.284(13)	-O(7)	120.1(9)
				-O(7)	1.295(13)	O(6)-O(7)	119.9(9)
				Average	1.284		

Note: Esd's are in parentheses.

O(2), O(3), O(4), O(5), and O(8) sites. This interpretation yields the structural formula

$$^{[6]}(Zn,Mg,Mn)_2 {}^{[6]}(Zn,Mg,Mn)_2 {}^{[4]}Zn_2 {}^{[4]}Zn(CO_3)_2(OH)_{10}$$

with Z = 4 for sclarite compared to structural formula

$$^{[6]}Mn_2 {}^{[6]}Mn_2 {}^{[4]}Zn_2 {}^{[4]}(Zn,Mg)(CO_3)_2(OH)_{10}$$
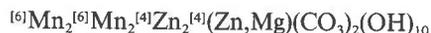
with Z = 4 for loseyite.

The topology of the loseyite structure type, which consists of stepped sheets of octahedra oriented parallel to (001) and connected to each other by isolated tetrahedral and carbonate groups, is discussed in detail by Hill (1981). There are a few unique features in the sclarite structure, and only these are described here.

Sclarite is one of the few minerals that has Zn in both tetrahedral and octahedral coordination sites. Ghose (1964) and Allmann (1968) described a similar feature in hydrozincite, $Zn_5(OH)_6(CO_3)_2$, and synthetic simonkolleite, $Zn_5(OH)_8Cl_2·H_2O$, respectively. Although Zn readily fills either a 4- or 6-coordinated site, it is evident from the loseyite and sclarite structures that it has a preference for the tetrahedral site. In loseyite, all the Zn is tetrahedrally coordinated, and Mg fills in for any deficiency in Zn occupancy. This phenomenon is even more evident in sclarite where the tetrahedral sites are fully occupied by Zn and only in the octahedral sites is any deficiency in Zn content compensated for by enough Mg to fill the site.

The final point concerns the problem of refining the y atomic coordinates of all of the atoms in the sclarite structure. This parameter corresponds to the elongate axis, [010], of the crystal. Hill (1981) attributed this morpho-

logical feature to edge-sharing octahedral ribbons. It is quite possible that during crystal growth, which is most rapid in this direction, defects occur in the ribbons, which are composed of Zn(1) and Zn(2) octahedra and vacant-site octahedra, which are overlain by Zn(3) tetrahedra. Such disorder in the [010] direction would account for the anomalously large esd's noted for the y parameters. Also, Ghose (1964) referred to stacking-ordered and stacking-disordered phases in hydrozincite, a structure more distantly related to sclarite and perhaps exemplifying the same features.

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