

THE STRUCTURE OF SPURRITE, TILLEYITE AND SCAWTITE, AND RELATIONSHIPS TO OTHER SILICATE–CARBONATE MINERALS

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ABSTRACT

Spurrite, $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$, tilleyite, $\text{Ca}_5(\text{Si}_2\text{O}_7)(\text{CO}_3)_2$, and scawtite, $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3)\cdot 2\text{H}_2\text{O}$, are the only calcium carbonate–silicate minerals known to date; all three form in high-temperature skarns. Crystals of spurrite and tilleyite from Cornet Hill, Metaliferi Massif, Apuseni Mountains, Romania, and scawtite from the type locality in Scawt Hill, Ireland, were used to refine the structures to *R* values of 0.036, 0.021 and 0.018, respectively. All three structures are monoclinic: spurrite, space group $P2_1/a$, *a* 10.484(1), *b* 6.712(1), *c* 14.156(2) Å, β 101.27(1)°, *V* 977.1(2) Å³; tilleyite, space group $P2_1/a$, *a* 15.082(3), *b* 10.236(2), *c* 7.572(1) Å, β 105.17°, *V* 1128.3(3) Å³, and scawtite, space group *Im*, *a* 6.631(1), *b* 15.195(3), *c* 10.121, β 100.59(3)°, *V* 1002.4(1) Å³. The calcium silicate–carbonate structures are layered. The structure of spurrite has two layers; $[\text{CaO}_8]$ polyhedra adjoin $[\text{CO}_3]$ groups in one layer, whereas $[\text{CaO}_7]$ polyhedra adjoin isolated $[\text{SiO}_4]$ tetrahedra in the second layer. The structure of tilleyite has $[\text{CaO}_8]$ polyhedra adjoining $[\text{CO}_3]$ groups in one layer, whereas $[\text{CaO}_8]$ polyhedra intertwine $[\text{Si}_2\text{O}_7]$ pairs of tetrahedra in the other layer. The structure of scawtite has $[\text{CO}_3]$ triangles sharing a layer with $[\text{Si}_6\text{O}_{18}]$ rings and a second layer with $[\text{CaO}_n]$ polyhedra (*n* between 6 and 8). The second layer has space to accommodate the H atoms of the H_2O molecule. The 13 described structures in the silicate–carbonate chemical class are compared. The high bond-strength and rigid nature of the carbonate group prevent carbonate–carbonate bonds and carbonate–silicate bonds, as the “bridging oxygen” would be over-bonded. Polymerization of the silicate polyhedra is possible; the degree of polymerization depends on the cation-to-anion ratio and Lewis-base strength of the silicate group. The alkali, alkaline-earth and rare-earth elements have low Lewis-acid strengths, thus forming large polyhedra that act as connectors between the carbonate and silicate groups. As the degree of polymerization of the silicate groups increases, the Lewis base-strength decreases from 0.33 *vu* for nesosilicates to 0.06 *vu* for a double-sheet silicate. In general, all these structures are layered, with high-coordination polyhedra and carbonate groups in one slab and the silicate groups with lower-coordination polyhedra in the second layer. As the Lewis base-strength decreases in the silicate layer, there is an increase in the number of large cations within the layer.

Keywords: crystal structure, silicate–carbonate, Apuseni Mountains, Romania, Scawt Hill, Ireland, classification of structures.

SOMMAIRE

La spurrite, $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$, la tilleyite, $\text{Ca}_5(\text{Si}_2\text{O}_7)(\text{CO}_3)_2$, et la scawtite, $\text{Ca}_7(\text{Si}_6\text{O}_{18})(\text{CO}_3)\cdot 2\text{H}_2\text{O}$, sont les seuls minéraux carbonatés–silicatés de calcium connus à date; les trois sont caractéristiques de skarns de haute température. Des cristaux de spurrite et de tilleyite de la colline Cornet, massif Metaliferi, montagnes Apuseni, en Roumanie, et la scawtite provenant de la localité type, Scawt Hill, en Irlande, ont servi pour l'affinement des structures jusqu'aux résidus *R* de 0.036, 0.021 et 0.018, respectivement. Les trois structures sont monocliniques: spurrite, groupe spatial $P2_1/a$, *a* 10.484(1), *b* 6.712(1), *c* 14.156(2) Å, β 101.27(1)°, *V* 977.1(2) Å³; tilleyite, groupe spatial $P2_1/a$, *a* 15.082(3), *b* 10.236(2), *c* 7.572(1) Å, β 105.17°, *V* 1128.3(3) Å³, et scawtite, groupe spatial *Im*, *a* 6.631(1), *b* 15.195(3), *c* 10.121, β 100.59(3)°, *V* 1002.4(1) Å³. Ce sont des structures en couches. La structure de la spurrite a deux niveaux; des polyèdres $[\text{CaO}_8]$ sont voisins de groupes $[\text{CO}_3]$ dans une couche, tandis que les polyèdres $[\text{CaO}_7]$ sont adjacents à des tétraèdres $[\text{SiO}_4]$ isolés dans la deuxième couche. Dans la structure de la tilleyite, les polyèdres $[\text{CaO}_8]$ sont voisins de groupes $[\text{CO}_3]$ dans une couche, tandis que les polyèdres $[\text{CaO}_8]$ sont inter-agencés avec des groupes $[\text{Si}_2\text{O}_7]$ dans l'autre couche. La structure de la scawtite possède des triangles $[\text{CO}_3]$ partageant une couche avec des anneaux $[\text{Si}_6\text{O}_{18}]$, et une deuxième couche de polyèdres $[\text{CaO}_n]$ (*n* de 6 à 8). La seconde couche peut accommoder les atomes H du groupe H_2O . On compare les treize structures décrites faisant partie de la classe des silicates–carbonates. La force des liaisons et la nature rigide des groupes carbonate empêchent la formation des liaisons carbonate–carbonate et carbonate–silicate, parce que l'atome agissant de lien entre les deux polyèdres serait surchargé. La polymérisation des polyèdres silicatés est possible; le degré de polymérisation dépend du rapport des rayons de cation à anion et de la puissance en termes de la base de Lewis du groupe silicaté. Les éléments alcalins, alcalino-terreux et les terres rares possèdent de faibles puissances en termes d'acides de Lewis, et forment ainsi des polyèdres volumineux qui agissent de connecteurs entre les groupes carbonatés et silicatés. À mesure qu'augmente le degré de polymérisation des groupes silicatés, la puissance de la base de Lewis diminue de 0.33 *vu* pour les néosilicates à 0.06 *vu* pour les silicates en feuillets doubles. En général, toutes ces structures sont stratifiées, avec des polyèdres

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à coordination élevée et des groupes carbonatés dans un feuillet, et les groupes silicatés avec les polyèdres à coordination plus faible dans l'autre. A mesure que la force de la base de Lewis diminue dans la couche contenant les tétraèdres silicatés, il y a une augmentation du nombre de gros cations dans la couche.

(Traduit par la Rédaction)

Mots-clés: structure cristalline, silicate-carbonate, montagnes Apuseni, Roumanie, Scawt Hill, Irlande, classification des structures.

INTRODUCTION

As part of an ongoing research project on carbonate minerals, samples of the three silicate-carbonates, spurrite, tilleyite and scawtite, were obtained for crystal-structure refinement. The crystal structures of spurrite and tilleyite described here were established with samples collected by Dr. Ștefan Marincea at Cornet Hill, Apuseni Mountains, Romania (Marincea *et al.* 2001). One additional sample of tilleyite from the type locality, at Crestmore, Riverside County, California, USA, was obtained to verify that the space group of the structure described by Louisnathan & Smith (1970) is the same as that of the material from Romania. Scawtite has not been recognized in either of these localities, thus material for this mineral came from the type locality, Scawt Hill, near Larne, County Antrim, Ireland. Unfortunately, the initial samples of tilleyite and spurrite provided by Dr. Mehmet Tanner from near Güneyce-Ikizdere, Trabzon Region, Pontides, Turkey, did not permit a good crystal-structure refinement because of poor crystallinity. The large mosaic spread for these crystals is likely due to the fact that they were removed from thin sections.

BACKGROUND INFORMATION

The structure of spurrite, as determined by Smith *et al.* (1960), is characterized by large R indices, 0.189 for all data and 0.131 for observed reflections, because film data were used, and the crystal chosen was polysynthetically twinned. The structure of tilleyite reported by Louisnathan & Smith (1970) refined to $R = 0.11$ and $wR = 0.06$. The crystal structure of scawtite was determined by Pluth & Smith (1973) in the centrosymmetric space-group, $I2/m$. Its structure, refined to $R = 0.083$ and $wR = 0.074$, indicated disordered carbonate groups. The structure of scawtite determined by Zhang *et al.* (1992) resolved this problem by reducing the symmetry to a noncentrosymmetric space-group. Although Zhang *et al.* (1992) published a good refinement, they were unable to determine the positions of H atoms. The shortcomings described in these important structures motivated the new refinements.

The spurrite-, tilleyite-, and gehlenite-bearing skarns of Cornet Hill, part of the Metaliferi Massif, Apuseni Mountains, Romania, were described in detail by Marincea *et al.* (2001). The high-temperature skarns were emplaced at the contact between a quartz

monzonitic to monzodioritic body and limestone. The primary assemblage of minerals consists largely of tilleyite, spurrite and gehlenite, with lesser amounts of garnet and wollastonite; perovskite, monticellite and hydroxyllestadite are rare. Scawtite, from Scawt Hill, is associated with melilite, calcite and thomsonite (Tilley & Hey 1930).

EXPERIMENTAL

Description of the samples

The sample from which a single crystal of spurrite was selected consists of blue-gray to gray patches of spurrite up to 2 cm across. The mineral has a good cleavage and is translucent. Interstitial to spurrite are veinlets of dull, white calcite. The tilleyite sample selected (Geological Survey of Romania sample #2430) has large knots, to 5 cm in diameter, of blue-gray tilleyite. The translucent tilleyite displays large surfaces with a perfect cleavage. The dark reddish brown to black, sugary grains within the tilleyite knots are a mixture of quartz and garnet. Gray patches of gehlenite are associated with greenish black vesuvianite. The sample of scawtite (Smithsonian Institution sample #106185) was received as a vial of cleavage fragments.

Electron-microprobe analysis

Chemical analyses of spurrite and tilleyite were done on a JEOL 733 electron microprobe in wavelength-dispersion (WD) mode using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine in XMAQNT (C. Davidson, CSIRO, pers. commun.). The operating voltage was 15 kV, and the beam current was 20 nA; the beam diameter was 30 μm . The following standards were used: sodic amphibole ($\text{NaK}\alpha$), gehlenite ($\text{CaK}\alpha$), almandine ($\text{AlK}\alpha$, $\text{FeK}\alpha$) and diopside ($\text{SiK}\alpha$). Several 100 s energy-dispersion (ED) scans indicated the absence of elements with $Z > 8$ other than those reported here. Magnesium, Ti and F were sought, but not detected. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. The concentration of CO_2 was established by stoichiometry considerations.

The chemical composition of spurrite (average of two analyses, with ranges) is: Na_2O 0.04 (0.00–0.08), CaO 64.25 (63.26–65.25), FeO trace, Al_2O_3 trace, SiO_2 27.19 (26.61–27.78) and CO_2 (10.04), total

101.51 wt.%. The empirical formula based on 11 oxygen anions is $(\text{Ca}_{5.02}\text{Na}_{0.01})_{\Sigma 5.03}\text{Si}_{1.99}\text{O}_8(\text{CO}_3)$, ideally $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$. The composition of tilleyite (average of two analyses, with ranges) is: CaO 58.13 (56.86–57.39), FeO trace, SiO_2 24.11 (23.82–24.39), CO_2 (17.81), total 99.05 wt.%. The empirical formula based on 13 oxygen anions is $\text{Ca}_{5.03}\text{Si}_{1.98}\text{O}_7(\text{CO}_3)_2$, ideally $\text{Ca}_5(\text{Si}_2\text{O}_7)(\text{CO}_3)_2$.

X-ray crystallography and crystal-structure determination

The single crystal of spurrite used for the collection of X-ray-diffraction intensity data is a ground sphere of radius 0.18 mm; the single crystal of tilleyite is a fragment measuring $0.26 \times 0.20 \times 0.08$ mm, and the single crystal of scawtite is a fragment measuring $0.30 \times 0.20 \times 0.05$ mm. For spurrite and tilleyite, the intensity data were collected on a fully automated Siemens P3/P4 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $\text{MoK}\alpha$ radiation. A set of 30 reflections was used to orient the crystal and to subsequently refine the cell dimensions. One asymmetric unit of intensity data was collected up to $2\theta = 60^\circ$ using a $\theta:2\theta$ scan-mode, with scan speeds inversely proportional to intensity, varying from 4 to $29.3^\circ/\text{minute}$. For scawtite, the intensity data were collected on a fully automated Siemens P4 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $\text{MoK}\alpha$ radiation. With the CCD detector, a full sphere of intensity data was collected out to $2\theta = 60^\circ$ using a 15 s frame-time and a crystal-to-detector distance of 4 cm. Data pertinent to all three intensity-data collections are given in Table 1.

All calculations were done with the Siemens SHELXTL Version 5.03 system of programs, which incorporates scattering factors of neutral atoms taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Data reduction included corrections for background, scaling, Lorentz, polarization and linear absorption. For the ellipsoidal absorption correction, nine (spurrite) and twelve (tilleyite) intense

diffraction-maxima in the range 6 to $50^\circ 2\theta$ were chosen for Ψ diffraction-vector scans after the method of North *et al.* (1968). The merging R for the Ψ -scan data set decreased from 0.052 (spurrite), 0.015 (tilleyite) and 0.032 (scawtite) before absorption corrections, to 0.015 (spurrite), 0.013 (tilleyite) and 0.017 (scawtite) after absorption corrections. The convergence for ground-spherical crystals was not significantly better than that of the crystal fragment.

In the final least-squares refinement, all atom positions were refined with anisotropic displacement-factors except for the H atoms in scawtite. The addition of an isotropic extinction-correction improved the refinements slightly. There was no evidence of twinning in either spurrite or tilleyite, but the introduction of a merohedral twin in the scawtite structure improved the R value slightly from 0.022 to 0.018. The H atoms in scawtite were refined with soft constraints to limit the H–O bond distance. The final positional and anisotropic-displacement parameters are given in Table 2, and selected bond-lengths and angles, in Table 3. Tables listing the observed and calculated structure-factors and the anisotropic-displacement parameters may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1b. TILLEYITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Simplified formula: $\text{Ca}_5(\text{Si}_2\text{O}_7)(\text{CO}_3)_2$	
Space group: $P2_1/a$	Number of reflections collected: 3519
Radiation: $\text{MoK}\alpha$	Unique reflections: 2990
Graphite monochromator	Observed reflections ($>4\sigma F_o$): 2677
a 15.082(3) Å	$R(\text{int}) = 0.0246$
b 10.236(2) Å	Goof = 1.038 (all data)
c 7.572(1) Å	$R = \Sigma(F_o - F_c) / \Sigma F_o =$
β 105.17(1) $^\circ$	0.021 (for F_o), and 0.024 (for all F)
V 1128.3(3) Å 3	$wR^2 = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2] = 0.055$
$Z = 1$	$w = 1/[\sigma^2 F_o^2 + (0.032 \times P)^2 + 0.39 \times P]$
μ 2.66 mm $^{-1}$	$P = [\text{Max}(F_o^2, 0) + 2 F_c^2] / 3$

TABLE 1a. SPURRITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Simplified formula: $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$	
Space group: $P2_1/a$	Number of reflections collected: 3014
Radiation: $\text{MoK}\alpha$	Unique reflections: 2863
Graphite monochromator	Observed reflections ($>4\sigma F_o$): 2500
a 10.484(1) Å	$R(\text{int}) = 0.0145$
b 6.712(1) Å	Goof = 1.078 (all data)
c 14.156(2) Å	$R = \Sigma(F_o - F_c) / \Sigma F_o =$
β 101.27(1) $^\circ$	0.036 (for F_o), and 0.041 (for all F)
V 977.1(2) Å 3	$wR^2 = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2] = 0.093$
$Z = 4$	$w = 1/[\sigma^2 F_o^2 + (0.060 \times P)^2 + 0.62 \times P]$
μ 3.05 mm $^{-1}$	$P = [\text{Max}(F_o^2, 0) + 2 F_c^2] / 3$

TABLE 1c. SCAWTITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Simplified formula: $\text{Ca}_5(\text{Si}_2\text{O}_{18})(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	
Space group: Im	Number of reflections collected: 4971
Radiation: $\text{MoK}\alpha$	Unique, merged reflections: 1517
Graphite monochromator	Observed reflections ($>4\sigma F_o$): 2890
a 6.631(1) Å	$R(\text{int}) = 0.0103$
b 15.195(3) Å	Goof = 0.934 (all data)
c 10.121(2) Å	$R = \Sigma(F_o - F_c) / \Sigma F_o =$
β 100.59(3) $^\circ$	0.018 (for F_o), and 0.020 (for all F)
V 1002.4(1) Å 3	$wR^2 = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2] = 0.0576$
$Z = 2$	$w = 1/[\sigma^2 F_o^2 + (0.046 \times P)^2 + 1.06 \times P]$
μ 2.32 mm $^{-1}$	$P = [\text{Max}(F_o^2, 0) + 2 F_c^2] / 3$

TABLE 2a. SPURRITE: ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (\AA^2)

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca1	0.14005(5)	0.66295(8)	0.07182(4)	0.0090(2)	0.0065(2)	0.0140(2)	-0.0014(2)	-0.0001(2)	0.0001(2)	0.0101(1)
Ca2	0.03225(5)	0.24170(8)	0.61152(4)	0.0109(2)	0.0121(2)	0.0107(2)	0.0004(2)	0.0006(2)	-0.0050(2)	0.0114(1)
Ca3	0.23999(5)	0.05991(8)	0.45584(4)	0.0058(2)	0.0060(2)	0.0159(2)	0.0002(2)	0.0021(2)	0.0001(2)	0.0092(1)
Ca4	0.04556(5)	0.99104(7)	0.83065(4)	0.0068(2)	0.0067(2)	0.0119(2)	-0.0002(2)	0.0009(2)	0.0009(2)	0.0086(1)
Ca5	0.13164(5)	0.50700(7)	0.82619(4)	0.0069(2)	0.0063(2)	0.0116(2)	-0.0005(2)	0.0011(2)	0.0005(2)	0.0084(1)
Si1	0.13420(6)	0.2241(1)	0.05667(5)	0.0047(3)	0.0044(3)	0.0100(3)	0.0001(2)	0.0005(9)	-0.000(2)	0.0065(1)
Si2	0.02636(6)	0.7494(1)	0.60459(5)	0.0049(3)	0.0043(3)	0.0092(3)	-0.0000(2)	0.0005(2)	0.0003(2)	0.0062(1)
C	0.1891(2)	0.6990(4)	0.2804(2)	0.007(1)	0.007(1)	0.013(1)	0.0002(8)	0.0014(8)	-0.0013(8)	0.0090(4)
O1	0.1235(2)	0.24165(3)	0.9404(1)	0.0133(8)	0.0078(8)	0.0111(8)	0.0001(6)	0.0022(6)	-0.0005(7)	0.0107(3)
O2	0.1401(2)	0.9973(3)	0.0970(1)	0.0093(8)	0.0059(8)	0.0141(8)	0.0010(6)	0.0031(7)	-0.0000(6)	0.0097(3)
O3	0.0079(2)	0.3372(3)	0.0836(1)	0.0093(8)	0.0094(8)	0.0152(8)	-0.0008(7)	0.0035(6)	0.0027(7)	0.0111(4)
O4	0.2671(2)	0.3326(3)	0.1078(1)	0.0079(8)	0.0118(9)	0.0208(9)	0.0007(7)	-0.0019(7)	-0.0043(7)	0.0142(4)
O5	0.8843(2)	0.1530(3)	0.4662(1)	0.0068(8)	0.0108(9)	0.0143(8)	0.0031(7)	0.0024(6)	-0.0002(7)	0.0106(4)
O6	0.8907(2)	0.4305(3)	0.3346(1)	0.0102(8)	0.0074(8)	0.0132(8)	0.0028(7)	0.0008(6)	0.0017(7)	0.0105(4)
O7	0.0227(2)	0.0774(3)	0.3300(1)	0.0111(8)	0.0074(8)	0.0142(8)	-0.0024(7)	0.0025(7)	0.0012(7)	0.0109(4)
O8	0.1006(2)	0.3383(3)	0.4690(1)	0.0067(8)	0.0102(9)	0.0130(8)	-0.0020(7)	0.0010(6)	-0.0011(7)	0.0101(4)
O9	0.2858(2)	0.6966(3)	0.2354(1)	0.0082(8)	0.0104(8)	0.0149(8)	-0.0002(7)	0.0030(6)	-0.0001(7)	0.0111(4)
O10	0.0713(2)	0.6899(3)	0.2304(1)	0.0062(8)	0.0110(9)	0.0154(9)	0.0005(7)	-0.0012(7)	-0.0003(7)	0.0113(4)
O11	0.2088(2)	0.7183(3)	0.3710(1)	0.0141(9)	0.0137(9)	0.0127(8)	-0.0006(7)	0.0023(7)	0.0002(8)	0.0135(4)

TABLE 2b. TILLEYITE: ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (\AA^2)

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca1	0.00343(2)	0.99395(3)	0.75024(4)	0.0096(2)	0.0096(1)	0.0084(1)	-0.0012(1)	0.0037(1)	-0.0021(1)	0.00896(8)
Ca2	0.17682(2)	0.21349(3)	0.09115(4)	0.0099(2)	0.0100(1)	0.0077(1)	0.0008(1)	0.0027(1)	0.0018(1)	0.00912(8)
Ca3	0.18116(2)	0.20649(3)	0.60855(4)	0.0100(2)	0.0080(1)	0.0087(1)	-0.0002(1)	0.0029(1)	0.0010(1)	0.00882(8)
Ca4	0.12417(2)	0.58934(3)	0.04534(4)	0.0090(2)	0.0082(1)	0.0076(1)	-0.0005(1)	0.0031(1)	0.0003(1)	0.00810(8)
Ca5	0.13621(2)	0.57880(3)	0.55926(4)	0.0108(2)	0.0076(1)	0.0092(1)	-0.0004(1)	0.0035(1)	-0.0013(1)	0.00905(8)
Si1	0.20174(3)	0.92086(4)	0.13855(6)	0.0077(2)	0.0053(2)	0.0058(2)	0.0000(1)	0.0031(2)	0.0003(1)	0.00603(9)
Si2	0.20390(3)	0.91414(4)	0.56867(5)	0.0077(2)	0.0054(2)	0.0057(2)	0.0001(1)	0.0031(2)	0.0003(1)	0.00603(9)
C1	0.0301(1)	0.3088(2)	0.3388(2)	0.0105(9)	0.0091(6)	0.0098(6)	0.0023(5)	0.0055(6)	0.0001(5)	0.0093(3)
C2	0.0220(1)	0.3027(2)	0.8176(2)	0.0119(9)	0.0079(6)	0.0103(6)	0.00134(5)	0.0064(6)	0.0004(5)	0.0094(3)
O1	0.07397(9)	0.2081(1)	0.29945(2)	0.0139(6)	0.0083(5)	0.0144(5)	-0.00059(5)	0.0066(5)	0.0013(4)	0.0117(2)
O2	0.07153(8)	0.2047(1)	0.7882(2)	0.0119(6)	0.0082(5)	0.0121(5)	-0.0007(4)	0.0049(5)	0.0015(4)	0.0104(2)
O3	0.06991(9)	0.3767(1)	0.4799(2)	0.0210(7)	0.0092(5)	0.0146(5)	-0.0025(4)	0.0044(5)	-0.0021(5)	0.0150(2)
O4	0.05589(9)	0.3760(1)	-0.0424(2)	0.0194(7)	0.0099(5)	0.0137(5)	-0.0033(4)	0.0046(5)	-0.0002(4)	0.0143(2)
O5	0.05021(9)	0.6655(2)	0.7530(2)	0.0115(7)	0.0340(8)	0.0117(5)	0.0049(5)	0.0030(5)	0.0076(5)	0.0191(3)
O6	0.05884(9)	0.6805(1)	0.2792(2)	0.0106(7)	0.0249(6)	0.0122(5)	0.0012(5)	0.0030(5)	0.0056(5)	0.0159(3)
O7	0.22519(8)	0.7744(1)	0.0876(2)	0.0122(6)	0.0069(5)	0.0121(5)	-0.0019(4)	0.0054(5)	-0.0002(4)	0.0100(2)
O8	0.22688(8)	0.7642(1)	0.6289(2)	0.0118(6)	0.0073(5)	0.0126(5)	0.0023(4)	0.0019(5)	-0.0004(4)	0.0108(2)
O9	0.09944(8)	0.9761(1)	0.0560(2)	0.0115(6)	0.0149(6)	0.0106(5)	0.0005(4)	0.0032(5)	0.0036(4)	0.0123(2)
O10	0.10274(8)	0.9720(1)	0.5534(2)	0.0106(6)	0.0132(5)	0.0118(5)	-0.0000(4)	0.0045(5)	0.0028(4)	0.0115(2)
O11	0.22507(8)	0.5306(1)	0.8846(2)	0.0127(6)	0.0078(5)	0.0145(5)	-0.0009(4)	0.0076(5)	0.0019(4)	0.0109(2)
O12	0.22205(8)	0.5210(1)	0.3213(2)	0.0114(6)	0.0096(5)	0.0123(5)	0.0030(4)	0.0024(4)	0.0017(4)	0.0112(2)
O13	0.22538(9)	0.9174(1)	0.3651(2)	0.0157(6)	0.0185(6)	0.0063(5)	0.0000(4)	0.0045(4)	0.0008(5)	0.0132(2)

TABLE 2c. SCAWTITE: ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (\AA^2)

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca1	0.20664(5)	0.14449(3)	0.21917(4)	0.0132(2)	0.011(2)	0.011(2)	-0.0007(1)	0.0040(1)	-0.0007(1)	0.0117(8)
Ca1B	0.80760(6)	0.86435(3)	0.79532(4)	0.0142(2)	0.0103(2)	0.0158(2)	-0.0002(1)	0.0062(2)	0.0003(1)	0.0130(1)
Ca2	0.49976(7)	0.25090(2)	0.00167(5)	0.0118(1)	0.0100(1)	0.0103(1)	0.0001(2)	0.0032(1)	0.0003(2)	0.0106(1)
Ca3	0.4787(9)	0	-0.00451(6)	0.0165(3)	0.0099(2)	0.0109(2)	0	0.0040(2)	0	0.0123(1)
Si1	0.70664(8)	0.10401(4)	0.27399(6)	0.0084(2)	0.0087(2)	0.0078(2)	-0.0008(2)	0.0015(2)	-0.0003(2)	0.0083(1)
Si1B	0.29443(8)	0.10419(3)	0.72753(6)	0.00824	0.0085(2)	0.0084(2)	0.0008(2)	0.0017(2)	0.0002(2)	0.0084(10)
Si2	-0.00006(9)	0.32340(3)	0.00377(7)	0.0081(2)	0.0106(2)	0.0079(2)	0.0005(2)	0.0018(1)	0.0003(2)	0.0088(1)
C	0.0032(5)	0	-0.0065(3)	0.011(1)	0.025(1)	0.011(1)	0	0.0004(9)	0	0.0160(5)
O1	0.9013(2)	0.3953(1)	0.0939(2)	0.0202(7)	0.015(6)	0.0147(7)	-0.0008(6)	0.0101(6)	-0.0000(6)	0.0156(3)
O1B	0.5857(2)	0.1087(1)	0.4012(2)	0.0204(7)	0.0166(7)	0.0149(7)	-0.0043(6)	0.0112(6)	-0.0012(6)	0.0163(3)
O2	0.1865(2)	0.2725(1)	0.0951(2)	0.0119(6)	0.0127(6)	0.0125(6)	0.0022(5)	0.0003(5)	0.0004(5)	0.0126(3)
O2B	0.8196(2)	0.7348(1)	0.91781	0.0081(6)	0.0157(6)	0.0126(7)	0.0022(5)	-0.0013(6)	0.00153	0.0126(3)
O3	0.5344(3)	0.8768(1)	0.1430(2)	0.0125(7)	0.0129(6)	0.0096(6)	0.0007(5)	-0.0020(5)	-0.0004(5)	0.0122(3)
O3B	0.4714(2)	0.8729(1)	0.8538(2)	0.0119(7)	0.0119(7)	0.0123(7)	-0.0000(5)	0.0007(6)	0.0008(5)	0.0122(3)
O4	0.5917(2)	0.6614(1)	0.2004(2)	0.0114(7)	0.0138(6)	0.0187(8)	0.0043(6)	0.0053(6)	0.0035(5)	0.0143(3)
O4B	0.9100(2)	0.8383(1)	0.3031(2)	0.0120(7)	0.0134(6)	0.0178(8)	0.0038(6)	0.0038(6)	0.0030(5)	0.0143(3)
O5	0.2300(3)	0	0.7481(2)	0.0159(9)	0.0101(8)	0.0182(3)	0	0.0086(8)	0	0.0141(4)
O5B	0.7794(3)	0	0.2660(2)	0.0125(9)	0.0088(8)	0.0205(9)	0	0.0058(8)	0	0.0136(4)
OW6	0.2015(4)	0	0.3356(3)	0.0151(9)	0.0139(9)	0.024(1)	0	0.0019(8)	0	0.0181(4)
OW6B	0.7931(4)	0	0.6479(3)	0.018(1)	0.018(1)	0.022(1)	0	0.0014(8)	0	0.0196(5)
O7	0.0937(5)	0.0725(2)	0.0162(3)	0.103(2)	0.095(2)	0.041(1)	-0.047(2)	0.044(2)	-0.085(2)	0.076(1)
O8	0.3187(4)	0.5	0.4332(2)	0.013(1)	0.053(2)	0.016(1)	0	0.0033(8)	0	0.0274(6)
H61	0.061(8)	0	0.333(7)							0.07(2)
H62	0.17(2)	0	0.424(5)							0.22(5)
H6B1	0.719(8)	0	0.563(4)							0.05
H6B2	0.923(7)	0	0.633(6)							0.05

TABLE 3a. SPURRITE: SELECTED BOND-LENGTHS (\AA) AND ANGLES ($^\circ$)

Ca polyhedra									
Ca1-O2	2.272(2)	Ca2-O5	2.359(2)	Ca3-O5	2.333(2)	Ca4-O4	2.253(2)	Ca5-O6	2.281(2)
Ca1-O3	2.432(2)	Ca2-O8	2.397(2)	Ca3-O8	2.349(2)	Ca4-O7	2.294(2)	Ca5-O3	2.365(2)
Ca1-O10	2.495(2)	Ca2-O7	2.406(2)	Ca3-O5*	2.402(2)	Ca4-O1	2.327(2)	Ca5-O1	2.418(2)
Ca1-O9	2.523(2)	Ca2-O6	2.416(2)	Ca3-O8*	2.436(2)	Ca4-O2	2.371(2)	Ca5-O2	2.428(2)
Ca1-O1	2.573(2)	Ca2-O11	2.601(2)	Ca3-O6	2.551(2)	Ca4-O10	2.534(2)	Ca5-O9	2.479(2)
Ca1-O4	2.586(2)	Ca2-O9	2.610(2)	Ca3-O11	2.580(2)	Ca4-O9	2.559(2)	Ca5-O10	2.500(2)
Ca1-O3*	2.611(2)	Ca2-O11*	2.682(2)	Ca3-O7	2.606(2)	Ca4-O3	2.628(2)	Ca5-O4	2.527(2)
Ca1-O1*	2.809(2)	Ca2-O10	2.710(2)	Ca3-O11*	2.629(2)	<Ca4-O>	<2.424>	<Ca5-O>	<2.428>
<Ca1-O>	<2.538>	<Ca2-O>	<2.523>	<Ca3-O>	<2.486>				
Silicate polyhedra					Carbonate polyhedron				
Si1-O4	1.613(2)	O2-Si1-O4	107.2(1)	Si2-O7	1.630(2)	O8-Si2-O7	108.2(1)	C-O11	1.266(3)
Si1-O2	1.623(2)	O1-Si1-O4	107.7(1)	Si2-O8	1.631(2)	O6-Si2-O7	115.0(1)	C-O9	1.299(3)
Si1-O1	1.632(2)	O3-Si1-O4	110.7(1)	Si2-O6	1.631(2)	O5-Si2-O7	110.1(1)	C-O10	1.299(3)
Si1-O3	1.634(2)	O1-Si1-O2	114.4(1)	Si2-O5	1.637(2)	O6-Si2-O8	110.7(1)	<C-O>	<1.288>
<Si1-O>	<1.626>	O3-Si1-O2	109.3(1)	<Si2-O>	<1.632>	O5-Si2-O8	104.2(1)	O9-C-O11	120.6(2)
		O3-Si1-O1	107.6(1)			O5-Si2-O6	108.0(1)	O10-C-O11	120.4(2)
		<O-Si1-O>	<109.5>			<O-Si2-O>	<109.4>	O10-C-O9	118.9(2)
								<O-C-O>	<120.0>

TABLE 3b. TILLEYITE: SELECTED BOND-LENGTHS (Å) AND ANGLES (°)

Ca polyhedra									
Ca1-O1	2.356(1)	Ca2-O8	2.294(1)	Ca3-O12	2.369(1)	Ca4-O11	2.264(1)	Ca5-O3	2.308(1)
Ca1-O2	2.375(1)	Ca2-O7	2.335(1)	Ca3-O2	2.400(1)	Ca4-O12	2.328(1)	Ca5-O8	2.318(1)
Ca1-O10	2.384(1)	Ca2-O11	2.363(1)	Ca3-O3	2.438(1)	Ca4-O5	2.336(1)	Ca5-O5	2.370(1)
Ca1-O9	2.395(1)	Ca2-O2	2.426(1)	Ca3-O7	2.464(1)	Ca4-O7	2.400(1)	Ca5-O6	2.376(1)
Ca1-O9*	2.418(1)	Ca2-O4	2.480(1)	Ca3-O1	2.472(1)	Ca4-O6	2.427(1)	Ca5-O11	2.526(1)
Ca1-O10*	2.459(1)	Ca2-O1	2.486(1)	Ca3-O13	2.557(1)	Ca4-O4	2.431(1)	Ca5-O12	2.548(1)
<Ca1-O>	<2.398>	Ca2-O9	2.678(1)	Ca3-O8	2.610(1)	Ca4-O4 *	2.733(1)	Ca5-O13	2.606(1)
		<Ca2-O>	<2.437>	Ca3-O10	2.660(1)	<Ca4-O>	<2.417>	<Ca5-O>	<2.436>
				<Ca3-O>	<2.496>				
Silicate polyhedra									
Si1-O9	1.608(1)	O7-Si1-O9	118.88(7)	Si2-O10	1.612(1)	O8-Si2-O10	119.95(7)		
Si1-O7	1.610(1)	O11-Si1-O9	109.03(7)	Si2-O8	1.613(1)	O12-Si2-O10	107.42(7)		
Si1-O11	1.617(1)	O13-Si1-O9	109.53(6)	Si2-O12	1.628(1)	O13-Si2-O10	109.74(7)		
Si1-O13	1.659(1)	O11-Si1-O7	114.96(6)	Si2-O13	1.656(1)	O12-Si2-O8	115.26(7)		
<Si1-O>	<1.624>	O13-Si1-O7	103.10(6)	<Si2-O>	<1.627>	O13-Si2-O8	101.68(7)		
		O13-Si1-O11	99.16(6)			O13-Si2-O12	100.82(7)		
		<O-Si1-O>	<109.11>			<O-Si2-O>	<109.08>		
Carbonate polyhedra									
C1-O5	1.256(2)	O3-C1-O5	121.3(2)	C2-O6	1.260(2)	O4-C2-O6	120.9(2)		
C1-O3	1.285(2)	O1-C1-O5	120.9(2)	C2-O4	1.290(2)	O2-C2-O6	121.1(2)		
C1-O1	1.301(2)	O1-C1-O3	117.6(2)	C2-O2	1.304(2)	O2-C2-O4	117.8(2)		
<C1-O>	<1.281>	<O-C1-O>	<119.9>	<C2-O>	<1.285>	<O-C2-O>	<119.9>		

DISCUSSION OF THE STRUCTURES

Comparison of the present atom-coordinates for the spurrite and tilleyite structures with values determined by Smith *et al.* (1960) and Louisnathan & Smith (1970), respectively, may be made directly, as their site assignments have been maintained. For scawtite, the present atom-coordinates may be compared to those originally determined by Pluth & Smith (1973), who refined the structure in the centrosymmetric space-group, *I2/m*, although they did note that the structure is more likely to belong to the noncentrosymmetric space-group *Im*. This in fact is the case, as determined by Zhang *et al.* (1992). In this paper, the original crystallographic setting of Pluth & Smith (1973) is maintained, with the β angle closer to 90° , and the atoms generated by removing the center of symmetry are designated by B in the atom label in Table 2c. The topological features of the three structures are the same as previously determined, but standard deviations in the atom coordinates and bond lengths have improved greatly owing to improvements in the experiments. Reducing the symmetry of the space group for scawtite gives the expected trigonal coordination for the carbonate group as opposed six-fold planar coordination of C in the Pluth & Smith (1973) structure.

In the crystal structure of spurrite, there are five Ca sites with two types of coordination polyhedron: *Ca1*, *Ca2* and *Ca3* have 8-fold coordination with oxygen, and *Ca4* and *Ca5* have 7-fold coordination with oxygen. Interspersed amongst the Ca polyhedra are independent $[\text{SiO}_4]$ tetrahedra and $[\text{CO}_3]$ with the typical triangular coordination. The spurrite structure is layered on (001). The layered topology (Fig. 1) has the 8-fold coordinated polyhedra of *Ca1*, *Ca2* and *Ca3* adjoining a (CO_3) group, whereas the 7-fold coordinated polyhedra of *Ca4* and *Ca5* adjoins three (SiO_4) and two (CO_3) groups.

In the structure of tilleyite, there are five Ca sites with three types of coordination; *Ca1* has 6-fold coordination with oxygen, *Ca2*, *Ca4* and *Ca5* have 7-fold coordination with oxygen, and *Ca3* has 8-fold coordination with oxygen. The two $[\text{SiO}_4]$ tetrahedra share a common oxygen atom, *O13*, to form a sorosilicate $[\text{Si}_2\text{O}_7]$ group. As is typical of sorosilicates, the Si atoms repel each other toward the base of each tetrahedron (Fig. 2). The $[\text{Si}_2\text{O}_7]$ groups are aligned along the *c* axis, and the $[\text{CO}_3]$ triangles are roughly perpendicular to $[001]$. As for spurrite, the tilleyite structure consists of slabs parallel to (100) with $[\text{CO}_3]$ groups interspersed along the *b* axis. Wrapped around the $[\text{Si}_2\text{O}_7]$ groups and the $[\text{CO}_3]$ triangles is a continuous mesh of $[\text{CaO}_n]$ polyhedra (Fig. 2).

TABLE 3c. SCAWTITE: SELECTED BOND-LENGTHS (Å) AND ANGLES (°)

Ca polyhedra									
Ca1-O4B	2.295(2)	Ca1B-O	2.301(2)	Ca2-O3B	2.390(2)	Ca3-O3	2.381(2)		
Ca1-O2	2.305(2)	Ca1B-O2B	2.319(2)	Ca2-O4B	2.391(2)	Ca3-O3*	2.381(2)		
Ca1-O7	2.327(2)	Ca1B-O3B	2.413(2)	Ca2-O3	2.396(2)	Ca3-O3B	2.400(2)		
Ca1-O2B	2.437(2)	Ca1B-O2	2.471(2)	Ca2-O4	2.396(2)	Ca3-O3B*	2.400(2)		
Ca1-O3	2.457(2)	Ca1B-O8	2.482(1)	Ca2-O2B	2.434(2)	Ca3-O8	2.449(2)		
Ca1-OW6	2.495(2)	Ca1B-OW6B	2.535(2)	Ca2-O2	2.457(2)	Ca3-O5	2.733(3)		
Ca1-O1B	2.882(2)	Ca1B-O7	2.821(4)	<Ca2-O>	<2.471>	Ca3-O7	2.823(4)		
<Ca1-O>	<2.457>	<Ca1B-O>	<2.477>			Ca3-O7*	2.823(4)		
						<Ca3-O>	<2.549>		
Silicate polyhedra									
Si1-O4B	1.591(2)	O3-Si1-O4B	120.13(10)	Si1B-O4	1.582(2)	O3B-Si1B-O4	119.51(10)		
Si1-O3	1.609(2)	O1B-Si1-O4B	110.56(9)	Si1B-O3B	1.607(2)	O1-Si1B-O4	109.68(9)		
Si1-O1B	1.639(2)	O5B-Si1-O4B	106.86(9)	Si1B-O1	1.638(2)	O5-Si1B-O4	108.38(10)		
Si1-O5B	1.659(1)	O1B-Si1-O3	105.24(9)	Si1B-O5	1.663(1)	O1-Si1B-O3B	106.99(9)		
<Si1-O>	<1.624>	O5B-Si1-O3	107.58(10)	<Si1B-O>	<1.622>	O5-Si1B-O3B	105.84(10)		
		O5B-Si1-O1B	105.58(10)			O5-Si1B-O1	105.56(10)		
		<O-Si1-O>	<109.32>			<O-Si1B-O>	<109.33>		
Silicate polyhedron			Carbonate polyhedra			O-H bonds			
Si2-O2	1.601(2)	O2B-Si2-O2	117.69(7)	C-O7	1.254(3)	O7*-C-O7	122.7(5)	OW6-H62	0.87(4)
Si2-O2B	1.609(2)	O1-Si2-O2	110.31(9)	C-O7*	1.254(3)	O8-C-O7	121.1(3)	OW6-H61	0.88(4)
Si2-O1	1.635(2)	O1B-Si2-O2	110.43(9)	C-O8	1.265(4)	O8-C-O7*	118.4(3)	OW6B-H6B2	0.97(4)
Si2-O1B	1.637(2)	O1-Si2-O2B	109.61(10)	<C-O>	<1.258>	<O-C-O>	<120.7>	OW6B-H6B1	0.97(4)
<Si2-O>	<1.620>	O1B-Si2-O2B	108.30(10)						
		O1B-Si2-O1	98.85(7)						
		<O-Si2-O>	<109.20>						

The structure of scawtite has four Ca sites with three types of coordination; *Ca1* and *Ca1B* have 7-fold coordination, *Ca2* has 6-fold coordination, and *Ca3* has 8-fold coordination. The three (SiO₄) tetrahedra form [Si₆O₁₈] rings (Fig. 3), separated by triangular [CO₃] groups. The structure is layered on (101), with the silicate rings and carbonate groups in one layer, and the [CaO_n] polyhedra in the other (Fig. 4).

COMPARISON OF SPURRITE, TILLEYITE AND SCAWTITE STRUCTURES TO OTHER SILICATE-CARBONATE STRUCTURES

At present, there are thirteen well-refined crystal structures in the silicate-carbonate chemical class. This class is defined by the presence of major proportions of silicate and carbonate groups, and excludes those minerals that also contain other anionic groups such as borate, sulfate and phosphate; members of this group are listed in Table 4. The Pauling bond-strength received at each anion is high for the two anionic complexes [1.33 *vu* for (CO₃)²⁻ and 1.0 *vu* for (SiO₄)⁴⁻]. The high bond-strength and rigid nature of the carbonate group prevents carbonate-carbonate bonds and carbo-

nate-silicate bonds as the “bridging oxygen” would be overbonded. Polymerization of the silicate polyhedra is possible; the degree of polymerization depends on the cation-to-anion ratio and the Lewis-base strength (LBS) of the silicate group. The alkali, alkaline earth and rare-earth elements have low Lewis-acid strengths, and thus form large polyhedra that act as connectors between the carbonate and silicate groups. In silicate-carbonate structures, the [CO₃] groups act as “separators” and tend to depolymerize the silicate and cationic groups. Ranking the structures according to the degree of polymerization of the silicate tetrahedra gives the order listed in Table 4.

In the independent-tetrahedra subgroup, tundrite-(Ce), iimoriite-(Y) and spurrite consist of slabs and cross-linking ribbons of large-cation polyhedra, [YO_n], [CaO_n] and [CeO_n]. Thus the template for the structure is defined by the cationic polyhedra, whereas the [SiO₄] and [CO₃] groups fill gaps. Tundrite-(Ce) has its silicate tetrahedra in a layer with the [TiO₆] and [NaO₆] polyhedra of higher Lewis-acid strength, and the carbonate group is layered with the [CeO₉] polyhedra, of lower Lewis-acid strength. Iimoriite-(Y) has silicate tetrahedra in a layer with [Y₂O₁₄] dimers. These dimers would

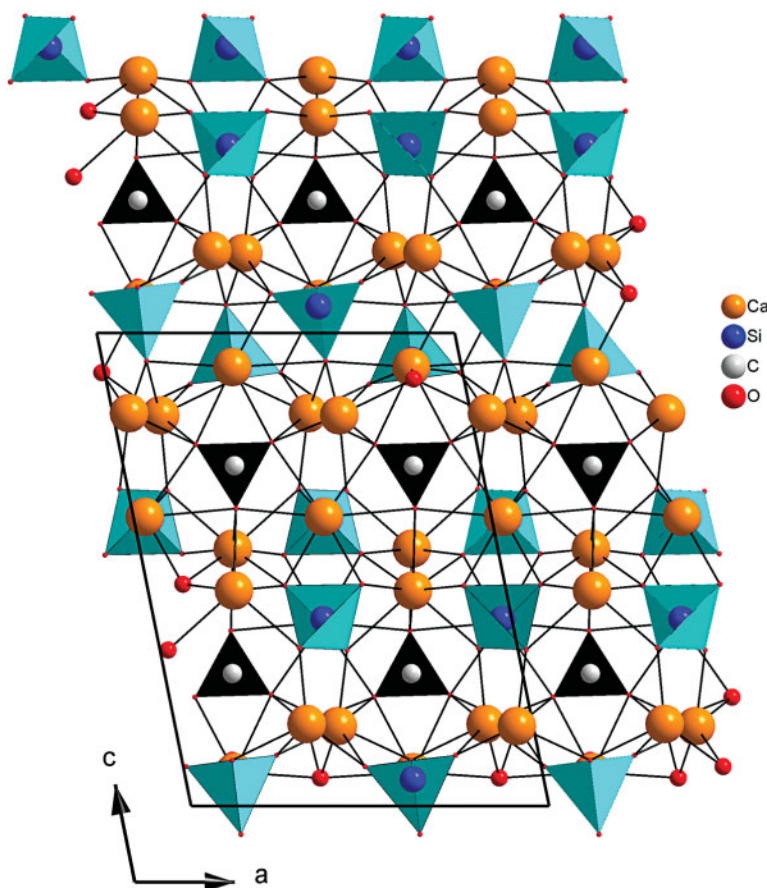


FIG. 1. The structure of spurrite projected along [010], with the unit cell outlined. The $[\text{SiO}_4]$ tetrahedra are cyan-colored, and the $[\text{CO}_3]$ triangles are black.

have a stronger Lewis-acid strength than the ribbons of edge-sharing $[\text{YO}_9]$ polyhedra in the carbonate layer. In spurrite, the silicate tetrahedra are linked to the $[\text{CaO}_7]$ polyhedra, which have a higher Lewis-base strength than the $[\text{CaO}_8]$ polyhedra linked to $[\text{CO}_3]$ groups.

The double tetrahedra (sorosilicate) subgroup, $[\text{Si}_2\text{O}_7]$, is represented by bussenite and tilleyite, both of which are composed of slabs. Bussenite adopts the expected arrangement, in which $[\text{CO}_3]$ groups accompany the cation polyhedra of lowest Lewis-acid strength, $[\text{BaO}_9]$, $[\text{BaO}_{11}]$ and $[\text{NaO}_7]$. The $[\text{Si}_2\text{O}_7]$ group crosslinks the $[\text{MnO}_6]$ and $[\text{TiO}_6]$ cation polyhedra of higher Lewis-acid strength. The tilleyite structure must accommodate an additional (CO_3) group relative to spurrite. To accomplish this, the carbonate slab incorporates the $[\text{CaO}_6]$ polyhedron that has a slightly higher Lewis-acid strength than the $[\text{CaO}_7]$ and $[\text{CaO}_8]$ polyhedra of the silicate slab.

There are three ring-silicates, ashburtonite, kainosite-(Y) and scawtite. The structure of ashburtonite (Grice *et al.* 1991) is layered, with $[\text{CuO}_6]$ octahedra occupying one layer, and the four-membered-silicate ring, bicarbonate group and Pb-oxychloride polyhedra occupying the other layer. Kainosite-(Y) also is layered, with the four-membered-silicate ring and the carbonate groups occupying one layer, and the $[\text{CaO}_n]$ polyhedra or alternately the $[\text{YO}_n]$ polyhedra occupying a second layer. In scawtite, the six-membered rings of silicate tetrahedra and the carbonate groups occupy one layer, and the Ca polyhedra, the second layer. The $[\text{Si}_8\text{O}_{22}]$ cluster in the fencooperite structure is a unique island (sorosilicate) building block (Grice 2001). The silicate islands are cross-linked by a second layer consisting of $[\text{Fe}_3\text{O}_{13}]$ pinwheel trimers. Sitting in the pockets created by these two layers are Ba atoms, Cl atoms, H_2O groups and (CO_3) groups. The silicate layer has all of these

“inclusions”, whereas the $[\text{Fe}_3\text{O}_{13}]$ pinwheel layer has only Ba polyhedra.

There are two types of chain-silicate structure with carbonate groups. Caysichite-(Y) is similar to kainosite-(Y) in chemical constituents, but very different in the topology of the structure. In caysichite-(Y), the double chain of silicate tetrahedra runs down square tubes bounded by Y and Ca polyhedra. The $[\text{CO}_3]$ groups are interspersed in these walls (Mellini & Merlino 1978). The tube-like chain in the ashcroftine-(Y) structure was elegantly described by Moore *et al.* (1987). This chain silicate is tube-like with enormous bulbs. As in caysichite-(Y), the tubes are bounded by K, Na and Y polyhedra encrusted with $[\text{CO}_3]$ groups.

There are two sheet-structure silicate-carbonates, both of which have double silicate layers. Kampfite (M.A. Cooper, pers. commun.) has a $[\text{Si}_4\text{O}_8]$ layer with the remaining carbonate group, H_2O group, and Ba polyhedra in the interlayer. Carletonite (Chao 1972) has a more open double layer of $[\text{Si}_8\text{O}_{18}]$ containing Na and K atoms and H_2O groups and a non-silicate interlayer with Na atoms, an H_2O group and the carbonate groups.

SUMMARY

A number of trends are notable in the silicate-carbonate structures.

(1) All silicate-carbonate structures are layered. Usually, there are only two types of layer.

(2) In the independent tetrahedron and double-tetrahedron structure-types, the silicate and carbonate

groups occupy separate layers because their Lewis-base strength is quite different; for the silicate group, $[\text{SiO}_4]$ has 0.33 valence units (*vu*), and $[\text{Si}_2\text{O}_7]$ has 0.30 *vu*, whereas the $[\text{CO}_3]$ group has 0.22 *vu*. The silicate group occupies the layer with cationic groups of higher Lewis-acid strength, and the carbonate group occupies the layer with cationic groups of lower Lewis-acid strength.

(3) In the ring- and island-type structures, the silicate and carbonate groups occupy the same layer, whereas the cationic groups occupy a second sheet. In these structures, the Lewis-base strength of the silicate group is approximately equal to that of the carbonate group. For the chain silicates, the silicate unit forms a tube, and the carbonate groups and cationic polyhedra act as sleeves around these tubes. In the silicate-island structure, the carbonate group fills spaces between islands, and the remaining cations form a separate layer.

(4) For the sheet-silicate structure type, the carbonate groups are again separated into a layer of cation-bearing polyhedra, whereas the silicate layer is a separate feature. In these structures, the silicate layer has a Lewis-base strength significantly less than that of the carbonate layer.

(5) As the degree of polymerization of the silicate groups increases, the Lewis-base strength on each apical oxygen within the silicate groups decreases from 0.33 *vu* for an independent $[\text{SiO}_4]$ group to 0.06 *vu* for a $[(\text{Si},\text{Al})\text{O}_2]$ double-sheet unit.

(6) As the polymerization of silicate tetrahedra increases, the ratio of silicate groups to carbonate plus large cation groups decreases.

TABLE 4. SILICATE-CARBONATE CRYSTAL STRUCTURES

Species	Formula	Structure type	LBS* [SiO _n]	Si : M** + C	Ref.
tundrite-(Ce)	$\text{Na}_2\text{Ce}_2\text{TiO}_2(\text{SiO}_2)(\text{CO}_3)_2$	independent $[\text{SiO}_4]$	0.33	1 : 4	(1)
iimoriite-(Y)	$\text{Y}_2(\text{SiO}_3)(\text{CO}_3)$	independent $[\text{SiO}_4]$	0.33	1 : 3	(2)
spurrite	$\text{Ca}_3(\text{SiO}_3)_2(\text{CO}_3)$	independent $[\text{SiO}_4]$	0.33	1 : 3	(3)
tilleyite	$\text{Ca}_4(\text{Si}_2\text{O}_7)(\text{CO}_3)_2$	double tetrahedra $[\text{Si}_2\text{O}_7]$	0.30	1 : 3	(3)
bussenite	$\text{Na}_2\text{Ba}_2\text{FeTi}(\text{Si}_2\text{O}_7)(\text{CO}_3)(\text{OH})_3\text{F}$	double tetrahedra $[\text{Si}_2\text{O}_7]$	0.30	1 : 2	(4)
ashburtonite	$\text{Cu}_2\text{Pb}_4(\text{SiO}_3)_4(\text{HCO}_3)_4(\text{OH})_4\text{Cl}$	ring $[\text{Si}_4\text{O}_{12}]$	0.25	1 : 2	(5)
kainosite-(Y)	$\text{Ca}_2\text{Y}_2(\text{SiO}_3)_4(\text{CO}_3)\cdot\text{H}_2\text{O}$	ring $[\text{Si}_4\text{O}_{12}]$	0.25	1 : 1.25	(6)
scawtite	$\text{Ca}_7(\text{SiO}_3)_6(\text{CO}_3)\cdot 2\text{H}_2\text{O}$	ring $[\text{Si}_6\text{O}_{18}]$	0.25	1 : 1	(3)
fencooperite	$\text{Ba}_4\text{Fe}_3(\text{Si}_8\text{O}_{23})(\text{CO}_3)_2\text{Cl}_3\cdot\text{H}_2\text{O}$	island $[\text{Si}_8\text{O}_{23}]$	0.20	1 : 1	(7)
caysichite-(Y)	$\text{Ca}_2\text{Y}_4(\text{Si}_2\text{O}_7)_4(\text{CO}_3)_6(\text{OH})\cdot 7\text{H}_2\text{O}$	double chain $[\text{Si}_4\text{O}_{20}]$	0.18	1 : 1.75	(8)
ashcroftine-(Y)	$\text{K}_3\text{Na}_3\text{Y}_{12}(\text{Si}_2\text{O}_7)_4(\text{CO}_3)_4(\text{OH})_2\cdot 8\text{H}_2\text{O}$	tube chain $[\text{Si}_{56}\text{O}_{140}]$	0.18	1 : 1.07	(9)
carletonite	$\text{KNa}_4\text{Ca}_4(\text{Si}_8\text{O}_{18})(\text{CO}_3)_2\text{F}\cdot\text{H}_2\text{O}$	double sheet $[\text{Si}_8\text{O}_{18}]$	0.12	1 : 1.25	(10)
kampfite	$\text{Ba}_6(\text{Si},\text{Al})_8\text{O}_{16}(\text{CO}_3)_2\text{Cl}_2\cdot\text{H}_2\text{O}$	double sheet $[(\text{Si},\text{Al})_2\text{O}_8]$	0.06	1 : 1	(11)

LBS* Lewis-base strength (in valence units) (Brown 1981). M** number of large anion(s) with coordination number(s) greater than [VI]. References: (1) Shumyatskaya *et al.* (1976), (2) Hughes *et al.* (1996), (3) this study, (4) Zhou *et al.* (2002), (5) Grice *et al.* (1991), (6) Giuseppetti *et al.* (1989), (7) Grice (2001), (8) Mellini & Merlino (1978), (9) Moore *et al.* (1987), (10) Chao (1972), (11) M.A. Cooper (pers. commun., 2004).

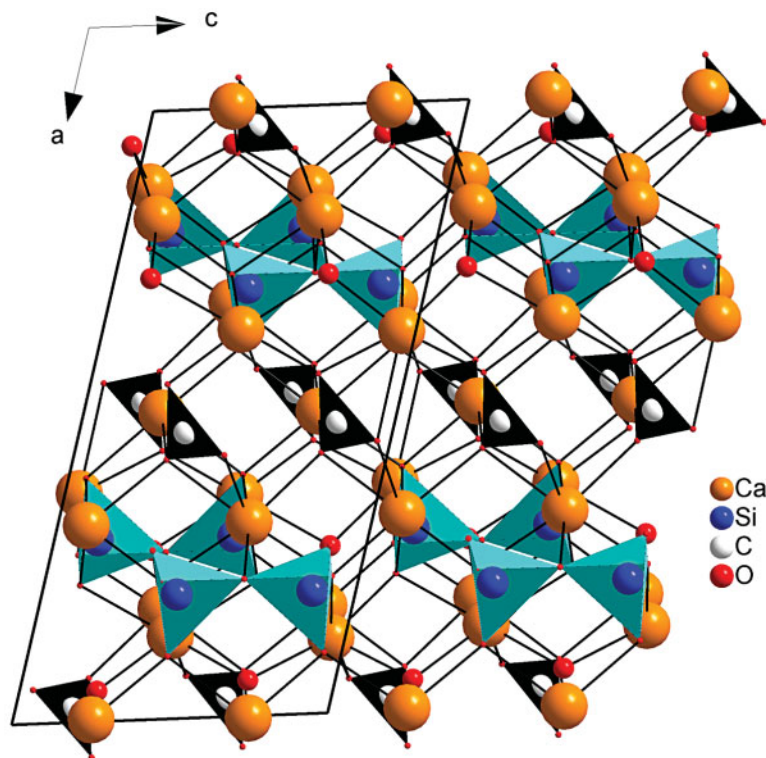


FIG. 2. The structure of tilleyite projected along [010], with the unit cell outlined. The $[\text{SiO}_4]$ tetrahedra are cyan-colored, and the $[\text{CO}_3]$ triangles are black.

Mineral species within the silicate-carbonate chemical class have crystal-structure topologies that are dependent on the Lewis-base strength of the silicate and carbonate anionic groups. The Lewis-base strength of the carbonate group is fixed, but that of the silicate group varies, depending on the degree of polymerization within the group. The Lewis-base strength of the silicate group can be greater than, equal to, or less than that of the carbonate group, and this variation defines the anionic and cationic composition within each layer. In general, as the silica activity increases, the total number of cations and carbonate groups decreases, the Lewis-base strength of the silicate groups decreases, and the layered topology becomes better defined into a silicate layer and a cation-carbonate layer.

ACKNOWLEDGEMENTS

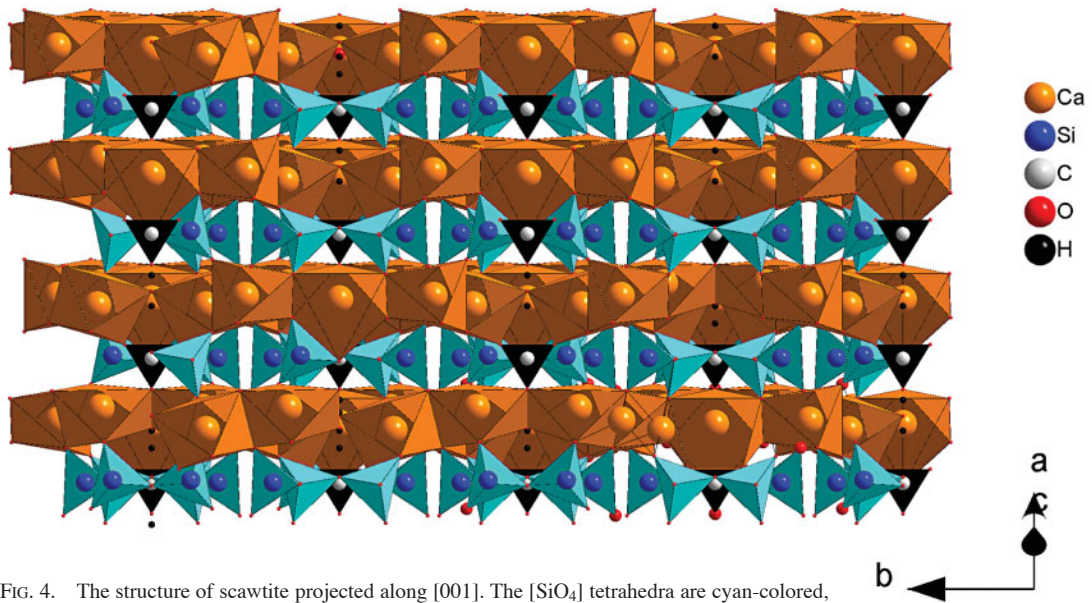
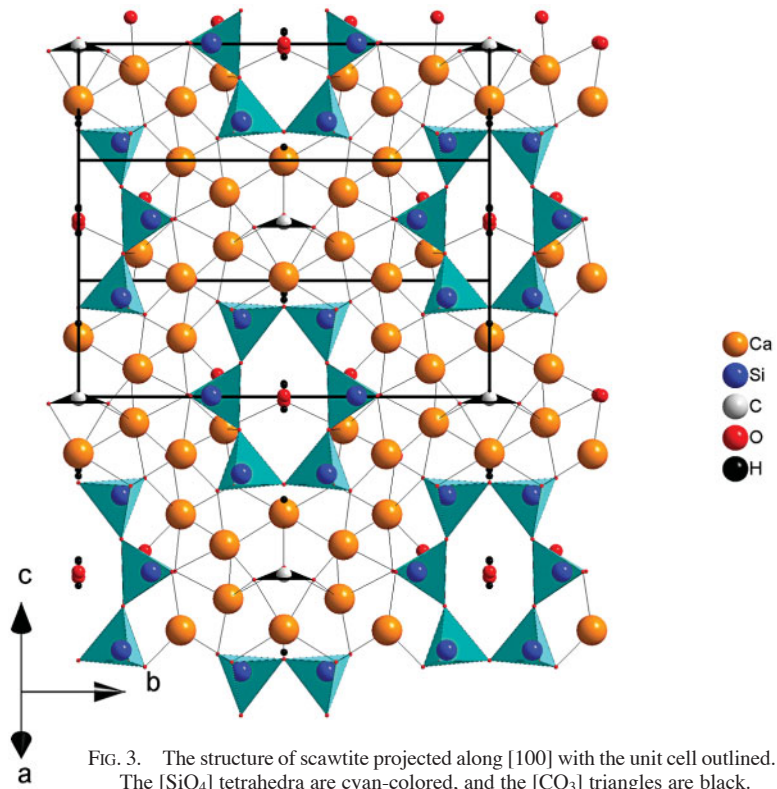
It gives me great pleasure to dedicate this paper to Mike Fleet on the occasion of his retirement. Mike has been a friend and an inspiration to me throughout my career. I have a tremendous admiration for Mike's

ability to contribute to such a wide variety of scientific fields. This paper on crystal chemistry represents but one small facet of his interests.

I gratefully acknowledge Dr. Pete Dunn, Smithsonian Institution, Dr. Ștefan Marincea, Geological Institute of Romania, and Dr. Mehmet Taner, Ottawa, for providing specimens. I thank Dr. Frank C. Hawthorne, University of Manitoba for the use of the single-crystal diffractometer. Helpful comments from the referees, Drs. Peter C. Burns and Frank C. Hawthorne and from the guest editor, Dr. Grant Henderson, improved the quality of the manuscript.

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Received August 10, 2004, revised manuscript accepted June 28, 2005.