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The crystal structures of helvite group minerals, $(Mn,Fe,Zn)_8(Be_6Si_6O_{24})S_2$

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Abstract

The structures of six members of the helvite–genthelvite series $(Mn,Fe,Zn)_8(Be_6Si_6O_{24})S_2$ have been refined in the space group $P\bar{4}3n$ to R factors between 0.024 and 0.029 for observed reflections measured on an automated single-crystal 4-circle X-ray diffractometer using Mo$K\alpha$ radiation. The 1:1 BeO_4 and SiO_4 tetrahedra are completely ordered. The Be–O, Si–O and O–O distances of the two distinct tetrahedra are constant throughout the compositional series, indicating that the interframework cations have no effect on the dimensions of the framework tetrahedra. Thus the geometrical sodalite model of Hassan and Grundy (1984) is applicable to the helvite group minerals and is used for a thorough analysis of the variations in crystal parameters. The results also indicate that pure danalite is probably stable and that complete miscibility should exist between the Mn, Fe and Zn end-members.

Introduction

The chemical composition of the helvite group minerals can be expressed as $C_8(Be_6Si_6O_{24})S_2$, with C = Mn (helvite), Fe^{2+} (danalite) and Zn (genthelvite). The helvite group minerals are isotypic with cubic sodalite, $Na_8(Al_6Si_6O_{24})Cl_2$ and their structures are characterized by four-membered rings of BeO_4 and SiO_4 tetrahedra in each of the faces of the unit cell; these rings are linked together, forming six-membered rings about each of the cell corners. The Al atoms in sodalite correspond to Be atoms in the helvite group minerals, the Na atoms to Mn, Fe^{2+} or Zn atoms and the Cl atoms to S atoms (see Fig. 1 of Hassan and Grundy, 1984).

Barth (1926) and Gottfried (1927) reported that helvite has space group $P\bar{4}3n$ and Pauling (1930) determined the structure of a helvite from Schwarzenberg, Saxony by making full use of the isotypic relationship with sodalite. A sample of helvite from the same locality was refined to an R-factor of 0.04 by Holloway et al. (1972).

Dunn (1976) analyzed seventy-five members of the helvite group from world-wide localities and also used fifty-seven analyses from the literature, and concluded that the chemical analyses indicate complete miscibility between the Fe- and Mn-members and between the Fe- and Zn-members but not between the Mn- and Zn-members. Essentially pure helvite and genthelvite occur naturally but the nearest approach to pure danalite is a sample with 86% of the Fe end-member. Danalite was the only end-member of the helvite group that could not be synthesized by Mel'nikov, Latvia and Fedosova (1968). This would suggest that pure danalite is unstable. Structural analyses and the sodalite model of Hassan and Grundy (1984) may be useful in considering the existence of pure danalite and the absence of miscibility between the Mn- and Zn-members of the Helvite group.

Hassan and Grundy (1984) have developed a geometrical model for structures based on the sodalite framework topology. In this model, they assumed that the interframework ions (Na^+, K^+, Ca^{2+}, Cl^-, OH^-, H_2O, SO_4^{2-}, etc.) have no effect on the Si–O and Al–O distances. The helvite group minerals provide an ideal opportunity to examine the isolated effect of the interframework cations on analogous Be–O and Si–O distances, together with the application of the sodalite model to variations of crystal parameters and thermal expansion behavior.

The sodalite structure has also been modelled by Taylor (1968, 1972), Taylor and Henderson (1978), Dempsey and Taylor (1980) and Beagley, Henderson and Taylor (1982). These models, including that of Hassan and Grundy (1984) have been used to analyze the thermal expansion behavior of aluminosilicate-sodalites; using thermal expansion data of Taylor (1968, 1972) and Henderson and Taylor (1978). The sodalite-type framework topology is usually in a partially collapsed state due to the relatively small interframework ions (Pauling, 1930). Heating (or substitution) causes the framework tetrahedra to rotate. This rotational mechanism is described in terms of ψ_{Si} and ψ_{Al}, the angles through which the distinct framework tetrahedra are rotated relative to their position

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Table 1. Localities of minerals in the helvite group

Sample No.	Mineral Name	Locality	ROM Collection No.	Dunn's sample No.
1	Helvite	Lexington Mine, Butte, Montana	M30349	46
2	Helvite	Sunnyside, San Juan Co., Colorado	M36390	
3	Danalite	Mt. Francisco Pegmatite, Ribawa Area, Western Australia	M37261	74
4	Danalite	Government Pits, Conway, New Hampshire	M34769	33
5	Genthelvite	Diamond Hill, Rhode Island	M37267	16
6	Genthelvite	Mt. St. Hilaire, Rouville Co., Quebec	M32727	2

in the fully expanded state (see Fig. 2 of Hassan and Grundy, 1984).

Experimental

The materials used in this study (Table 1) were donated by the Royal Ontario Museum. The six species selected for structural study represent compositions closest to the end-members, together with others within the ternary system (Table 2). The samples were chosen on the basis of the locality and chemical analyses of Dunn (1976); as the materials used in both of these studies are from the same general localities, the chemical analyses of Dunn (1976) should be representative of our materials.

Dunn (1976) used the electron microprobe to analyse the helvite group minerals and since beryllium could not be measured on the probe, Dunn (1976) calculated a BeO content assuming an ideal ratio [Mn, Fe^{2+}, Zn, Ca, Mg]: Be = 4:3. His chemical analyses were reported in terms of wt.% oxides and we use these values to calculate the number of ions on the basis of 12(Al+Be+Si), that is, the unit cell contents (Table 2). The number of Al atoms is insignificant (Table 2); Be atoms total more than six and Si atoms less than six. If the number of ions were calculated on the basis of 26(O+S), the same trends would exist. Moreover, the analyses also show that the sum of the interframework cations exceeds the maximum value of 8 (from 8.17 to 8.46) even if the Ca ions are subtracted. However, the numbers of S atoms reported by Dunn (1976) seem reasonable with values close to the maximum of 2. These trends in Dunn's (1976) analyses are due to the method used to calculate the BeO context. It seems that the interframework cations have been overestimated and due to the assumed Be:C = 3:4, the calculated Be content is greater than six, and due to the basis used in normalizing the unit cell contents, the amount of Si is less than six.

Precession photographs of all the samples show sharp reflections and no superstructure reflections. The symmetry of all the minerals is consistent with space group $P\bar{4}3n$ with *hhl*, *lhh*, and *hlh* absent when $l \neq 2n$. The cell parameters were determined using the least-squares method, monochromatic MoKα radiation and at least fifteen reflections ($15° < 2\theta < 30°$) automatically centered on a 4-circle single-crystal X-ray diffractometer. The cell parameters are presented in Table 3, together with other information pertinent to X-ray data collection and refinement. All reflection intensities were measured in the positive octant with $0 < h,k,l < 12$, out to a maximum 2θ of 65° on either a Nicolet P3 or a Syntex $P2_1$ diffractometer operating in the θ–2θ scan mode, with a 2θ scan range of $(K\alpha_1 - 0.85°)$ to $(K\alpha_2 + 0.85°)$ and variable scan rates of 3° to 29.3° min^{-1}, depending on the intensity of a prescan.

The two standard reflections of each sample which were monitored after every 50 reflections collected did not change. The data were corrected for Lorentz, polarization, background effects and spherical absorption (Table 3). Equivalent reflections were then averaged to produce unique data sets. All crystallographic calculations were made using XRAY 76 Crystallographic system (Stewart, 1976).

Structure refinement

Initial positional parameters and isotropic temperature factors for helvite (M30439) were those of Holloway,

Table 2. Chemical analyses[†] of the helvite group minerals after Dunn (1976) for specimens corresponding to those used in the present study

	Helvite 1.	Danalite 3	Danalite 4	Genthelvite 5	Genthelvite 6
ZnO	0.38	4.13	9.68	41.44	54.43
FeO	0.21	24.00	32.07	10.79	0.00
MnO	52.50	24.97	10.65	1.93	0.95
CaO	0.17	0.05	0.04	0.10	0.08
BeO	13.51	13.40	13.29	12.79	12.58
SiO_2	31.29	30.56	30.71	29.97	29.66
Al_2O_3	0.33	0.10	0.02	n.d.	n.d.
S	5.65	5.73	5.54	5.64	5.61
Total*	101.22	100.08	99.23	99.84	100.51
Number of ions on the basis of 12(Al + Be + Si)					
Zn	0.05	0.58	1.37	6.05	8.05
Fe	0.03	3.83	5.14	1.78	0.00
Mn	8.32	4.04	1.73	0.32	0.16
Ca	0.03	0.01	0.01	0.02	0.02
C	8.43	8.46	8.25	8.17	8.23
Be	6.07	6.14	6.11	6.07	6.06
Si	5.85	5.83	5.88	5.93	5.94
Al	0.07	0.02	0.00	—	—
S	1.98	2.05	1.99	2.09	2.11

[†] Dunn's collection numbers are given in Table 1. The number of ions were calculated in this study. * All totals less O=S.

Table 3. Crystal data† and data collection information for minerals in the helvite group

Miscellaneous	Helvite 1	Helvite 2	Danalite 3	Danalite 4	Genthelvite 5	Genthelvite 6
a(Å)	8.2913(6)	8.2365(4)	8.2317(9)	8.2182(2)	8.1493(5)	8.1091(4)
V(Å^3)	570.0	558.8	557.9	555.1	541.2	533.2
D_{calc}(gcm^{-3})	3.23	—	3.40	3.41	3.64	3.72
Crystal size (mm)	0.10 x 0.13 x 0.15	0.15 x 0.20 x 0.20	0.15 x 0.15 x 0.20	0.12 x 0.15 x 0.20	0.20 x 0.20 x 0.20	0.12 x 0.16 x 0.18
μ(cm^{-1})	49.7	—	60.2	64.3	87.8	96.7
Total no. of I	1283	1273	1271	1271	1224	1214
No. of non-equivalent $\|F\|$	256	254	254	254	245	243
No. of non-equivalent $\|F_o\|$ $>3\sigma\|F\|$	156	163	166	162	164	152
Isotropic Refinement $^*R_{(o)}$	2.5	3.7	2.6	2.7	2.6	2.9
Isotropic Refinement $^{**}Rw_{(o)}$	3.2	4.3	2.9	3.2	3.2	3.3
Anisotropic Refinement $R_{(o)}$	2.4	2.9	2.4	2.5	2.5	2.8
Anisotropic Refinement $Rw_{(o)}$	3.1	3.7	2.7	3.1	3.1	3.4

†Space group $P\bar{4}3n$; Z = 1; Radiation/monochromator is Mo/C; λ(MoKα) = 0.71069Å; $^*R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$;
$^{**}Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, w = 1.

Giordano and Peacor (1972); thereafter, the final results were used as starting parameters for the other sample closest in chemical composition. Atomic scattering factors for neutral atoms were taken from Cromer and Mann (1968).

The full-matrix least-squares refinement was similar in all cases. The first stage involved refinement of atomic positions, isotropic temperature factors and a variable overall scale factor using unit weights. In the second stage, the isotropic temperature factors were converted to the anisotropic form and the refinement continued until convergence. The *R*-factors at convergence in both stages are given in Table 3. During the final stages, both the occupancy factor and temperature factor for each Si, S and the interframework cation C (in terms of the dominant interframework cation) were refined while holding the remaining part of the structural model invariant. The refined occupancy factor for Si in each specimen was 1.00(1), indicating that this site is fully occupied by Si ions. This is further confirmed by the observed Si–O distances and bond-valence calculations. It was not possible to successfully refine together the occupancy factor and temperature factor for the Be position; however, the chemical analyses show insignificant amounts of Al ions and thus this site can be assumed to be fully occupied by Be ions. Moreover, this is justified in all the refined structures by the constancy of the Be–O and Si–O distances, which is unlikely if variable amounts of other ions were substituted at these tetrahedral sites. The occupancy factor for the S site was 1.00(1) and that for the C site in each of the samples was close to 1.00 (Table 4), indicating full occupancy of these sites. These results show that the number of interframework cations per unit cell is quite close to the maximum value of 8 as is the number of S atoms at the maximum value of 2. Consequently the chemical formula for the helvite group minerals may be written as (Mn, Fe, Zn)$_8$(Be$_6$Si$_6$O$_{24}$)S$_2$. The results presented here are not in good agreement with the chemical analyses of Dunn (1976), which seem to have overestimated the amount of interframework cations; due to the assumption made in calculating the beryllium content, the amounts of Be and Si shown by the chemical analyses also seem unsatisfactory. Unfortunately, the relative amounts of Mn, Fe and Zn in each specimen of the helvite group could not be calculated from the refinement as Mn and Fe have a difference of only one electron and also Zn may be present. Sample (M37261) was classified as helvite-rich by Dunn (1976). The refinement gave population and *R*-values of 1.06(1) and 0.024 respectively in terms of Fe; and 1.12(1) and 0.025 respectively in terms of Mn which indicates that the Fe-rich variety is a better fit to the structural data.

The final atomic parameters and isotropic temperature factors are given in Table 4, anisotropic thermal parame-

Table 4. Atomic parameters*, C site population parameters and isotropic temperature factors ($\times 10^4$) for the helvite group of minerals

		Helvite 1	Helvite 2	Danalite 3	Danalite 4	Genthelvite 5	Genthelvite 6
C Coordinate	x	0.1709(1)	0.1687(1)	0.1693(1)	0.1687(1)	0.1674(1)	0.1668(1)
O Coordinates	x	0.1407(6)	0.1393(6)	0.1395(4)	0.1394(5)	0.1382(6)	0.1377(7)
	y	0.1411(6)	0.1400(6)	0.1401(5)	0.1400(5)	0.1385(6)	0.1381(7)
	z	0.4168(4)	0.4134(4)	0.4126(3)	0.4114(4)	0.4029(4)	0.4060(5)
C Population Parameter		$0.97(1)_{Mn}$	$1.03(1)_{Mn}$	$1.06(1)_{Fe}$	$1.05(1)_{Fe}$	$1.00(1)_{Zn}$	$1.00(2)_{Zn}$
Isotropic temperature factors ($U \times 10^4$)	C	79(1)	82(3)	69(2)	68(2)	60(2)	59(3)
	S	112(5)	140(9)	103(7)	96(5)	68(7)	62(14)
	Si	72(6)	46(6)	32(5)	31(4)	25(4)	36(8)
	Be	85(26)	77(29)	65(21)	69(17)	57(19)	59(24)
	O	100(7)	79(8)	66(7)	63(6)	49(7)	61(12)

*The atoms are on the following sites in the space group $P43\bar{n}$: Be on 6(d); Si on 6(c) O on 24(i); S on 2(a) and C on 8(e). Estimated standard errors refer to the last digit.

ters in Table 5, and the interatomic distances and angles are presented in Table 6. The structure factors are in Table 7.[2]

Discussion

The general features of the structure of minerals in the helvite group are similar to those of sodalite (Hassan and Grundy, 1984) and basic sodalite (Hassan and Grundy, 1983). The average Be–O and Si–O distances of the six structures are 1.634Å and 1.629Å respectively (Table 6) and they are constant within the experimental errors. This indicates that BeO_4 and SiO_4 tetrahedra are completely ordered. The refinements therefore provide a useful Be–O distance which may be used to indicate Be site occupancy in a similar way to Al–O and Si–O distances (Jones, 1968).

The six members of the helvite group investigated cover the entire range of cell dimensions: end-member helvite (8.291Å) to end-member genthelvite (8.109Å), and throughout the compositional series, the Be–O, Si–O and tetrahedral O–O distances (Table 6) are constant within the estimated error. These are important features of the geometrical sodalite-type model (Hassan and Grundy, 1984). The constancy of the framework tetrahedra dimensions clearly show that they are unaffected by the different interframework ions—Mn, Fe^{2+} and Zn. Although Mn and Fe^{2+} have very similar chemical behavior, they are usually dissimilar to Zn. However, in the helvite group all three interframework cations behave as "hard-spheres" and the two distinct framework tetrahedra as rigid groups with purely geometrical interactions. This is clearly due to the rotational freedom of the framework tetrahedra.

In sodalite (Hassan and Grundy, 1984), the difference in rotation angles between the two distinct framework tetrahedra is quite large ($\psi_{Si} - \psi_{Al} = 1.6°$) due to the significant difference in dimensions of the SiO_4 (Si–O = 1.620Å) and AlO_4 (Al–O = 1.742Å) tetrahedra; this contrasts with the small difference in rotational angles ($\psi_{Si} - \psi_{Be} = 0.1°$) between the similar dimensions of the SiO_4 (Si–O = 1.629Å) and BeO_4 (Be–O = 1.634Å) tetrahedra in the helvite group. Moreover, for a given change in ψ, there is a larger change in cell edge for the beryllosilicate framework than the aluminosilicate framework. Therefore, the framework tetrahedra in the helvite group have greater rotational freedom than in the aluminosilicate sodalites, particularly near the maximum cell edge where ψ_{Si} is closer to zero in helvite than in sodalite (see equation (4') of Hassan and Grundy, 1984). The rotation angle, ψ, varies from about 30° to 34° from pure helvite to pure genthelvite, while the Si–O–Be angle varies from about 128° to 123° (Table 6). These variations must be directly related to the size of the interframework cations which in turn affects the cell edge. The effective ionic radii for the four coordinate interframework cations are: Mn^{2+} (H.S.)= 0.66, Fe^{2+}(H.S.) = 0.63, Zn^{2+} = 0.60 (Shannon, 1976). The decrease in the cell edge parallels the decrease in the radii of the interframework cations. As the radii decrease, the effective charge on the cation increases, as a result the C–O distance shortens and the following trends are observed: (1) the angle of rotation, ψ, increases, that is, the framework moves towards a more collapsed state and the Be–O–Si angle decreases; (2) the dimensions of the interframework (CO_3S) trigonal pyra-

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[2] To obtain a copy of Table 7, order Document AM-85-261 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N. W., Washington, D. C. 20009. Please remit $5.00 in advance for the microfiche.

Table 5. Anisotropic temperature factors† ($\times 10^4$) for the helvite group of minerals

		Helvite 1	Helvite 2	Danalite 3	Danalite 4	Genthelvite 5	Genthelvite 6
C	U_{11}	79(3)	82(3)	69(2)	68(3)	60(2)	59(3)
	U_{22}	79	82	69	68	60	59
	U_{33}	79	82	69	68	60	59
	U_{12}	2(3)	18(3)	3(2)	4(3)	5(2)	3(3)
	U_{13}	2	18	3	4	5	3
	U_{23}	2	18	3	4	5	3
S	U_{11}	112(8)	140(9)	103(7)	96(8)	68(7)	65(9)
	U_{22}	112	140	103	96	68	65
	U_{33}	112	140	103	96	68	65
	U_{12}	0	0	0	0	0	0
	U_{13}	0	0	0	0	0	0
	U_{23}	0	0	0	0	0	0
Si	U_{11}	62(14)	50(15)	37(12)	34(14)	30(15)	33(18)
	U_{22}	77(9)	44(8)	29(7)	30(8)	23(8)	40(10)
	U_{33}	77	44	29	30	23	40
	U_{12}	0	0	0	0	0	0
	U_{13}	0	0	0	0	0	0
	U_{23}	0	0	0	0	0	0
Be	U_{11}	69(63)	85(75)	78(58)	97(69)	66(72)	24(82)
	U_{22}	93(35)	74(38)	59(30)	55(34)	53(37)	79(46)
	U_{33}	93	74	59	55	53	79
	U_{12}	0	0	0	0	0	0
	U_{13}	0	0	0	0	0	0
	U_{23}	0	0	0	0	0	0
O	U_{11}	109(23)	77(24)	70(19)	71(22)	50(24)	67(32)
	U_{22}	114(23)	83(25)	68(19)	70(22)	57(24)	77(33)
	U_{33}	77(13)	78(14)	58(11)	47(13)	40(14)	38(16)
	U_{12}	24(13)	31(13)	23(10)	26(11)	22(12)	27(14)
	U_{13}	4(17)	12(18)	12(14)	8(15)	22(16)	-15(21)
	U_{23}	-24(17)	4(18)	12(14)	9(15)	14(16)	-24(21)

†The anisotropic temperature factors are coefficients in the expression $\exp-[U_{11}h^2+U_{22}k^2+U_{33}\ell^2+2U^{12}kh+2U^{13}h\ell+2U^{33}k\ell]$. Estimated standard errors refer to the last digit.

mid decrease; (3) the dimensions of the interframework (SC_4) tetrahedron decrease. The same trends hold for the intermediate members of the helvite group, using the weighted average cation radii.

End-member danalite probably has a cell edge that is midway between the other two end-members as the radius of Fe^{2+} is the mean of Mn^{2+} and Zn^{2+}. Therefore pure danalite should have a cell edge of 8.200Å and thus a mean $\psi = 32°$. Due to the small difference in radii among the interframework cations and the small difference in rotation angle among the three end-members compared to the difference between Na_8Cl_2- and K_8Cl_2-aluminosilicate sodalites (Hassan and Grundy, 1984) and in view of the rotational freedom of the framework tetrahedra, the results indicate that pure danalite should exist and that there should be no miscibility gap in the ternary system. These results indicate the need for further experimental work on the synthesis of selected chemical compositions, as in nature certain compositions seems to be preferred. For example, the Mn-member is more common than the Fe-member whereas the Zn-member is the rarest. This may be related to the chalcophile-lithophile tendencies of the elements (Burt, 1974), and as was pointed out by Burt (1980), it may also explain the otherwise puzzling gap between natural Mn- and Zn-members noted by Dunn (1976).

Finally, the results obtained from this study clearly show that the geometrical sodalite model of Hassan and Grundy (1984) is quite applicable to the minerals of the helvite group. Therefore, using equation (4) of Hassan and Grundy (1984) and the average parameters given in Table 6, a maximum cell edge of 9.053Å is predicted for the beryllosilicate sodalites. If we choose 8.220Å as a typical cell edge at room temperature for the helvite group, we can consider if a change of 0.833Å in the cell edge is possible through thermal expansion. Using the maximum cell edge, a hypothetical cation, C, at (1/4, 1/4, 1/4) and equations (5) and (7) of Hassan and Grundy (1984), the calculated C–O and C–S distances are 2.591Å and 3.920Å respectively. All of the changes from room temperature to the maximum cell edge are quite large compared to those occurring in the aluminosilicate sodalites, suggesting that the beryllosilicate sodalites would break down before the maximum cell edge is reached. However, it is possible that the cation may reach x = 1/4 and give rise to a discontinuity in the cell edge expansion

Table 6. Interatomic distances and angles† in the helvite group of minerals

		Helvite 1	Helvite 2	Danalite 3	Danalite 4	Genthelvite 5	Genthelvite 6	Selected Averages
SiO_4 tetrahedra								
Si-O	4 x	1.629(4)	1.627(5)	1.629(4)	1.631(4)	1.630(4)	1.628(5)	1.629
O-O	4 x	2.634(6)	2.634(6)	2.635(5)	2.637(6)	2.640(6)	2.636(8)	2.636
	2 x	2.711(6)	2.703(6)	2.710(5)	2.714(6)	2.706(6)	2.703(7)	2.708
O-Si-O	4 x	107.9(2)	108.1(2)	107.9(2)	107.9(2)	108.1(2)	108.1(2)	
	2 x	112.7(2)	112.3(2)	112.6(2)	112.7(2)	112.2(2)	112.1(3)	
BeO_4 tetrahedra								
Be-O	4 x	1.633(4)	1.634(5)	1.636(4)	1.637(4)	1.633(4)	1.632(5)	1.634
O-O	4 x	2.641(6)	2.646(6)	2.647(5)	2.649(6)	2.645(6)	2.643(7)	2.645
	2 x	2.717(6)	2.712(6)	2.719(5)	2.723(6)	2.710(6)	2.708(7)	2.715
O-Be-O	4 x	107.9(2)	108.1(2)	108.0(2)	108.0(2)	108.1(2)	108.2(2)	
	2 x	112.6(2)	112.2(2)	112.4(2)	112.5(2)	112.2(2)	112.1(3)	
Si-O-Be		128.0(2)	126.5(2)	126.1(2)	125.5(2)	124.0(2)	123.1(2)	
Si-Be		2.931(1)	2.912(1)	2.910(1)	2.906(1)	2.881(1)	2.867(1)	
Si/Be-O		1.631	1.631	1.633	1.634	1.632	1.630	1.632
ϕ_{Si}		30.6	31.9	32.1	32.4	33.7	34.3	
ϕ_{Be}		30.5	31.7	31.9	32.3	33.6	34.3	
CO_3S trigonal pyramid								
C-S		2.454(1)	2.407(1)	2.413(1)	2.402(1)	2.362(1)	2.342(1)	
C-O	3 x	2.069(3)	2.043(4)	2.033(3)	2.023(3)	1.989(3)	1.968(4)	
S-O	3 x	3.830(4)	3.774(4)	3.767(3)	3.751(3)	3.687(4)	3.652(4)	
O-O	2 x	3.235(6)	3.188(6)	3.176(5)	3.159(5)	3.107(6)	3.095(7)	
S-C-O	3 x	115.5(1)	115.7(1)°	115.6(1)	115.7(1)	115.6(1)	115.6(2)	
O-C-O	3 x	102.8(1)	102.6(2)	102.8(1)	102.6(2)	102.7(2)	102.7(2)	

† Estimated standard errors refer to the last digit.

with the framework still in a partially collapsed state. To consider this possibility, we may fix the C–O distance at some reasonable value (see Table 6), as Hassan and Grundy (1984) have shown that the C–O distance is constant (particularly in Na_8I_2- and Na_8Br_2-sodalites) up to where the cation just reaches x = 1/4 and thereafter it begins to expand. If we set the C–O value to 2.020Å, the cation just reaches x = 1/4 with the cell edge being 8.540Å and the C–S distance being 3.698Å. From room temperature to this state, C–S and cell edge change about 1.30Å and 0.32Å respectively. Such changes for the beryllosilicate sodalites are unlikely before breakdown because the aluminosilicate sodalites (e.g., Na_8I_2-sodalite) undergo changes that are about one-half these values (Hassan and Grundy, 1984) before they breakdown (Henderson and Taylor, 1978). Moreover, the doubly charged interframework ions in the beryllosilicate sodalites form bonds that are considerably stronger than the singly charged interframework ions in the alkali halide aluminosilicate sodalites. Therefore, the thermal expansion curves for the helvite group of minerals are highly unlikely to show discontinuities as the framework at room temperature is in a highly collapsed state.

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