# The structure of slawsonite, a strontium analog of paracelsian

Dana T. Griffen[1], P. H. Ribbe, and G. V. Gibbs

*Department of Geological Sciences, Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061*

## Abstract

Slawsonite is a new mineral from the Triassic Martin Bridge Formation in Wallowa County, Oregon. Its composition ($Sr_{0.87}Ca_{0.13}Al_2Si_2O_8$), cell dimensions ($a = 8.888$, $b = 9.344$, $c = 8.326$ Å, $\beta = 90.33°$), and $P2_1/a$ space group suggest it is isostructural with paracelsian, $BaAl_2Si_2O_8$. A structure refinement using 1617 twice-measured reflections with $|F_{obs}| > 3\hat{\sigma}$ was undertaken by conventional methods to $R = 0.048$. Like paracelsian, slawsonite has a completely ordered Al/Si distribution in its infinite 3-D framework of corner-sharing tetrahedra. The mean Al–O distances at $T10$ and $T2m$ are both 1.748 Å; mean Si–O distances are 1.623 and 1.624 Å for the $T1m$ and $T20$, respectively. The former are equal to those in paracelsian, while the latter are 0.004 Å longer on the average. The Sr atom is 7-coordinated; $\langle Sr-O \rangle = 2.630$ Å. There is a high correlation among individual $T$–O distances, the mean intertetrahedral angle $T$–O–$T$, and the mean of the three O–$T$–O angles involved in the $T$–O bond.

## Introduction

The structure of paracelsian ($BaAl_2Si_2O_8$, $P2_1/a$), originally solved by Smith (1953), was refined by Craig *et al.* (1973) who found it to have a completely ordered Al/Si distribution in its framework of corner-sharing tetrahedra. Recently structures of several paracelsian analogs have been reported, in particular hurlbutite ($CaBe_2P_2O_8$; Lindbloom *et al.*, 1974), and synthetic $SrGa_2Si_2O_8$[2] and $SrGa_2Ge_2O_8$ (Phillips *et al.*, 1975). Danburite ($CaB_2Si_2O_8$), which has paracelsian topology but a different $T^{3+}/T^{4+}$ ordering scheme and space group (*Pnam*), was refined by Phillips *et al.* (1974). In addition, work is in progress on the paracelsian modifications of $SrAl_2Ge_2O_8$ (Kroll and Phillips, in preparation) and $BaGa_2Ge_2O_8$ (Calleri, personal communication). This study presents the structure of a new mineral, slawsonite ($SrAl_2Si_2O_8$), the Sr analog of paracelsian.

Barrer and Marshall (1964) synthesized pseudo-orthorhombic $SrAl_2Si_2O_8$ from gels in hydrothermal experiments. The lattice parameters determined by them are listed in Table 1. Erd *et al.* (1977) have described natural slawsonite from metamorphosed limestones of the Triassic Martin Bridge Formation in Wallowa County, Oregon. Its cell dimensions and space group, $P2_1/a$, suggest that slawsonite is isostructural with paracelsian (Table 1).

## Experimental procedures

The crystal used for this structure refinement came from the type locality (Wallowa County, Oregon) and was provided by Richard C. Erd of the U. S. Geological Survey. It is a clear, flat triangular prism $62\mu m$ thick with sides measuring $140 \times 217 \times 155\mu m$. The lattice parameters shown in Table 1 were determined by least-squares refinement of sixteen reflections measured with a fully automated four-circle Picker diffractometer using Zr-filtered Mo$K\alpha$ radiation. Electron microprobe analysis gave an Al:Si ratio of 1:1, within the limits of error. The only other cations detected in significant concentrations were Sr and Ca, accounting for 0.82 and 0.12 atoms, respectively, in the formula unit. Because of some uncertainty about the Sr content of the "standard" used for microprobe analysis and because no substituents other than 0.04 weight percent Fe were detected, the values for Sr and Ca were scaled upward so that Sr + Ca = 1.0, giving an approximate formula of $Sr_{0.87}Ca_{0.13}Al_2Si_2O_8$.

Table 1. Crystallographic data for slawsonite

|  | Barrer and Marshall (1964) | Erd, Nolf, and Smith (pers. comm.) | This study |
|---|---|---|---|
| a (Å) | 8.91$_0$ | 8.895(1)* | 8.888(2) |
| b (Å) | 9.34$_3$ | 9.359(1) | 9.344(2) |
| c (Å) | 8.34$_5$ | 8.333(1) | 8.326(3) |
| β (°) | ∿90 | 90.24(1) | 90.33(2) |
| Vol. (Å$^3$) | – | 693.7(1) | 691.5 |

* e.s.d.'s, given in parentheses, refer
to last decimal place.

Table 4. Isotropic and anisotropic temperature factors

| Atom | B (Å$^2$) | Anisotropic temperature factors ($\times 10^4$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Sr | 0.66(1)* | 30(1) | 20(1) | 29(1) | 0(1) | 0(1) | 1(1) |
| T1o | 0.34(2) | 9(2) | 10(2) | 12(2) | 1(1) | 0(1) | 2(2) |
| T1m | 0.31(2) | 6(2) | 9(1) | 11(2) | 0(1) | 2(1) | 0(1) |
| T2o | 0.27(2) | 8(2) | 6(1) | 10(2) | -2(1) | 0(1) | 1(1) |
| T2m | 0.30(2) | 9(2) | 7(2) | 10(2) | -1(1) | 1(1) | 0(1) |
| O1o | 0.62(6) | 21(4) | 15(4) | 22(5) | 7(3) | 3(4) | 0(4) |
| O1m | 0.67(6) | 25(5) | 10(4) | 28(5) | 8(4) | 8(4) | 5(4) |
| O2o | 0.48(6) | 13(4) | 7(4) | 22(5) | -2(3) | -7(4) | 3(3) |
| O2m | 0.59(6) | 17(5) | 12(4) | 20(5) | -1(3) | 11(4) | -2(3) |
| O3o | 0.51(6) | 13(4) | 16(4) | 15(5) | -2(3) | 3(4) | -2(4) |
| O3m | 0.63(6) | 10(4) | 16(4) | 29(5) | 0(3) | 1(4) | 4(4) |
| O4 | 0.89(6) | 42(5) | 27(4) | 13(5) | -12(4) | 0(4) | 0(4) |
| O5 | 0.61(6) | 12(4) | 25(4) | 17(5) | -6(4) | 3(4) | 2(4) |

* e.s.d.'s, given in parentheses, refer to last
decimal place.

Computer programs used during this study, as listed in the *World List of Crystallographic Computer Programs* (Third Edition) were DATALIB, DATASORT, OR XFLS3, and OR FFE3. For the refinement of the structure, 4168 intensities were collected from two equivalent quadrants. A $\theta$–$2\theta$ scanning rate of 1°/min was used and intensities were measured in the range $0.12 < \sin\theta/\lambda < 1.22$. Observed intensities were corrected for Lorentz-polarization effects and for absorption ($\mu_L = 93.4$ cm$^{-1}$), and converted to $F^2_{obs}$ with the program DATALIB. These were weighted according to $1/\hat{\sigma}^2$, and the weighted values for symmetry equivalent reflections were averaged using the program DATASORT, to give 1870 non-zero symmetry-independent observations.

The atomic coordinates of SrGa$_2$Si$_2$O$_8$ (Phillips *et al.*, 1975) were used as starting values in the least-

squares refinement program OR XFLS3, and scattering factors for neutral atoms were employed (Doyle and Turner, 1968). Reflections for which $|F_{obs}|$ was less than $3\hat{\sigma}$ were omitted, and the remaining reflections were weighted according to $1/\hat{\sigma}^2$. An extinction correction was applied, and refinement with isotropic temperature factors yielded an unweighted residual of 0.050 ($wR = 0.055$) for 1617 reflections. With the introduction of anisotropic temperature factors, the refinement converged to $R = 0.048$ ($wR = 0.053$). No significant correlations were noted among the parameters. The final $F_{obs}$ and $F_{calc}$ values are listed in Table 2,[3] and the fractional atomic coordinates are shown in Table 3. Table 4 gives the isotropic and anisotropic temperature factors. The important interatomic distances and bond angles (Table 5) were calculated with the computer program OR FFE3.

## Discussion

### Lattice parameters of paracelsian analogs

The lattice parameters for five paracelsian analogs and danburite are listed in Table 6.[4] Multiple linear regression analyses of the cell parameters as functions

Table 3. Final atomic positional parameters

| Atom | x | y | z |
|---|---|---|---|
| Sr | 0.8902(1)* | 0.4122(1) | 0.2503(1) |
| T1o | .2321(2) | .9249(2) | .9311(2) |
| T1m | .2405(2) | .9199(2) | .5605(2) |
| T2o | .0595(2) | .2006(2) | .9440(2) |
| T2m | .0541(2) | .1944(2) | .5706(2) |
| O1o | .1910(4) | .0934(4) | .0100(5) |
| O1m | .1875(4) | .0740(4) | .4937(5) |
| O2o | .1192(4) | .3658(4) | .9458(5) |
| O2m | .1236(4) | .3699(4) | .5573(5) |
| O3o | .9202(4) | .1919(4) | .0699(4) |
| O3m | .8979(4) | .1923(4) | .4399(5) |
| O4 | .0092(5) | .1545(4) | .7662(5) |
| O5 | .3139(4) | .9252(4) | .7407(5) |

* e.s.d.'s, given in parentheses,
refer to last decimal place.

[3] To obtain a copy of this table, order Document AM-76-018 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

[4] Danburite is topologically identical to paracelsian, but topochemically different: whereas paracelsian contains $T^{3+}$–O–$T^{4+}$ linkages but no $T^{3+}$–O–$T^{3+}$ or $T^{4+}$–O–$T^{4+}$ linkages, all three types occur in danburite (Phillips *et al.*, 1974). It is nonetheless valid to include it in a comparison of paracelsian-type structures, as demonstrated in the following discussion.

Table 5. Interatomic distances (Å) and angles (°)

| | *T*–O | | O···O | O–*T*–O |
|---|---|---|---|---|
| **T10 tetrahedron** | | | | |
| T10–O10 | 1.745(4)* | O10–O20 | 2.738(5) | 102.8(2) |
| –O20 | 1.757(4) | –O30 | 2.922(5) | 113.9(2) |
| –O30 | 1.741(4) | –O5 | 2.953(5) | 115.4(2) |
| –O5 | 1.749(4) | O20–O30 | 2.914(6) | 112.8(2) |
| | | –O5 | 2.732(6) | 102.4(2) |
| | | O30–O5 | 2.840(5) | 108.9(2) |
| Mean | 1.748 | | 2.850 | 109.4 |
| **T1m tetrahedron** | | | | |
| T1m–O1m | 1.612(4) | O1m–O2m | 2.579(5) | 105.4(2) |
| –O2m | 1.629(4) | –O3m | 2.663(6) | 111.1(2) |
| –O3m | 1.618(4) | –O5 | 2.716(5) | 113.6(2) |
| –O5 | 1.633(4) | O2m–O3m | 2.698(5) | 112.4(2) |
| | | –O5 | 2.597(6) | 105.5(2) |
| | | O3m–O5 | 2.642(5) | 108.7(2) |
| Mean | 1.623 | | 2.649 | 109.5 |
| **T20 tetrahedron** | | | | |
| T20–O10 | 1.634(4) | O10–O20 | 2.678(5) | 110.2(2) |
| –O20 | 1.631(4) | –O30 | 2.628(5) | 107.4(2) |
| –O30 | 1.628(4) | –O4 | 2.649(6) | 109.9(2) |
| –O4 | 1.602(4) | O20–O30 | 2.615(5) | 106.8(2) |
| | | –O4 | 2.659(6) | 110.6(2) |
| | | O30–O4 | 2.675(5) | 111.8(2) |
| Mean | 1.624 | | 2.651 | 109.5 |
| **T2m tetrahedron** | | | | |
| T2m–O1m | 1.756(4) | O1m–O2m | 2.871(5) | 109.6(2) |
| –O2m | 1.757(4) | –O3m | 2.835(5) | 107.5(2) |
| –O3m | 1.758(4) | –O4 | 2.873(6) | 111.4(2) |
| –O4 | 1.720(4) | O2m–O3m | 2.774(5) | 104.2(2) |
| | | –O4 | 2.853(6) | 110.2(2) |
| | | O3m–O4 | 2.909(6) | 113.5(2) |
| Mean | 1.748 | | 2.853 | 109.4 |

| **Sr–O distances** | | **_T_–O–_T_ angles** | |
|---|---|---|---|
| Sr–O10 | 2.662(4) | T10–O10–T20 | 125.2(2) |
| –O1m | 2.723(4) | T1m–O1m–T2m | 130.0(2) |
| –O20 | 2.641(4) | T10–O20–T20 | 123.1(2) |
| –O2m | 2.594(4) | T1m–O2m–T2m | 124.6(2) |
| –O30 | 2.562(4) | T10–O30–T20 | 128.5(2) |
| –O3m | 2.591(4) | T1m–O3m–T2m | 127.3(2) |
| –O5 | 2.635(4) | T20–O4–T2m | 138.7(3) |
| | | T10–O5–T1m | 131.9(2) |
| Mean | 2.630 | | 128.7 |

*e.s.d's, given in parentheses, refer to last decimal place.



Fig. 1. Observed *vs.* calculated lattice parameters for five para-celsian-type structures and danburite. Lines are drawn at 45°; symbols and observed values are listed in Table 6. Correlation coefficients $r$ are given in the figures. Calculated values $y$ came from linear regressions equations of the type $y = a_0 + a_1 \langle M{-}O \rangle + a_2 \langle\langle T{-}O \rangle\rangle$; the constants are listed below:

| | $a_0$ | $a_1$ | $a_2$ |
|---|---|---|---|
| $a$ | −0.9535 | 1.3246 | 3.7516 |
| $b$ | 0.8823 | 1.2943 | 3.0072 |
| $c$ | 0.1615 | 1.5119 | 2.4818 |
| Volume | −1281.4 | 307.85 | 690.54 |



Fig. 2. Mean *T*–O–*T* angle as a function of mean *M*–O and grand mean *T*–O bond lengths for parcelsian-type structures and danburite. Symbols are listed in Table 6.

of mean *M*–O and grand mean *T*–O distances gave multiple correlation coefficients > 0.99 for *a*, *b*, *c*, and volume. Figure 1 shows plots of observed values versus values calculated from the various regression equations listed in the figure legend. An examination
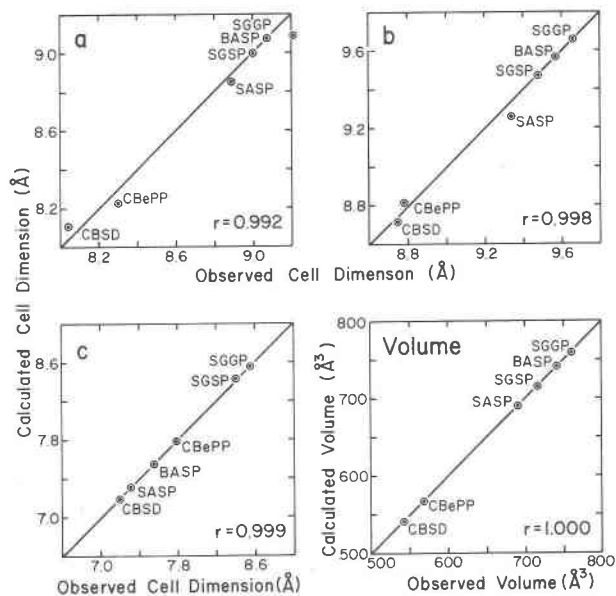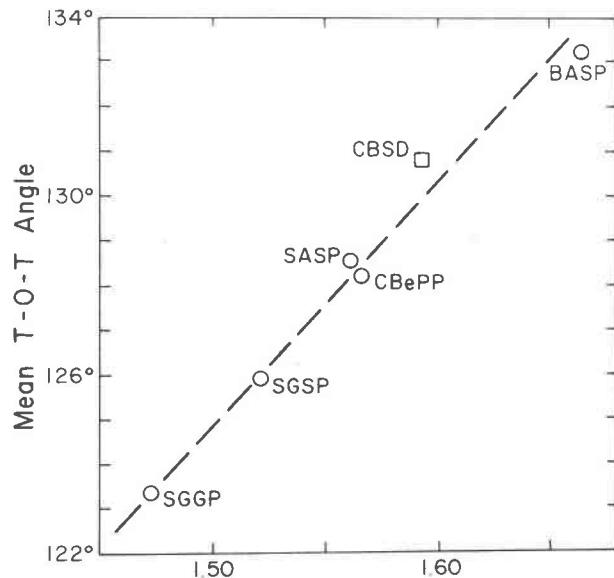
Table 6. Crystallographic data for five paracelsian analogs and danburite

| | Paracelsian $BaAl_2Si_2O_8$ | Slawsonite $SrAl_2Si_2O_8$ | (Synthetic) $SrGa_2Si_2O_9$ | (Synthetic) $SrGa_2Ge_2O_8$ | Hurlbutite $CaBe_2P_2O_8$ | Danburite $CaB_2Si_2O_8$ |
|---|---|---|---|---|---|---|
| $a$ (Å) | 9.065(3)* | 8.888(2) | 9.001(1) | 9.206(1) | 8.299(1) | 8.038(3) |
| $b$ (Å) | 9.568(1) | 9.344(2) | 9.484(1) | 9.660(1) | 8.782(2) | 8.752(5) |
| $c$ (Å) | 8.574(5) | 8.326(3) | 8.399(1) | 8.581(1) | 7.798(3) | 7.730(3) |
| $\beta$ (°) | 90.00(1) | 90.33(2) | 90.68(1) | 90.43(1) | 90.5 | 90.0 |
| $\langle M^{VII}$–O$\rangle$ (Å) | 2.801 | 2.630 | 2.626 | 2.630 | 2.469 | 2.461 |
| $\langle T^{3+}$–O$\rangle$ (Å) | 1.747 | 1.748 | 1.823 | 1.825 | --- | 1.474 |
| $\langle T^{4+}$–O$\rangle$ (Å) | 1.619 | 1.624 | 1.628 | 1.748 | --- | 1.617 |
| $\langle\langle T$–O$\rangle\rangle$ (Å) | 1.683 | 1.686 | 1.726 | 1.786 | 1.577 | 1.546 |
| Symbol | BASP | SASP | SGSP | SGGP | CBePP | CBSD |

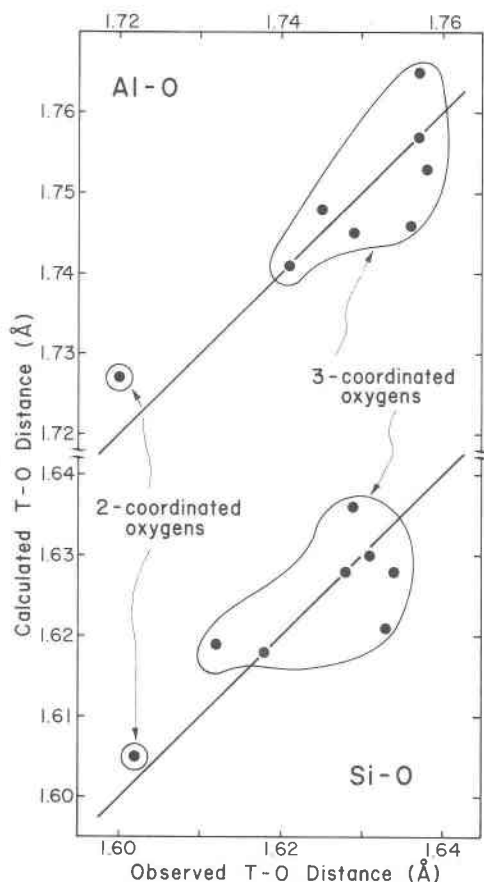* e.s.d.'s, given in parentheses, refer to last decimal place.



Fig. 3. Least-squares regression lines showing the relationship between the calculated and observed Al–O and Si–O distances in slawsonite. Calculated values came from these multiple linear regression equations:

$$(Al{-}O)_{calc} = 2.354 - 0.0055\,\langle O{-}T{-}O\rangle_3 - 0.0010\,(T{-}O{-}T)$$
$$(Si{-}O)_{calc} = 2.239 - 0.0029\,\langle O{-}T{-}O\rangle_3 - 0.0013\,(T{-}O{-}T)$$

of the regression coefficients indicates that the cell parameters are approximately twice as dependent on $\langle\langle T$–O$\rangle\rangle$ as they are on $\langle M$–O$\rangle$.

*The Sr atom*

As in the other paracelsian structures and danburite, the $M$ cation in slawsonite may be considered seven-coordinated. Phillips *et al.* (1975) have established the sympathetic relationship between mean $T$–O–$T$ angles and $\langle M$–O$\rangle/\langle\langle T$–O$\rangle\rangle$ for paracelsian analogs and danburite (Fig. 2). By examining changes in individual $T$–O–$T$ angles Phillips and Kroll (in preparation) have shown that the tetrahedral framework collapses (*i.e.*, individual $T$–O–$T$ angles decrease) with decreasing $\langle M$–O$\rangle$ and with increasing $\langle\langle T$–O$\rangle\rangle$, thus providing a physical interpretation for the parameter $\langle M$–O$\rangle/\langle\langle T$–O$\rangle\rangle$. In light of this it is interesting to note that the *mean* Sr–O distances for the three Sr paracelsian analogs are statistically identical despite the increase in framework size in the order $SrAl_2Si_2O_8 < SrGa_2Si_2O_8 < SrGa_2Ge_2O_8$. The *range* in individual Sr–O distances, however, increases in the same order, suggesting that the collapse of the framework about the Sr atom causes some Sr–O distances to increase while others decrease, leaving the mean essentially unchanged. The same is true for the Ca–O distances in danburite and hurlbutite, where the framework size increases for $CaB_2Si_2O_8$ to $CaBe_2P_2O_8$.

*Al/Si order in the tetrahedral framework*

The mean Si–O and Al–O distances in fully-ordered anorthite have been generally used as standards

for the estimation of order in framework aluminosilicates. The mean Al–O distances in slawsonite, paracelsian and anorthite are statistically identical (1.748Å, 1.747Å, and 1.747Å, respectively), whereas the mean Si–O distances are 1.624Å, 1.619Å, and 1.614Å, respectively. Phillips *et al.* (1975) found a mean Si–O distance of 1.628Å in $SrGa_2Si_2O_8$, and they attributed this increase over $\langle Si-O \rangle$ in $BaAl_2Si_2O_8$ to inductive effects of the much larger Ga atoms. Because silicon and gallium possess quite different X-ray scattering characteristics, they were able to determine by site refinement techniques that $SrGa_2Si_2O_8$ is completely ordered. Since the mean Si–O distance in this paracelsian analog is 0.004Å larger than that in slawsonite, it may be concluded with some confidence that slawsonite is also fully-ordered. Thus the significantly larger mean Si–O bond length in $SrAl_2Si_2O_8$ relative to $BaAl_2Si_2O_8$ suggests that the *M* cation may also be influential in determining the sizes of the tetrahedral sites.

### Correlations between *T*–O distances and *T*–O–*T* and O–*T*–O angles

The *T*–O bond length variations in the feldspars correlate with the angles within and between the tetrahedral ions of the framework, shorter bonds tending to involve wider angles (Ribbe *et al.*, 1974; Gibbs *et al.*, 1974). The same correlation can be made for the tetrahedral bond lengths in slawsonite as evinced by Figure 3 where observed *T*–O bond lengths are plotted against bond lengths calculated as a function of the intertetrahedral angle *T*–O–*T* and the mean of the three O–*T*–O angles common to the *T*–O bond. As expected, the shortest Al–O and Si–O bonds in slawsonite are both to the only 2-coordinated oxygen (O4) and are involved in the widest *T*–O–*T* and $\langle O-T-O \rangle_3$ angles.

## References

Barrer, R. M. and D. J. Marshall (1964) Hydrothermal chemistry of silicates. Part XII. Synthetic strontium aluminosilicates. *J. Chem. Soc.*, 485–497.

Craig, J. R., S. J. Louisnathan and G. V. Gibbs (1973) Al/Si order in paracelsian (abstr.), *Trans. Am. Geophys. Union, 54,* 496

Erd, R. C., B. O. Nolf and V. C. Smith (1977) Slawsonite, $(Sr,Ca)Al_2Si_2O_8$, a new mineral from the Wallowa Mountains, Oregon. *Am. Mineral. 62,* in press.

Gibbs, G. V., S. J. Louisnathan, P. H. Ribbe and M. W. Phillips (1974) Semiempirical molecular orbital calculations for the atoms of the tetrahedral framework in anorthite, low albite, maximum microcline and reedmergnerite. In, *The Feldspars,* W. S. MacKenzie and J. Zussman, eds. Manchester University Press, p. 25–48.

Lindbloom, J. T., G. V. Gibbs and P. H. Ribbe (1974) The crystal structure of hurlbutite: A comparison with danburite and anorthite. *Am. Mineral., 59,* 1267–1271.

Phillips, M. W., G. V. Gibbs and P. H. Ribbe (1974) The crystal structure of danburite: A comparison with anorthite, albite, and reedmergerite. *Am. Mineral., 59,* 79–85.

———, H. Kroll, H. Pentinghaus and P. H. Ribbe (1975) The structures of synthetic paracelsian analogs, $SrGa_2Si_2O_8$ and $SrGa_2Ge_2O_8$. *Am. Mineral., 60,* 659–666.

Ribbe, P. H., M. W. Phillips and G. V. Gibbs (1974) Tetrahedral bond length variations in feldspars. In, *The Feldspars,* W. S. MacKenzie and J. Zussman, eds. Manchester University Press, p. 25–48.

Smith, J. V. (1953) The crystal structure of paracelsian, $BaAl_2Si_2O_8$ *Acta Crystallogr., 6,* 613–620.

# Vibrational spectra of the alkaline earth double carbonates

Barry E. Scheetz and William B. White

*Materials Research Laboratory and Department of Geosciences*
*The Pennsylvania State University, University Park, Pennsylvania 16802*

## Abstract

Raman spectra and mid-range and far infrared spectra have been measured on poly-crystalline norsethite [$BaMg(CO_3)_2$], barytocalcite [$BaCa(CO_3)_2$], the high-temperature modification of barytocalcite, huntite [$CaMg_3(CO_3)_4$], benstonite [$Ca_7Ba_6(CO_3)_{13}$], and alstonite [$CaBa(CO_3)_2$]. Factor-group calculations permit the assignment of the internal modes of the known structures. Effects of ordering in these derivative structures appear mainly in the IR spectra. A degree of translational disorder in the high-temperature modification of barytocalcite and in alstonite appears as a line broadening of the symmetric stretching mode in the Raman spectra.

## Introduction

Seven known minerals containing alkaline-earth cations possess derivative or superstructures based on the calcite or aragonite structures (Table 1).

Two distinct types of ordering occur in the double carbonates. The first type represents an ordering of cation layers, while the second type is based on a superstructure of calcite with an ordering of cations within the layers. The high-temperature barytocalcite, barytocalcite, norsethite, and dolomite belong to the first type, and benstonite and huntite belong to the second type.

Barytocalcite (Dickens and Bowen, 1971) has a monoclinic cell, with space group $P2_1/m$ and $Z = 2$, that is related to the rhombohedral cell of calcite. If one considers Ca and Ba as identical, then a pseudo-cell can be constructed along the monoclinic $\{10\bar{1}\}_{mono} = a_{pc}$; $\{010\}_{mono} = b_{pc}$; and $\{101\}_{mono} = c_{pc}$. The pseudocell matches well with the orthohexagonal cell of calcite. The barytocalcite cell possesses alternating layers of Ca and Ba ions and two non-equivalent carbonate ions, one associated with the Ba ion and one with the Ca ion. The carbonate groups are non-planar and rotated 30° about "3-fold axis" with respect to the calcite carbonate groups. In addition, the carbonate group related to the calcium layer is tilted by 20° with respect to (101). Perpendicular to the layering, barytocalcite possesses a three-layer repeat similar to calcite, but because of the 30° rotation of the carbonate groups, the structure in this respect is similar to aragonite.

Prior to the structural determination of Dickens and Bowen (1971), Alm (1960) had investigated the structure and determined the space group to be $P2_1$. A second-harmonic generation test performed on a specimen verified the centrosymmetric cell and supports Dickens and Bowen's assignment of space group $P2_1/m$.

Norsethite (Lippmann, 1973) has a cell (space group $R32$) similar to dolomite, with alternating $Mg$–$CO_3$–$Ba$–$CO_3$ layers. In norsethite, however, the planar carbonate groups are rotated by 17.5° about the "3-fold axis" with respect to calcite, and the carbonate ions follow a fundamentally different stacking pattern than in dolomite. The carbonate groups in norsethite are related by two fold axes, while in dolomite they are related by a center of symmetry.

The second type of ordering includes ordered cation sites within the cation layers. Of the two examples studied, only the structure of huntite is known in detail (Graf and Bradley, 1962). Huntite is related to calcite by $a_{hex} = 9.505 = 2 \times 4.752$; $c_{hex} = 7.821 = 15.642/2$. The relationship to calcite arises from the ordering of the cations on the expanded cation layer (Fig. 1). Two crystallographically distinct carbonate groups are present—one in the basal plane of the cell and three symmetry-related $CO_3^{2-}$ canted to the basal plane.

No detailed structural data are available for benstonite, which possesses a superstructure of calcite, or for alstonite, an aragonite-related, polymorphic