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The Structures of Synthetic Paracelsian Analogs, $SrGa_2Si_2O_8$ and $SrGa_2Ge_2O_8$

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Abstract

The crystal structures of two synthetic paracelsian analogs, $SrGa_2Si_2O_8$ (SGSP)[2] and $SrGa_2Ge_2O_8$ (SGGP), have been refined by conventional methods. These compounds are pseudo-orthorhombic; completely ordered T^{3+}, T^{4+} distributions in their respective tetrahedral frameworks result in $P2_1/a$ symmetry for both. Pertinent crystal data are:

	a (Å)	b (Å)	c (Å)	β	R factor
SGSP	9.001	9.484	8.399	90.68°	0.036
SGGP	9.206	9.660	8.583	90.43°	0.050

Mean Sr–O and T–O distances (in Å) are:

	⟨Sr–O⟩	$\langle Ga–O\rangle_{T_1}$	$\langle Ga–O\rangle_{T_2}$	$\langle Si–O\rangle_{T_1}$	$\langle Si–O\rangle_{T_2}$	$\langle Ge–O\rangle_{T_1}$	$\langle Ge–O\rangle_{T_2}$
SGSP	2.626	1.822	1.824	1.627	1.629	—	—
SGGP	2.630	1.823	1.826	—	—	1.746	1.750

These structures are compared in detail with hurlbutite ($CaBe_2P_2O_8$), another paracelsian-type structure, and with danburite ($CaB_2Si_2O_8$) whose T^{3+}, T^{4+} ordering is distinctly different. One-fourth of the T–O–T linkages in danburite are of the type T^{3+}–O–T^{3+} or T^{4+}–O–T^{4+}; three-fourths are of the type T^{3+}–O–T^{4+}. In paracelsian all linkages are of the latter type. Consideration of charges on bridging oxygen atoms in $T_2O_7^{n-}$ groups (as calculated by extended Hückel molecular orbital approximations) indicates that the charges on oxygen atoms involved in T^{3+}–O–T^{3+} linkages are substantially different from those in T^{4+}–O–T^{4+} linkages except for the case T^{3+} = boron. This suggests that in the presence of Si (or Ge) any T^{3+}–O–T^{3+} bonds involving Al or Ga (but not B) will result in a non-uniform charge distribution on the oxygen atoms. This is offered as an explanation for the absence of danburite analogs of ordered $M^{2+}\,T_2^{3+}\,T_2^{4+}\,O_8$ compounds containing Al or Ga which have thus far been observed as only feldspar or paracelsian-type structures.

Introduction

In order to determine the bonding properties of tetrahedral (T) cations which are involved in order-disorder transformations and the polymorphism of feldspars and related framework structures, it is important to obtain precise structural data, not only for naturally occurring minerals but also for their synthetic analogs. It is particularly useful to investigate Ga and Ge analogs of alumino-silicates, as Goldsmith and Laves (1955) recognized in their study of GaGe ⇄ AlSi substitutions in anorthite. Ga and Ge not only have greater X-ray scattering powers than Al and Si, but they are distinctly larger and thus afford new insight into the role of cation size in framework structures. As part of an extensive program to characterize the crystal chemistry of

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[2] The abbreviated symbols are based on the initial letters of the M^{2+}, T^{3+}, and T^{4+} cations and the letter P which symbolizes the paracelsian structure type; by contrast, the feldspar, anorthite, is represented by CASF and celsian by BASF.

$M^{2+}T_2^{2+,3+}T_2^{5+,4+}O_8$ compounds, this paper presents the structures of $SrGa_2Si_2O_8$ (SGSP) and $SrGa_2Ge_2O_8$ (SGGP), which are analogs of paracelsian, $BaAl_2Si_2O_8$ (BASP).

Paracelsian is pseudo-orthorhombic, and Smith (1953) determined its average structure, refining it in space group *Pnam*. However, on the basis of optical observations he realized that paracelsian is monoclinic and that the true space group might be $P2_1/a$ and that an ordered distribution of Al and Si might account for the slight deviation from orthorhombic symmetry. Bakakin and Belov (1960) showed that Al and Si were indeed ordered, as in anorthite, and that the space group is $P2_1/a$. They also found (1959) that hurlbutite, $CaBe_2P_2O_8$, is isostructural with paracelsian and that danburite, $CaB_2Si_2O_8$, although topologically similar, has a distinctly different ordering scheme in which B_2O_7 and Si_2O_7 groups alternate in the tetrahedral framework. Recent refinements of paracelsian (Craig, Louisnathan, and Gibbs, 1973), hurlbutite (Lindbloom, Gibbs, and Ribbe, 1974), and danburite (Phillips, Gibbs, and Ribbe, 1974) provide the basic data for a comparison of paracelsian-like structures. When combined with refinements of slawsonite (SASP—Griffen, personal communication), $SrAl_2Ge_2O_8$ (SAGP—Kroll and Phillips, in preparation), and SGSP and SGGP (this paper), a good understanding of this group of compounds should emerge.

Experimental Methods

Sample Preparation

Crystals of both SGSP and SGGP were prepared in the following manner. First, a fine-grained material was produced by solid-state reaction of a stoichiometric mixture of $SrCO_3$, Ga_2O_3, and SiO_2 (or GeO_2). The reactant products were then crushed and sealed in a platinum capsule. Starting from a temperature 10–20°C above the melting points, the samples were individually cooled at a constant rate of several degrees per hour over a range of 125°C. This procedure yielded grains suitable for single crystal work.[3] The crystal of SGSP selected for study was ground to a sphere of diameter 0.185 ± 0.010 mm. For SGGP a crystal (0.09 × 0.10 × 0.16 mm) with well-developed faces was chosen. Precession photographs of both crystals confirmed the $P2_1/a$ space group.

TABLE 1. Lattice Parameters*

	SGSP	SGGP
a	9.0009(9)Å	9.2056(7)Å
b	9.4840(8)	9.6602(6)
c	8.3987(7)	8.5834(6)
β	90.682(7)°	90.432(5)°
V	716.90(7)Å³	763.28(6)Å³

* The estimated standard errors are given in parentheses and refer to the last decimal place.

Lattice Parameter Determination

Unit cell parameters (Table 1) were determined on the same samples from which the single crystals were chosen. Powder photographs were taken by the Guinier-Jagodzinski technique using monochromatized Cu$K\alpha_1$ radiation (λ = 1.54051 Å) and a 99.999 percent silicon metal standard which was tested against the Parrish (1960) silicon and found to have a statistically identical cell dimension. After correcting for systematic errors, 59 lines for SGSP and 46 lines for SGGP could be indexed unambiguously. The lattice parameters were refined using the program LCLSQ (Burnham, 1962).

Data Collection and Refinement

Intensity data for the range $\sin\theta/\lambda$ = 0.1 − 0.5 were collected from both SGSP and SGGP on a Picker automated four-circle diffractometer with a scintillation counter employing Nb-filtered Mo$K\alpha$ radiation. All reflections were measured using a θ-2θ scan at a speed of 1°2θ/min. and a scan width of 2.0°2θ + $\Delta 2\theta$, where $\Delta 2\theta$ is the calculated $\alpha_1 - \alpha_2$ peak separation. Background counts of 40 sec were taken at the beginning and end of each scan. A program written by C. T. Prewitt was used to correct the intensity data for background, Lorentz-polarization effects, and absorption, and to convert to $|F_{obs}|$. The linear absorption coefficients of 160.2 cm^{-1} for SGSP and 228.9 cm^{-1} for SGGP demonstrate the high absorption of Mo$K\alpha$ radiation by Sr, Ga, and Ge. Reflections of the type $|F_{obs}|$ less than four times the standard deviation in $|F_{obs}|$ as determined by counting statistics were considered to be unobserved and were not used in the refinements. Exclusion of these reflections left 1706 and 1723 nonequivalent structural amplitudes for SGSP and SGGP, respectively. A listing of $|F_{obs}|$ and F_{calc} values may be obtained from the authors.

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[3] A more detailed description of the synthesis of paracelsian-type compounds will be presented elsewhere (Pentinghaus, in preparation).

TABLE 2. Site Occupancies Obtained for SGSP Using Two Refinement Programs, MS-FLS and RFINE

	MS-FLS		RFINE	
Site	Ga	Si	Ga	Si
$T_1$0	0.996(6)	0.004(6)	0.995(6)	0.005(6)
T_1m	0.016(5)	0.984(5)	0.019(10)	0.981(10)
$T_2$0	-0.003(5)	1.003(5)	-0.002(6)	1.002(6)
T_2m	0.991(8)	0.009(8)	0.988(5)	0.012(5)

Starting coordinates were taken from a recent refinement of hurlbutite, $CaBe_2P_2O_8$ (Lindbloom *et al*, 1974), with Ga assigned to the Be sites and Si (or Ge) to the P sites. Atomic scattering factors for neutral atoms were taken from Doyle and Turner (1968), and anomalous dispersion corrections were made using coefficients from Cromer (1965). Dr. L. W. Finger's program RFINE was used throughout, although in the latter stages of refinement a least-squares program (MS-FLS) written by D. Stöckelmann was also employed. This program permits the use of double precision (on IBM systems) in the summation of derivatives used to form the normal equations matrix and in the inversion of the matrix itself.

After initial convergence was obtained using unit weights and isotropic temperature factors, the data were corrected for extinction effects using an angular independent approximation described by Stout and Jensen (1968, p. 409). The data were then weighted according to a scheme: $w = a_0 + a_1|F_{obs}| + a_2|F_{obs}|^2 + \ldots + a_i|F_{obs}|^i$, where the coefficients $a_0, a_1, \ldots, a_i$ are chosen in such a way that w has a minimum value of 1.0 and the variation of $w|\Delta F|^2$ with $|F_{obs}|$ is minimized as suggested by Cruickshank (1965).

The final refinements using isotropic temperature factors yielded weighted and unweighted R values of 0.045 and 0.044 for SGSP and 0.070 and 0.062 for SGGP. With the introduction of anisotropic temperature factors the weighted and unweighted R factors dropped to 0.037 and 0.036 for SGSP and 0.059 and 0.050 for SGGP. At this stage the occupancies of the tetrahedral (T) sites were included as variables along with the atomic coordinates and anisotropic temperature factors. The total occupancy of each T site was constrained at 1.0 and the Ga:Si (or Ga:Ge) ratio of 1:1 was maintained. The occupancies obtained for SGSP using both programs (see Table 2) are nearly identical and indicate that ordering is essentially complete. The occupancies obtained for SGGP have errors about 50 times greater than those of SGSP and therefore were not considered meaningful. This can be attributed mainly to the similar scattering powers of Ga and Ge, although a reasonable site refinement has been obtained in one instance (an ordered synthetic feldspar, $BaGa_2Ge_2O_8$; Kroll, Phillips, and Pentinghaus, in preparation).

The positional parameters and anisotropic temperature factors quoted in Tables 3 and 4 are taken from the final anisotropic refinements assum-

TABLE 3. Atomic Coordinates and Isotropic Temperature Factors (B)*

	SGSP				SGGP			
Atom	x	y	z	$B(Å^2)$	x	y	z	$B(Å^2)$
M (Sr)	0.8893(1)	0.4131(1)	0.2515(1)	0.68(1)	0.8857(1)	0.4125(1)	0.2499(1)	0.71(2)
T_1O (Ga)	.2284(1)	.9257(1)	.9302(1)	.50(2)	.2359(1)	.9242(1)	.9329(1)	.49(2)
T_1m	.2434(2)	.9185(1)	.5596(2)	.46(4)	.2425(1)	.9206(1)	.5622(1)	.44(2)
T_2O	.0611(2)	.2017(1)	.9463(2)	.39(4)	.0565(1)	.1992(1)	.9408(1)	.40(2)
T_2m (Ga)	.0530(1)	.1910(1)	.5732(1)	.45(2)	.0529(1)	.1945(1)	.5685(1)	.43(2)
O_1O	.1930(4)	.0980(4)	.0150(5)	.64(6)	.1926(7)	.0911(7)	.0179(8)	.78(11)
O_1m	.1899(5)	.0692(4)	.4894(5)	.76(7)	.1905(7)	.0784(7)	.4833(8)	.71(11)
O_2O	.1188(5)	.3651(4)	.9397(5)	.73(7)	.1162(7)	.3719(7)	.9340(8)	.59(11)
O_2m	.1230(5)	.3718(4)	.5594(5)	.73(7)	.1182(8)	.3729(7)	.5658(8)	.81(12)
O_3O	.9268(4)	.1961(4)	.0734(5)	.70(6)	.9134(7)	.1970(7)	.0737(8)	.70(11)
O_3m	.8930(4)	.1941(4)	.4365(5)	.73(6)	.9007(7)	.1972(7)	.4315(8)	.70(11)
O_4	.0061(5)	.1449(4)	.7742(5)	.91(7)	.0017(9)	.1363(8)	.7605(8)	1.01(12)
O_5	.3184(4)	.9256(4)	.7367(5)	.73(6)	.3282(7)	.9250(8)	.7450(8)	1.04(12)

* The estimated standard errors are given in parentheses and refer to the last decimal place.

TABLE 4. Anisotropic Temperature Factors (× 10^4)

	SGSP						SGGP					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M	29(1)*	15(1)	21(1)	1(1)	-1(1)	-1(1)	33(1)	15(1)	18(1)	1(1)	0(1)	0(1)
T_1O	17(1)	13(1)	17(1)	0(1)	-1(1)	-2(1)	20(1)	13(1)	11(1)	1(1)	0(1)	-1(1)
T_1m	15(1)	12(1)	15(1)	1(1)	1(1)	0(1)	18(1)	11(1)	10(1)	2(1)	0(1)	0(1)
T_2O	13(1)	11(1)	13(1)	-2(1)	0(1)	-2(1)	19(1)	9(1)	9(1)	0(1)	0(1)	0(1)
T_2m	19(1)	10(1)	14(1)	0(1)	0(1)	2(1)	20(1)	10(1)	10(1)	1(1)	1(1)	0(1)
O_1O	24(4)	12(3)	27(5)	4(3)	-5(4)	-3(3)	23(6)	15(6)	29(8)	5(5)	-6(6)	-2(6)
O_1m	31(4)	13(4)	30(5)	6(3)	4(4)	5(3)	34(7)	9(6)	24(8)	12(5)	4(6)	7(6)
O_2O	30(4)	12(3)	31(5)	-9(3)	-10(4)	5(3)	27(7)	4(6)	28(8)	-5(5)	-5(6)	7(5)
O_2m	26(5)	15(4)	33(5)	-12(3)	9(4)	1(3)	38(8)	17(7)	20(8)	-5(5)	9(6)	2(6)
O_3O	13(4)	24(3)	26(5)	-4(3)	8(3)	-9(3)	11(6)	21(7)	32(8)	-4(5)	1(5)	-7(6)
O_3m	20(4)	18(3)	28(5)	-4(3)	-3(4)	7(3)	22(6)	17(6)	25(8)	-13(5)	-10(6)	7(6)
O_4	48(5)	25(4)	18(5)	-15(4)	0(4)	-1(4)	57(9)	32(7)	10(7)	-21(6)	0(6)	2(6)
O_5	24(4)	33(4)	13(4)	-5(3)	6(3)	0(3)	26(7)	48(8)	21(8)	-2(6)	-3(6)	12(7)

* The estimated standard errors are given in parentheses and refer to the last digit.

TABLE 5. Interatomic Distances and Angles*

T-O distances (Å)

	SGSP	SGGP
T_1O-O_1O	1.812	1.815
O_2O	1.839	1.842
O_3O	1.813	1.806
O_5	1.824	1.829
Mean	1.822	1.823
T_1m-O_1m	1.617	1.734
O_2m	1.634	1.756
O_3m	1.627	1.742
O_5	1.629	1.752
Mean	1.627	1.746
T_1O-O_1O	1.641	1.757
O_2O	1.636	1.758
O_3O	1.623	1.749
O_4	1.615	1.734
Mean	1.629	1.750
T_2m-O_1m	1.835	1.847
O_2m	1.831	1.826
O_3m	1.832	1.823
O_4	1.799	1.807
Mean	1.824	1.826

O-O distances (Å) and O-T-O angles (°)

	SGSP	SGGP	SGSP	SGGP
O_1O-O_2O	2.807	2.783	100.5	99.1
O_3O	3.079	3.050	116.2	114.8
O_5	3.078	3.109	115.6	117.1
O_2O-O_3O	3.036	3.052	112.5	113.6
O_5	2.829	2.846	101.1	101.6
O_3O-O_5	2.971	2.968	109.5	109.5
O_1m-O_2m	2.544	2.689	103.6	100.8
O_3m	2.681	2.887	111.5	112.3
O_5	2.730	2.967	114.5	116.7
O_2m-O_3m	2.724	2.932	113.3	113.9
O_5	2.599	2.763	105.6	103.9
O_3m-O_5	2.639	2.842	108.3	108.9
O_1O-O_2O	2.693	2.892	110.6	110.7
O_3O	2.622	2.810	106.9	106.6
O_4	2.654	2.846	109.2	109.3
O_2O-O_3O	2.619	2.795	107.0	105.7
O_4	2.700	2.913	112.3	113.1
O_3O-O_4	2.665	2.875	110.8	111.3
O_1m-O_2m	2.992	3.008	109.4	110.0
O_3m	2.953	2.935	107.3	106.2
O_4	3.010	3.009	111.9	110.9
O_2m-O_3m	2.854	2.861	102.4	103.3
O_4	3.006	3.032	111.8	113.2
O_3m-O_4	3.039	3.024	113.7	112.8

T-O-T angles (°)

	SGSP	SGGP
O_1O	122.1	122.3
O_1m	127.9	124.6
O_2O	120.8	118.0
O_2m	123.3	119.9
O_3O	126.1	124.3
O_3m	124.4	123.2
O_4	133.4	129.0
O_5	129.1	125.5
Mean	125.9	123.4

Sr-O distances (Å)

	SGSP	SGGP
$Sr-O_1O$	2.646	2.660
O_1m	2.706	2.703
O_2O	2.646	2.614
O_2m	2.588	2.608
O_3O	2.568	2.587
O_3m	2.594	2.602
O_5	2.635	2.637
Mean	2.626	2.630

*Estimated Standard Errors

	SGSP	SGGP
Sr-O, T-O distances	0.004Å	0.007Å
O-O distances	0.006Å	0.010Å
O-T-O, T-O-T angles	0.2°	0.3°

ing complete order for SGGP and assuming the occupancies given in Table 2 for SGSP. The interatomic distances and angles (Table 5) were obtained from the same refinements using the program ORFFE (Busing, Martin, and Levy, 1964).

The atomic sites are labeled according to a scheme similar to that used for the triclinic alkali feldspars in which the O and *m* sites are related by a pseudo-mirror. The nomenclature is based on that of danburite (Phillips *et al*, 1974) and assumes that the T_2 site ($x = 0.0533$; $y = 0.1924$; $z = -0.0558$) which contains Si in danburite is the T_2O site containing Si in SGSP. The site occupancies then become:

	T_1O	T_1m	T_2O	T_2m
Danburite	B	B	Si	Si
Hurlbutite	Be	P	P	Be
Paracelsian	Al	Si	Si	Al
SGSP	Ga	Si	Si	Ga
SGGP	Ga	Ge	Ge	Ga

Discussion

Pseudo-symmetry

Both the paracelsian and danburite structures can be thought of as sheets of 4- and 8-membered tetrahedral rings parallel to (001) with a regular alternation of T^{3+} and T^{4+} (for hurlbutite, T^{2+} and T^{5+}) cations within each sheet (see Fig. 2, Phillips *et al,* 1974). Every tetrahedron within a sheet points either up or down, and the apical oxygens serve as bridging

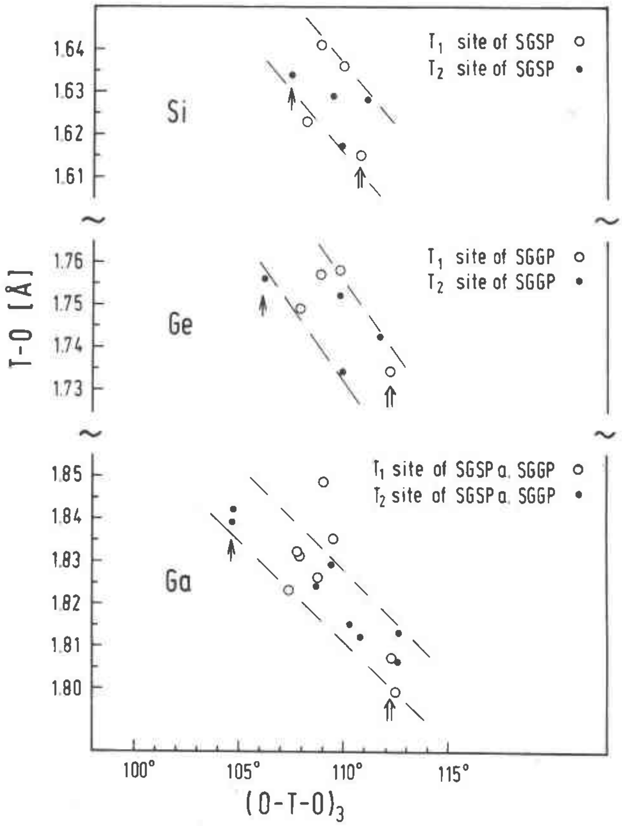

FIG. 1. The mean of the three O–*T*–O angles involved in a given *T*–O bond is plotted against that bond distance for each *T*–O bond distance in SGSP ($SrGa_2Si_2O_8$) and SGGP ($SrGa_2Ge_2O_8$). The vertical arrows point out the bond distances which have the smallest and largest values of $\langle O\text{-}T\text{-}O\rangle_3$, for each of the three *T*–O populations, whereas the dashed lines represent visually estimated boundaries for these populations.

atoms to adjacent sheets, thereby forming a three-dimensional framework of corner-sharing tetrahedra. In danburite (space group *Pnam*) these apical oxygens (O_4 and O_5) lie on mirror planes at $z = 0.25$ and 0.75, forming only linkages of the type Si–O–Si or B–O–B between the successive layers which result in Si_2O_7 and B_2O_7 groups (Bakakin and Belov, 1960a; Phillips *et al,* 1974). In the paracelsians (space group $P2_1/a$) these apical oxygens lie near pseudo-mirrors and form only linkages of the type T^{3+}–O–T^{4+} between the layers, resulting in alternation of T^{3+} and T^{4+} cations throughout the entire framework. Both structures are completely ordered but according to two different schemes (*cf* Fig. 2, Lindbloom *et al,* 1974). The shifts of atomic coordinates from those of danburite are only slight in the paracelsian-type structures, and β angles are very nearly 90°. Hence these structures are "strongly pseudo-orthorhombic" (Smith, 1953).

In SGSP and SGGP, which have β angles of 90.67° and 90.43° respectively, the crystallographic axes can be experimentally identified unequivocally, but in structures where β is close to 90° (as in paracelsian or hurlbutite) it may be difficult or impossible to distinguish the octants. In these cases there is an even chance the reflections may be assigned improper indices; *e.g.*, $h\ k\ l$ may be indexed as $h\ k\ \bar{l}$. Because β is nearly 90°, such an error will not appreciably affect the refinement and indeed cannot be detected by simply examining the resultant structure. However, to obtain the conventional orientation ($\beta > 90°$ in a right-handed system) if $h\ k\ l$ reflections were indexed as $h\ k\ \bar{l}$, it would be necessary to transform the z coordinates to $1 - z$. Using a four-circle diffractometer, Lindbloom *et al* (1974) were able to distinguish the octants in hurlbutite unambiguously, and in order to obtain convergence they found it was necessary to transform the z coordinates of the Bakakin and Belov (1960b) refinement in just this way.

In the space group $P2_1/a$ it is equally valid to choose as the origin the center of symmetry at either (0,0,0) or (0,0,1/2). In practice this is determined by the choice of starting coordinates used in the refine-

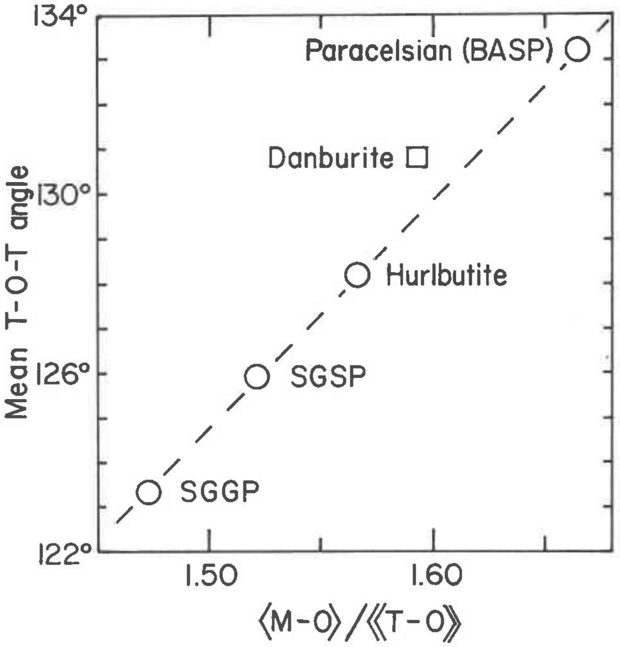

FIG. 2. A plot of the mean *T*–O–*T* angle *vs* the ratio of the mean *M*–O distance (*M* = Ca, Sr, or B) to the grand mean *T*–O distance for each of the structures. Danburite, which has an ordering scheme different from the rest, does not lie along the visually estimated dashed line.

ment, and because SGGP and SGSP were refined from the hurlbutite coordinates (Lindbloom *et al,* 1974), our final coordinates differ from those of Bakakin and Belov (1960a) by ½ + *z*.

One problem arising from the pseudo-symmetry is that if the β and β^* angles are unknowingly reversed in the data-collection procedure, and if the origin is chosen at (0,0,1/2), then the refined structure will have coordinates corresponding to those which would have been obtained had the β angle been properly assigned and the origin chosen at (0,0,0), except that the T^{3+} and T^{4+} sites will appear to be reversed. This explains why Bakakin and Belov (1960 a,b) were led to believe that P^{5+} and Al^{3+} (and Be^{2+} and Si^{4+}) occupy similar positions in the hurlbutite and paracelsian structures. Although this is not a serious matter, it is convenient for purposes of comparison to have the structures oriented in the same way.

Tetrahedral Ordering in Paracelsians and Danburite

As pointed out above, the paracelsians and danburite are ordered differently. Because both structure types are topologically so similar, danburite might be expected to have a regular three-dimensional alternation of T^{3+} and T^{4+} like that observed in paracelsians and in the ordered alkaline-earth feldspars where linkages of the type T^{3+}–O–T^{3+} (and T^{4+}–O–T^{4+}) tend to be avoided. Until now no satisfactory explanation for the occurrence of B–O–B linkages in danburite has been provided.

TABLE 6. Calculated Relative Charges [Q(O)] on Oxygen Atoms in a Variety of *T*–O–*T* Linkages

Linkage	Q(O)	Linkage
B-O-B	-1.25	
	-1.27	B-O-Si
Si-O-Si	-1.28	
Al-O-Al	-1.53	
	-1.40	Al-O-Si
Si-O-Si	-1.28	
Ga-O-Ga	-1.50	
	-1.39	Ga-O-Si
Si-O-Si	-1.28	
Al-O-Al	-1.53	
	-1.41	Al-O-Ge
Ge-O-Ge	-1.30	
Ga-O-Ga	-1.50	
	-1.40	Ga-O-Ge
Ge-O-Ge	-1.30	

As part of an investigation of the bonding in feldspars Gibbs, Louisnathan, Ribbe, and Phillips (1974) performed extended Hückel molecular orbital (EHMO) calculations on idealized $T_2O_7^{n-}$ groups containing different *T* cations. Examining the bond overlap populations (*n*) of the *T*–O bonds to the bridging oxygens they found that n(B–O)—n(Si–O) = 1/3[n(Al–O)—n(Si–O)] (see Fig. 5, Gibbs *et al,* 1974). Using the procedure outlined by Gibbs *et al,* we calculated the charges on the bridging oxygen atoms in a variety of $T_2O_7^{n-}$ linkages; the results are presented in Table 6. It is to be emphasized that although the absolute values of the charges probably have no physical significance, their relative values are meaningful.

It is expected that the tetrahedral cations in a framework structure would be arranged in such a way as to maintain a uniform charge distribution over all oxygen atoms. Inspection of Table 6 shows that if an Al–O–Al (or Ga–O–Ga) linkage were present (along with a corresponding T^{4+}–O–T^{4+} linkage which would necessarily occur in a $T_2^{3+}T_2^{4+}O_8$ framework), the bridging oxygens would have substantially different charges. On the other hand, formation of B–O–B and Si–O–Si linkages (rather than all B–O–Si) produces only small differences in the relative charges on the bridging oxygens. This indicates that although perfect alternation of B^{3+} and Si^{4+} may be slightly favored, there are not the serious restrictions on the formation of B–O–B and Si–O–Si linkages in danburite as there are on both Al–O–Al and Ga–O–Ga linkages in the presence of either Ge or Si.

Distortions of Tetrahedra

As already pointed out, confusion may arise in recognizing the analogous sites in the different paracelsian-type structures because of their orthorhombic pseudo-symmetry. An examination of the distortions of tetrahedra in the different structures indicates that the orientations chosen for SGSP and SGGP are consistent with both those of danburite and hurlbutite. As a quantitative measure of distortion, we define a parameter σ, where

$$\sigma^2 \equiv \sum_{i=1}^{6} [(\mathrm{O}-T-\mathrm{O})_i - \langle \mathrm{O}-T-\mathrm{O} \rangle]^2/6.$$

This is similar to the parameter σ^2_{tet} defined by Robinson, Gibbs, and Ribbe (1971).

Values of σ in Table 7 demonstrate that distortions arise from both structural and chemical factors. The T_1 sites are always more distorted than their corresponding, chemically identical T_2 sites. Regardless of whether a 7- or 9-fold coordination model is chosen for the large cation, the T_1 tetrahedra always have two more shared polyhedral elements than the T_2 tetrahedra, where "shared polyhedral elements" are defined as the sum of all edges and corners common to both the tetrahedron and the alkaline-earth polyhedron (Ribbe, Phillips, and Gibbs, 1974). Ribbe *et al* (1974) observed that in anorthite and in the alkali feldspars, the distortion of tetrahedra varies directly with the number of shared polyhedral elements, therefore the T_1 tetrahedra are expected to be the more distorted, as observed. The T_2 sites in both danburite and the paracelsians have very similar environments, and the same is true for the T_1 sites. This is reflected in the nearly constant ratios of distortions shown in the last line of Table 7, where $\sigma T_2 : \sigma T_1 \equiv 1/2[\sigma(T_2\mathrm{O})/\sigma(T_1m) + \sigma(T_2m)/\sigma T_1\mathrm{O})]$.

For pairs of *structurally* similar sites (T_1O,T_1m or T_2O, T_2m), the T^{3+} tetrahedra are more distorted than the T^{4+} tetrahedra; however, this does not necessarily imply that formal charge is the dominant factor controlling distortion. In fact, because T^{3+} cations are usually larger than T^{4+} cations, and because distortion increases with increasing cation size, it is not yet possible to separate the effects of charge and size on distortion, even though size appears to be the more important. The structure of SAGP (in preparation) may help to resolve this problem, because Al and Ge are similar in size. In addition it appears that the particular combination of T^{3+} and T^{4+} cations may also affect the distortions, although to a lesser degree. For example, respective Ga sites in SGSP are less distorted than in SGGP.

Despite the influence of these chemical factors, the dominant influence on distortion appears to be the environment of the tetrahedra, particularly with respect to the *M* polyhedra whose geometries, within a given structure type (paracelsian or feldspar), are remarkably similar, regardless of whether *M* is Ca, Sr, or Ba. For example, the distortion of tetrahedra which share equal numbers of polyhedral elements (edges plus corners) with *M* polyhedra in anorthite (CASF) and $SrAl_2Si_2O_8$ (SASF) are nearly identical (Chiari, Calleri, Bruno, and Ribbe, 1975, Fig. 4). Likewise, the mean distortion of tetrahedra in the feldspar SGSF (6.41°) (Kroll and Phillips, in preparation) is much more like that of BGSF (6.22°) than that of SGSP (3.91°).

It is interesting to note that the $\sigma T_2 : \sigma T_1$ distortion ratio for danburite is the same as those for the paracelsians, even though the averaging process used to obtain the paracelsian values has the effect of factoring out the influence of chemistry, which is not the case for danburite.

TABLE 7. Distortion Parameters for Tetrahedra in Danburite, Hurlbutite, SGSP, and SGGP

Distortion param.	Danburite	Hurlbutite	SGSP	SGGP
$\sigma(T_1\mathrm{O})$	3.87(B)	4.75(Be)	6.31(Ga)	6.75(Ga)
$\sigma(T_1\mathrm{m})$		3.66(P)	4.00(Si)	5.77(Ge)
$\sigma(T_2\mathrm{O})$	1.96(Si)	1.99(P)	2.01(Si)	2.61(Ge)
$\sigma(T_2\mathrm{m})$		2.36(Be)	3.31(Ga)	3.56(Ga)
Mean	2.92	3.20	3.91	4.62
$\sigma T_2 : \sigma T_1$	0.51	0.52	0.51	0.49

Variation of Bond Angles and Distances

The tetrahedral distortions described above are related to differences in O–*T*–O angles from their respective mean values for individual tetrahedra and generally may be related to polyhedral edge- and corner-sharing. Phillips *et al* (1974) found that $\langle \mathrm{O}-T-\mathrm{O}\rangle_3$, the mean of the three O–*T*–O angles common to a given *T*–O bond, is negatively correlated with the length of that *T*–O bond, especially for B in danburite. That same relationship is recognizable for $\langle \mathrm{O-Ga-O}\rangle_3$ and Ga–O bond lengths in SGSP and SGGP, and much less certainly for $\langle \mathrm{O-Si-O}\rangle_3$ and Si–O and $\langle \mathrm{O-Ge-O}\rangle_3$ and Ge–O (Fig. 1).

The mean *T*–O distances in these paracelsian analogs are consistent with completely ordered *T* atom distributions. The ⟨Ga–O⟩ distances of the individual tetrahedra in the two structures are statistically identical, ranging between 1.822 and 1.826 Å. The ⟨Ge–O⟩ distances in SGGP are 1.746 and 1.750 Å, only several thousandths of an Ångström larger than the ⟨Al–O⟩ distances in paracelsian BASP (Craig *et al,* 1973). The ⟨Si–O⟩ distances in SGSP are 1.627 and 1.629 Å, larger than expected for an ordered framework silicate. Though the grand mean Si–O distance in anorthite is only 1.613 Å, that value is 1.620 for BASP in which Al and Si are ordered. It is probable that the larger ⟨Si–O⟩ value for SGSP is due to inductive effects of the much larger Ga atoms in the four tetrahedra which share corners with each SiO_4 tetrahedron.

The fundamental difference between feldspar- and paracelsian-type structures is the manner in which the double crankshaft chains of 4-membered tetrahedral rings are connected (Smith and Rinaldi, 1962). In feldspars there are two types of 8-membered rings which are elongated normal to one another in adjacent layers, whereas in paracelsians there is only one type of 8-membered ring which is related by a pseudo-mirror to those in adjacent layers (Phillips *et al,* 1974, pp. 81–83 and Fig. 3). The environment of the *M* cation is much more constrained between adjacent 8-membered rings in paracelsians than in feldspars, as evidenced by more regular *M* polyhedra and generally smaller temperature factors for *M* cations in paracelsians. For example, in SGSP and SGGP the Sr–O distances exhibit a range of only 0.13 Å (B_{Sr} = 0.7 Å^2), whereas in SASF (Chiari *et al,* 1975) the range is 0.41 Å (B_{Sr} = 1.1 Å^2). Furthermore, the range of values of the individual *T*–O–*T* angles in the paracelsians is relatively small (up to 17°) compared to that in feldspars (up to 47°). However, in feldspars the mean *T*–O–*T* angle for individual structures shows less sensitivity to chemical variations (⟨*T*–O–*T*⟩ = 133° for BGGF, 136° for anorthite) than in comparable paracelsians. In the paracelsians, because of the relationship of the framework to the *M* site, the mean inter-tetrahedral angles depend strongly on the combination of *M* and *T* cation size. Figure 2 shows the manner in which the inter-tetrahedral angles respond to differences in the relative sizes of the *M* cation and the cations in the tetrahedral framework.

In SGSP and SGGP, as in danburite and hurlbutite, the 2-coordinated O_4 atom is involved in the widest *T*–O–*T* angle. The O_1 and O_3 atoms in the 4-membered rings have intermediate angles, while those at O_2, which occur only in the 8-membered rings, tend to be the smallest.

Further analysis of bond angle and bond length variation in Sr paracelsians awaits the completion of refinements of the structures of slawsonite (SASP—Griffen, personal communication) and SAGP (Kroll and Phillips, in progress).

Note Added in Proof

It has come to our attention that M. Calleri and G. Gazzoni have a paper in press (*Periodico di Mineralogia* XLIV) entitled "Part II. The crystal structure of the paracelsian modification of $SrGa_2Si_2O_8$."

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