Quartz: Variations on a theme

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There will always arise a need for another paper on quartz.
Peter G. Embrey
Quoted in Moore (1975)

ABSTRACT

Quartz as an aristotype has embraced relatively few derivative structures or structures with quartzlike fragments. This may have arisen from inadequate retrieval of such units, especially when the 3-fold screw is parallel to the plane of projection.

A fragment of the quartz aristotype closely resembles the $[AlSi_3O_{10}]$ sheet in prehnite. Differences in tetrahedral cation coordinates do not exceed 1 Å between the two structures.

Cation distributions in the very complex rhombohedral structures of steenstrupine and cerite are locally quartzlike and also have similar differences when referred to quartz. They usually match quartz within 1 Å. Although projections of these structures admit the $\{6 \cdot 3 \cdot 6 \cdot 3\}$ Kagomé net, rhombohedral symmetry forces alternate 3_1- and 3_2-screw operations of the related NbO net. Rhabdophane is an exploded version of quartz. The quartz-related subcells have $a' = 6.0$–7.0 Å, $c' = 3.2$–3.8 Å with stoichiometry of the Kagomé net $X_3\phi_{5.5-6}$, similar to quartz. Packing efficiencies range from 21.3–23.1 Å³ per anion, compared with 19.7 Å³ for quartz.

INTRODUCTION

During the course of developing a hierarchy of structure types for the mineral species, several important arrangements could not be rationalized, prehnite being one of them. That this rock-forming mineral could not be understood in the structural hierarchy was a vexing problem. However, I uncovered a remarkable relationship with quartz which is reported herein.

This contribution is a "left-handed" way of acknowledging the extensive work of Dick Jahns on pegmatites. One item in the genesis of pegmatites is the enormity of the crystals which compose them. In an extensive review on granitic pegmatites, Jahns (1953) discussed anhedral crystals of quartz to "several tons" in weight. Quartz is an essential component of granitic pegmatites, and much is known about its occurrences. Much less is known about its occurrences as a component or fundamental building block in diverse crystal structures, and it is to this occurrence that I address this presentation. As the occurrence of quartzlike units in crystal structures of some other minerals is as yet very incompletely explored, I discuss two interesting problems.

In relating quartz or any other fundamental structure or regions of it to other structures, it is necessary to evolve a connected hierarchy with the familiar aristotype by coloring it and applying graphical enumeration to the colorings. In this sense, a hierarchy of colorings or fragments of the aristotype evolves. If a fragment is found as a component in other structures, then the fragment is defined as a *fundamental building block*: it is a structural region that is topologically and geometrically relatively invariant over several structures. Fundamental building blocks may be intrinsically stable units of crystal structure. They tend to define regions of greatest bond strength and also tend to be the most stable parts of a crystal structure (e.g., relative resistance to disintegration, minor (if any) disorder, well-behaved thermal vibration parameters, etc.). In turn, fundamental building blocks can be combinatorially linked to form as yet undiscovered structures and can assist in selecting which unknown structure types to further study, a process that to this day is usually conducted in a haphazard fashion by crystallographers. Unfortunately, this fundamental aspect of structure study claims but few practitioners. Certain fundamental building blocks are appearing with considerable frequency, for example, the arrangements based on the octahedral cation (M), linked anionic ($\phi = H_2O$, OH^-, F^-, O^{2-}) unit, tetrahedral unit (TO_4) such as the octahedral *trans* edge-chain $M_2^{2+}\phi_2(TO_4)_2$ (Moore et al, 1985; Hawthorne, 1985); the $M_2^{2+}\phi_{4-6}(TO_4)_2$ 7-Å octahedral corner-chain (Moore, 1980); and fragments of the pyroxene structure type (Moore, unpub.).

Typical aristotypes include rocksalt, spinel, corundum, brucite, fluorite, perovskite, hexagonal tungsten bronze, and rutile. Curiously, the important rock-former, quartz, rarely makes an appearance. However, I discovered a simple relationship to the quartz structure in prehnite. The structure was initially reported by Peng et al. (1959) and

studied in further detail by Preisinger (1965) and by Papike and Zoltai (1967).

This study is by no means an exhaustive compilation of the structure genealogy of quartz, as the "language of crystals" is as yet poorly deciphered. The paper concludes with several exceedingly complex structures and their relation in cation distributions to that of quartz. Surely, a large and diverse array of structure types will be found derivative of quartz. The quartz structure type, at present apparently relatively barren of mineralogical children, may prove to rival the simple aristotypes rocksalt, fluorite, brucite, corundum, and rutile and their extensive genealogies.

PASSACAGLIA

The space group $P6_222$ has some interesting equivalences which lend themselves well to a variety of group-subgroup relationships. In this paper, when I employ the generic term "quartz," I mean *high* quartz that can exist in either $P6_222$ or the enantiomorphic $P6_422$ crystals. High quartz is best illustrated with the orthohexagonal representation of that cell. Define the orthohexagonal cell (A, B, C) where $\cos(A\angle B, B\angle C, C\angle A) = 0$. Define the hexagonal metric for $P6_222$ as $(a_1, a_2, c, \gamma = \frac{2}{3}\pi$ radians), or implicit in the hexagonal system as (a, c). Finally, $|A| = |a|, |B| = |a\sqrt{3}|, |C| = |c|$. The 6_2 operation admits additional relationships. For rotations of $\pm 2n\,\pi/6$ radians where n is an integer, the same symmetry-conserving pattern is obtained, translated up $(2n/6)|C|$ with each turn. For $\pm(2n + 1)\pi/6$ radian rotations, the cell (B, A, C) is chosen for superposition on (a, c) and enjoys the same translations along C as the preceding setting.

In this analysis of the prehnite structure, the orthohexagonal cell (A, B, C) for quartz will be used. Prehnite's cell translations will be used throughout in lower case (a, b, c). Note that I shall use prehnite cells as published by the earlier investigators and I will state the appropriate equivalences. The relation $(A \rightarrow b; B \rightarrow c; C \rightarrow a)$ will be most frequently employed and that in diagrams (a, c) will often be used for the conventional quartz parameters when ambiguity does not arise.

The orthohexagonal cell (A, B, C) is clearly centered and contains twice the number of equipoints—in this case 24—as its primitive hexagonal cell $P6_222$. What equipoints, or better yet, equivalences of symmetry operations are compatible with the orthorhombic crystal system? Clearly, these are only the rotations and translations in $P6_222$ that are parallel to the orthorhombic cell translations. The orthorhombic group of maximal symmetry is therefore $C222 \equiv C2_12_12$ and contains eight elements. This orthorhombic group is by no means rare among mineral structures. One wonders how many of these are in fact derivative of the quartz structure type.

The quartz structure has been discussed many times in the literature; Smith (1982) devoted considerable space to the quartz structure types. In this study, I find no reason to depart from the $P6_222$ group of high quartz. Its structure is sketched in Figure 1, along with peripheral designs and
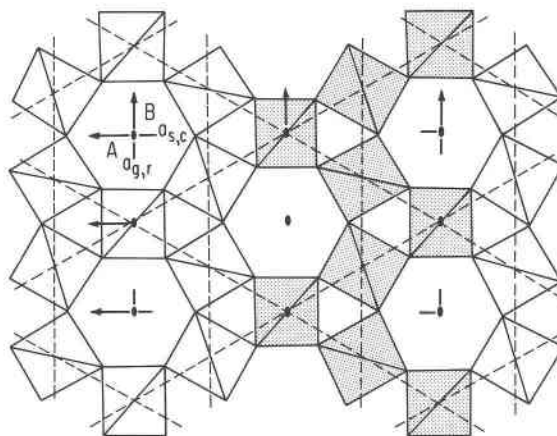

Fig. 1. Orthohexagonal cell of quartz with axes A and B. The $a_{q,r}$ is the axial translation for a_1 of the trigonal cells in quartz and rhabdophane, the $a_{s,c}$ is the axial translation for a_2 of the rhombohedral (hexagonal setting) cells of steenstrupine and cerite. The SiO_4 tetrahedra for quartz are drawn in. The Kagomé net (dashed), the prehnite fragment (stippled), and the 2-fold rotors common to the $P6_222$ and $C222$ space groups are shown.

some symbols. Perhaps the most important is the appearance of a Kagomé $\{6\cdot3\cdot6\cdot3\}$ semiregular net if the cations are connected when the structure is projected down [001]. This net is fundamental in relating the quartz structure type to certain structures of extraordinary complexity which for long have been a source of perplexity, such as steenstrupine, cerite, and rhabdophane—the first two among the most complex structures in the mineral kingdom. I shall demonstrate that these structures are stuffed elaborations of quartzlike cells, and demonstrate that aspects—in this case, cation distributions—of these exceedingly complex structures can be reduced to relative simplicity.

The prehnite species was structurally studied largely independently by three groups. Their efforts focused on structure determination and group-subgroup relationships consequent of order-disorder involving (Si,Al) populated tetrahedra in the fundamental sheets. Here we shall see a different kind of problem, a relation from one structure (e.g., prehnite) to another (e.g., high quartz).

The strategy was to first project prehnite's $[Si_3AlO_{10}]$ tetrahedral fragment down each of the three principal crystallographic axes in $Pncm$. I shall not focus on the problem of order-disorder in its crystal structure and will consider only the holosymmetric group. They reported (here rounded off to the second digit) $a = 4.65$, $b = 5.48$, $c = 18.49$ Å, with two molecules of $Ca_2Al(OH)_2[Si_3AlO_{10}]$ in the cell. The $Ca_2Al(OH)_2$ fraction of the structure shall be ignored in this study. The crucial test is to demonstrate that the $[Si_3AlO_{10}]$ fundamental building block in prehnite and a fragment of the quartz structure closely match metrically. This shall be demonstrated by taking appropriate regions of both structures and seeking their differences in ångström units of displacement. To effect this, I displaced the T(2) position of prehnite at $(0.192, \frac{1}{4}, \frac{1}{4})$ to $(0, 0, 0)$
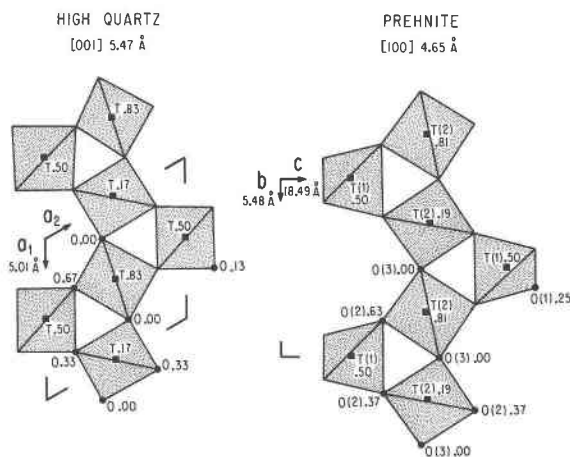
Fig. 2. Sections of high quartz and the [AlSi$_3$O$_{10}$] fraction of prehnite. The axes of projection and the cell translations in the plane are given. Heights shown in fractional coordinates. In quartz, ½ is added to z throughout. The prehnite is drawn from Papike and Zoltai (1967).
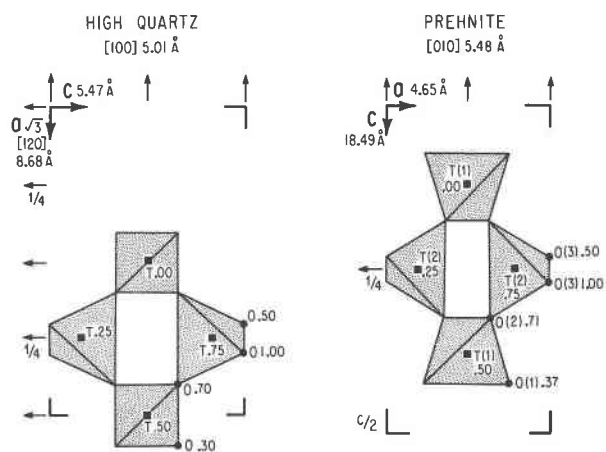

Fig. 3. Sections of high quartz (orthohexagonal unit) and prehnite. See Fig. 2 legend for details. The 2-fold rotors are drawn in. Prehnite from Papike and Zoltai (1967).

and adjusted all other coordinate parameters accordingly; the same was done for the related position of quartz.

A hint of the close structural relationship between high quartz and prehnite can be seen in Figure 2. Here, a fragment of quartz down [001] is compared with prehnite down [100]. Heights and axial translations are given in these diagrams to ease visualizing the structures when referred to the coordinates of Papike and Zoltai (1967). The coordinates for high quartz were obtained from Smith (1982, p. 263) and ½ was added to z to effect a direct comparison. This relationship requires a projection of the prehnite structure down [100], which was not done in the earlier studies. I suspect the relation between a high-quartz fragment and that for the tetrahedral fraction of prehnite was overlooked because projections of prehnite along any of the remaining two orthogonal directions would place the 3$_2$-pseudo–screw axis *in the plane* of the projection, making that operation very difficult to observe!

High quartz and prehnite, when appropriately translated, were each converted to absolute coordinates in ångström units, and the atomic displacements calculated for pairs of similar *cations*. The results are (referred to prehnite in Fig. 2, from top to bottom) ΔT(1) = 0.45 Å, ΔT(2) = 0.00 Å (arbitrarily set as the origin for the calculations), ΔT(1) = 0.45 Å, ΔT(2) = 0.76 Å. All other similar calculations are equivalent to these as they are all related by cell translations. Calculations were also performed for O(1), O(2), and O(3) in prehnite compared with quartz, and as expected their deviations are somewhat greater. Relations between cation populations shall constitute the essence of this study.

Other projections are also featured as these will surely show up in other crystal structures. Figure 3 is a projection down [010] in prehnite which corresponds to [100] in high quartz. Again, axial translations, heights in fractional atom

coordinates, and some of the symmetry operations are shown. In this diagram, some symmetry elements of quartz match those of prehnite. Incidentally, this projection is the one commonly featured in earlier literature, for example in Papike and Zoltai (1967).

Figure 4 is a geometrical fantasia. Selecting a perfect tetrahedron, a corner-linked array on the left with a central 4$_1$-screw has a *maximal* envelope of 5.5 Å (=3$l/\sqrt{2}$), providing the tetrahedral edge l = 2.6 Å (a good O–O average in silicates) is chosen. The directions t_1 and t_2 denote the orientations chosen in Figure 3. The *minimal* envelope would force rotation of the tetrahedra to the limiting configuration on the right, shown as a spoke or "bond" diagram. Here, the envelope is $\sqrt{2}\ l$ or 3.8 Å. The direction of the arrows of the envelope at the bottom of Figure 4 corresponds to c in quartz and a in prehnite, according to Figure 3. We therefore have the progression *max* 5.5 Å > c(q) 5.47 Å > a(p) 4.65 Å > *min* 3.8 Å. On the left is an idealization of Figure 3; a 4$_1$-screw cannot exist in quartz. Further widening of the envelope breaks the linkage at the joined corners. On the right, any further rotation either widens the envelope or leads eventually to overlap of the cations. As a projection, one pair of tetrahedra "share" a common edge.

The final projection of prehnite, Figure 5, is down [001]; this projection figures in the study of Preisinger (1965). Again, comparison with high quartz shows an obvious relationship. Certain equivalent polyhedra have been deliberately omitted to minimize visual clutter. In all these diagrams, high quartz itself is shown, and it is obvious that in any projection other than [001] in quartz, the geometrical relationships would not be immediately spotted. One wonders how many quartz fragments actually exist among structures that have already been determined. This question is important as quartz may loom forth as a significant aristotype for many hitherto unrationalized structure types.
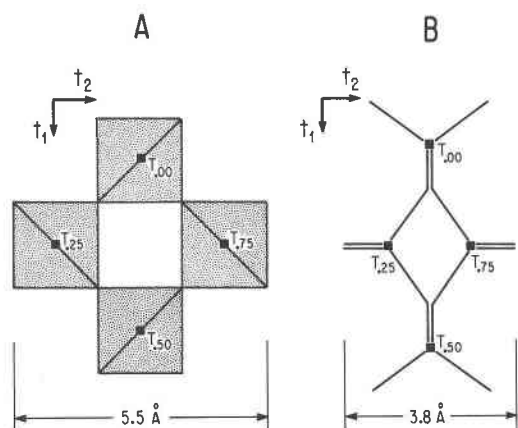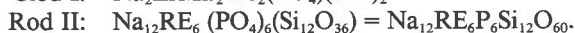
Fig. 4. An idealization of Fig. 3. Perfect tetrahedra are assumed, and the arrangement on the left has a 4_1-pseudo screw axis. For $l = 2.6$ Å, a maximum envelope of 5.5 Å is shown. On the right, rotation of tetrahedra lead to a minimum envelope of 3.8 Å, and a spoke diagram is drawn.
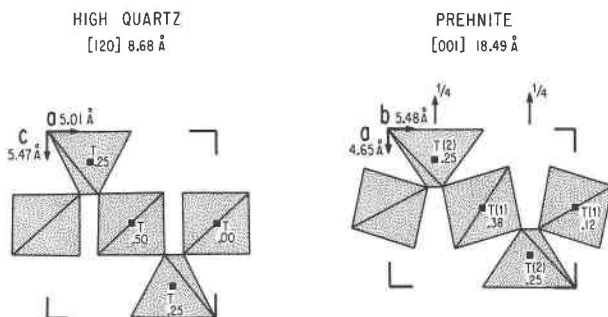

Fig. 5. The remaining principal projections of quartz and prehnite. Some 2-fold rotors for prehnite are shown. See Fig. 2 legend for details. Prehnite from Papike and Zoltai (1967).

FUGUE

Steenstrupine

Steenstrupine possesses an exceedingly complex structure. At least 21 different elements may play some role in the structure, and an end-member formula can be written along with cell criteria: $Na_{14}RE_6^{3+}Mn_2^{2.5+}Fe_2^{3+}Zr(PO_4)(PO_4)_6$ $(Si_6O_{18})_2(OH)_2 \cdot 3H_2O$, space group $R\bar{3}m$, $a = 10.46$, $c = 45.48$ Å, Z = 3; there is no evidence of substructure (Moore and Shen, 1983a). In that study, they stressed a $\{6 \cdot 3 \cdot 6 \cdot 3\}$ Kagomé semiregular design when the cations are projected down the **c** axis and connected in the plane. The structure was described as a *rod* structure as projection of the cations led to close superposition, with twelve cations superimposed in a *c*-axial repeat about the nodes of the Kagomé net. The maximum displacement in the *xy* plane for the cations about a node is 1.4 Å.

Two kinds of rods were discerned. Rod I at $(0\ 0\ z)$, etc., is at the centers of the hexagons, rod II at $(\frac{1}{3}\ \frac{1}{6}\ z)$, etc., is situated at the nodal points of $\{6 \cdot 3 \cdot 6 \cdot 3\}$. The ratio of rod II:rod I in the cell is exactly 3:1, the ratio of nodes to hexagon centers for the Kagomé net. For the end-member formula, the populations are

Rod I: $Na_2ZrMn_2\ Fe_2(PO_4)(OH)_2$
Rod II: $Na_{12}RE_6\ (PO_4)_6(Si_{12}O_{36}) = Na_{12}RE_6P_6Si_{12}O_{60}$.

The water molecules are hydrogen bonded only, and as they do not ligate to metals, they are ignored. Adding rods I and II together gives the end-member formula less the water molecules. Now the oxygens in rod I are also bonded to cations in rod II so they must be associated with rod II: $Na_{12}RE_6P_6Si_{12}O_{66}$. Setting X = cation and ϕ = anion, the composition $3X_{36}\phi_{66}$ obtains, or $18X_6\phi_{11}$.

A quartz-related cell (t_q^s) can be extracted from steenstrupine (t^s). This is $a_q^s = a^s/\sqrt{3}$, $c_q^s = c^s/12$ or $a_q^s = 6.04$, $c_q^s = 3.79$ Å. The quartz-cell stoichiometry is $3XO_2$. For steenstrupine, this would be $3X\phi_{1.83}$ or $X_3\phi_{5.5}$, Z = 36 (the

number of equivalences in $R\bar{3}m$, hexagonal setting). A true isomorphism of the quartz-related cell for rhombohedral cells (or cubic cells down [111]) to quartz itself cannot exist, because such cells impose both right- and left-handed senses to adjacent screw axes. In fact, the simplest such arrangement on a Kagomé net is the NbO net and is featured by Wells (1977, p. 110). This and the two quartz enantiomorphs are the only 4-connected 3D nets based on the Kagomé design. Smith (1979) appropriately called them "helix plus 2D nets." Regions in such nets can still be compared with cation distributions in quartz as only one rod with the same sense of the three-fold screw will be extracted.

The quartzlike volume is $V_q^s = 119.7$ Å³ and the packing efficiency $V_E = 21.8$ Å³. Thus, steenstrupine is an exceedingly dense structure. For example, CaO with the rocksalt structure (ccp), has $V_E = 27.8$ Å³. One reason for this is that steenstrupine is a stuffed version of quartz—better yet, NbO—as the cations remaining in rod I or $Na_2ZrMn_2Fe_2P$ were not taken into account. They provide additional chemical bonds in the structure.

Taking rod II at $(\frac{1}{3}\ \frac{1}{6}\ z)$, the *z* coordinates were extracted and normalized to quartz by subtracting (0.046) from each atomic position for steenstrupine:

Steenstrupine		Quartz ($\frac{1}{12}$ths)	Δ(Å, $c^s = 45.48$)
Na(3)	.000	.000	.00
P	.075	.083	.36
P	.167	.167	.00
Na(3)	.242	.250	.36
Si(2)	.318	.333	.68
Na(2)	.391	.417	.91
RE	.471	.500	1.32
Si(1)	.555	.583	.82
Si(1)	.687	.667	.91
RE	.771	.750	.96
Na(2)	.851	.883	.82
Si(2)	.924	.917	.32

The average is 0.62 Å. As all cations in rod II were listed and as there are nine equivalent rod II in the steen-

strupine cell, the *cation* distributions at least closely mimic the cation distributions in high quartz. Perhaps the puzzle of these rod structures of extraordinary complexity was largely solved through (at that time) serendipitous exploitation of the Kagomé net (see Moore, 1981; Moore and Shen, 1983a, 1983b) and through the equally serendipitous perusal of the Figure 7.16 (p. 263) in Smith (1982).

In this study, all calculations were performed on the cations. The anions were used only for calculating the packing efficiency. As coordination numbers of anions about cations in rod II range from 4 to 9, no sensible relationship could be found between anion packings in quartz and steenstrupine. This is probably one of the more pronounced examples of a structure where cation distributions and connectivities appear to play a more important role than anions in discussing structure systematology. It certainly lends credence to the growing awareness of the importance of cation distribution, as discussed for example by O'Keeffe and Hyde (1985).

As the average formula at the quartz nodes of the Kagomé net is $X_6\phi_{11}$, how is a quartzlike stoichiometry compatible with cations of higher order C.N. [Na(2) = 8; Na(3) = 8; RE = 9; P, Si = 4]? This can be qualitatively seen by noting that extensive edge- and face-sharing occur in this structure, and from the examples that follow.

Cerite

Cerite, another complex structure, was studied by Moore and Shen (1983b) who obtained $R = 0.03$. An end-member formula is $RE_{18}^{3+}Fe_2^{2+}(SiO_4)_{12}(SiO_3OH)_2(OH)_6$, space group $R3c$, $a = 10.78$, $c = 38.06$ Å, $Z = 3$. Although the {6·3·6·3} Kagomé net was mentioned in the study, no diagram was offered. Unfortunately, some confusion was created in earlier studies (Moore, 1981; Moore and Shen, 1983b) by confounding the glaserite structure type based on the {6³} hexagonal net with the {6·3·6·3} Kagomé design. The glaserite family of structures will be cursorily discussed at the end of this paper in light of the tridymite structure.

Two kinds of rods were discerned for cerite. Rod I at (0 0 z), etc., and rod II at (⅓ ⅙ z), etc., follow the same connotations as for steenstrupine, except there are ten successive cations within a rod II repeat along **c**. For the end-member formula, the populations are

Rod I: $Fe_2(SiO_3OH)_2(OH)_6$
Rod II: $RE_{18}(SiO_4)_{12} = RE_{18}Si_{12}O_{48}$.
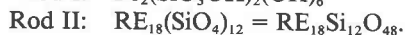
As these formulae require $Z = 3$ and as there are nine equivalent rod II in the cerite cell, each rod II has $RE_6Si_4O_{16}$ or ten cations in the c repeat. Excepting the $(OH)^-$ group bonded only to silicon in rod I, the remaining oxygens also bond to cations in rod II and must be added. $RE_{18}Si_{12}O_{48+12} = RE_{18}Si_{12}O_{60}$, or $3X_{30}\phi_{60}$, or $9X_{10}\phi_{20}$, or $30X_3\phi_6$ the quartz stoichiometry.

A quartz-related cell can be extracted from cerite. That is $a_q^c = a^c/\sqrt{3}$, $c_q^c = c^c/10$ or $a_q^c = 6.22$, $c_q = 3.81$ Å. The quartzlike volume is $V_q^c = 127.6$ Å³ and the packing efficiency $V_E = 21.3$ Å³, very similar to steenstrupine.

Discussion of cation distributions with respect to the high-quartz structure follows. The maximum displacement in the xy plane between the cations about a node is 1.5 Å. The c glide implicit in $R3c$ requires that a succession of only five cations need be examined, the z coordinates of cerite being normalized to quartz by setting $z = 0.000$ for RE(1):

Cerite		Quartz (¹⁄₁₀ths)	Δ(Å, c^c = 38.06)
RE(1)	.000	.000	.00
RE(3)	.108	.100	.30
RE(2)	.198	.200	.08
Si(1)	.296	.300	.15
Si(2)	.403	.400	.11

The average is 0.12 Å. Cerite is particularly interesting since the polyhedra involve extensive edge- and face-sharing between (SiO₄) tetrahedra and (REO₈) $D2d$ dodecahedra of order 8 (polyhedron no. 14 in Britton and Dunitz, 1973).

The final structure discussed in this section is rhabdophane, whose simplicity demonstrates that these related structures are, at least locally, stuffed versions of quartz.

Rhabdophane

Rhabdophane, owing to its relative simplicity and its quartzlike space group, is a key link to these more complicated structures. The structure was initially investigated by Mooney (1950). Its formula is $RE(PO_4)\cdot0$–0.5 H_2O, and the zeolitic water occurs in the relatively open channels along the hexagonal axis. The space group is $P6_222$, $a = 7.05$, $c = 6.44$ Å, $Z = 3$ for synthetic RE = Ce. Connecting the projections of cations down the **c** axis yields the {6·3·6·3} Kagomé net. Rod I at the centers of hexagons defines the disordered zeolitic water molecules. Rod II pierces RE and P. The coordinates of rhabdophane were adjusted by ($z + \frac{1}{2}$). Comparison of the atom coordinates between rhabdophane and high quartz shows that the greatest deviation occurs for the anions. A better match occurs if the z coordinates of rhabdophane are inverted, but this produces $P6_422$, which is left-handed so that the sense of the tetrahedra is reversed in rhabdophane relative to quartz in the same space group.

Rhabdophane				Quartz		
P	½	0	0	Si	½	0	0
RE	½	0	½		··	··	··
0	.446	.147	−.140	0	.394	.197	.167
V_{cell}	277.2 Å³				118.9 Å³		
	3RE(PO₄)				3SiO₂		
			$P6_222$				

It is seen that rhabdophane has 2.33 times the cell volume as quartz and twice the number of anions. The cations in both structures are situated on fixed positions of point symmetry 222. Whereas Si in quartz alternates with a

vacancy along rod II, rhabdophane has P alternating with RE. The (PO_4) tetrahedron and the (REO_8) $D2d$ dodecahedron (polyhedron no. 14) share edges pairwise normal to the direction of the rod, which is a 2-fold rotor implicit in the $\{\bar{4}\}$ point symmetry of the dodecahedron. In addition, four edges, those parallel to the 2-fold rotor and parallel to the c axis (called the lateral edges), are shared with other (REO_8) polyhedra. The (REO_8) polyhedron is the same type that constitutes the coordination polyhedra about the lanthanides in cerite.

Rhabdophane is an exploded version of the quartz structure type. In quartz, successive tetrahedra that twist about the 3_2-screw share corners on the 2-fold axes at $(2x, x, \frac{1}{6})$, etc., so that each oxygen is two-coordinated by silicon. In rhabdophane, this oxygen is split into two equivalences and becomes a general position. The distance between these oxygens in the xy plane is 1.07 Å; their absolute separation is 2.71 Å, which corresponds to a lateral shared edge between two (REO_8) polyhedra.

All atoms in high quartz are constrained by symmetry. Exploiting the 3_2-screw at $(\frac{2}{3}, \frac{1}{3}, z)$ and the 222 point symmetry which fixes the Si atom, the distance down the 2-fold axis in the (SiO_4) tetrahedron can be calculated. It is $c_q/3 = 5.47/3 = 1.82$ Å. This would be the distance between the centers of two perfect (SiO_4) edge-sharing tetrahedra. Infinite edge-sharing tetrahedral chains of composition $\frac{1}{\infty}[SiO_2]$ are known in the structure of "fibrous silica" or "silica-W" (Weiss and Weiss, 1954). Their reported Si–Si separation is 2.58 Å but the Si–O distance is 1.87 Å, considerably greater than Si–O = 1.62 Å in quartz. Weiss and Weiss noted that their value more closely resembles a homopolar bond than an ionic bond, at least for silica-W.

The quartz structure type can admit, at least as a geometrical construction, distorted silica-W type chains where each anion is coordinated by four Si atoms. Such a hypothetical stuffed derivative would be $3T_2O_2$ and for a rigid model, $c = \frac{2}{3} \times 5.47$ Å = 3.64 Å (or 2×1.82 Å, twice the tetrahedral thickness in this direction). It is reminiscent of the minimal distance in Figure 4 which is parallel to t_2 in that figure and to the c axis in quartz. However, tetrahedral edges are not shared in Figure 4, only corners, so these two representations are not equivalent.

A possible explanation for the quartzlike distribution of cations in these structures and the absence of any obvious relation of anions to those of quartz may arise from this lack of equivalence of the anions in the collapsed arrangement in Figure 4. The $t_2 = 3.8$ Å is strikingly similar to the quartzlike cells listed in Table 1. The structures are arranged according to decreasing c'/a' (the primes denoting quartzlike cells) ratios. We note a progressive increase in the a-axial dimensions which seems to reflect increasing average cation size in these structures. Compared with quartz, their c' axes are close to the collapsed model, with c' ranging from 3.2 to 3.8 Å. Their packing efficiencies range from 21.3 to 23.1 Å³, not far removed from 19.7 Å³ for quartz, again demonstrating that, for

Table 1. High quartz and the quartzlike subcells of some lanthanide oxysalts

	High Quartz	Steenstrupine	Cerite	Rhabdophane
a' (Å)	5.00	6.04	6.22	7.05
c' (Å)	5.47	3.79	3.81	3.22
c'/a'	1.09	0.63	0.61	0.46
V_E (Å³)	19.7	21.8	21.3	23.1
Formula	Si_3O_6	$X_3\phi_{5\cdot5}$	$X_3\phi_6$	$X_3\phi_6$

structures with many large cations, they are very efficiently packed indeed.

CODA

Prehnite is evidently a fragmented derivative of the quartz structure, and the tetrahedral cations match within 1 Å in both structures. The very complex structures of steenstrupine and cerite, and the simpler structure of rhabdophane, are based on $\{6\cdot3\cdot6\cdot3\}$ Kagomé nets of cations when projected down the c axes of their hexagonal cells. The distributions of the cations in these structures are usually within 1 Å when compared with quartz along unique rod II. Rod I seems also to accommodate additional cations, and some or all anions in that rod also bond to the cations in rod II. This probably explains the curious ratio of RE:OH = 3:1 reported in the earlier structure studies, as $\{6\cdot3\cdot6\cdot3\}$ has a ratio of rod II (nodes):rod I (hexagonal centers) of exactly 3:1. These complex hexagonal, rhombohedral, or trigonal structures tend to be very brittle, display no good cleavage direction, and are glassy in appearance, again emphasizing their quartzlike character. One could add names like okanoganite, tritomite, melanocerite, and many other minerals usually found in a metamict state and speculate that their structures are based on similar principles.

In this light, the glaserite derivative structures are being re-examined. These structures are based on the $\{6^3\}$ hexagonal net, and there is every indication that glaserite itself can be related to the quartz polymorph tridymite. It is possible that a chemical crystallographic genealogy may arise for these equally complex structures.

Finally, the complex distribution of cations has to be addressed. Were these crystals extensively disordered at the higher temperatures of their crystallization, and ordered at successively lower temperatures leading to cells of considerable complexity? Single-crystal experiments at high temperature would be informative.

ACKNOWLEDGMENTS

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