2810 *Inorg. Chem.* **1982**, *21*, 2810-2816

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Synthesis of the Tube Silicate Litidionite[1-3] and Structural Relationships between It and Some Other Silicates

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Received March 18, 1981

Two good syntheses of the rare tube silicate litidionite, $NaKCuSi_4O_{10}$, are reported. In one a 2:1:1:8 mole ratio mixture of CuO, Na_2CO_3, K_2CO_3, and SiO_2 is sintered and in the other a glass made from a mixture of these reagents in the same mole ratios is devitrified. The structures of the ion in this silicate and those in other known tube silicates are discussed in terms of their relationships to each other and to the ions in other silicates. It is pointed out that many latticework tubes like those which are the parents of these tube silicate ions exist, and it is concluded that silicate ions corresponding to some of them will be found.

While the scroll silicate chrysotile, $Mg_3Si_2O_5(OH)_4$,[4,5] is a familiar item of commerce (it is one of the silicates commonly called asbestos) and has been extensively studied,[6] tube silicates and aluminosilicates are unfamiliar and have been investigated relatively little. They are interesting, however, because tube structures in which the tube bonds are primary bonds have received little attention.

The most studied of the tube silicates and aluminosilicates is the aluminosilicate imogolite, $Al_2(OH)_3SiO_3OH$.[7] It is known to be composed of neutral tubes (the details of the structure of these tubes are, however, not understood).[8] Another aluminosilicate which can be viewed as belonging to the tube group, since it has an aluminosilicate ion that can be considered to be tubular, is bavenite, $Ca_4Be_2Al_2Si_9O_{26}(OH)_2$.[9-11]

Three silicates which have tube ions are litidionite, $NaKCuSi_4O_{10}$,[13] fenaksite, $NaKFeSi_4O_{10}$,[14] and the synthetic species, $Na_2CuSi_4O_{10}$.[15] Others are agrellite, $NaCa_2Si_4O_{10}F$,[16] narsarsukite, $Na_2TiSi_4O_{11}$,[17] miserite, $KCa_5Si_2O_7Si_6O_{15}(OH)F$,[18] and probably canasite, $Na_4K_2Ca_5Si_{12}O_{30}(OH,F)_4$.[19]

As implied, all but $Na_2CuSi_4O_{10}$ have been found naturally.[20-25] So far as is known fenaksite, agrellite, narsarsukite, miserite, and canasite are rare. Litidionite is apparently very rare, the only reported occurrence of it being in the crater of Mount Vesuvius.

Both litidionite[15,26] and narsarsukite[27] have been made in the laboratory by using hydrothermal techniques. Hydrothermal techniques have also been used to make $Na_2CuSi_4O_{10}$.[28-31]

Since compounds containing tube ions are uncommon, these silicates are of interest and good synthetic routes to them are of value. In this paper we report two good new syntheses for litidionite and point out the advantages of each.

In addition we discuss the structure of its silicate ion (Figure 1) and those of other known tube silicates in terms of their relationships to each other and to the ions in other silicates. We also point out the fact that many latticework tubes like those which are the parents of these tube silicate ions exist and conclude that silicate ions corresponding to some of them will be found.

Experimental Section

Synthesis of $NaKCuSi_4O_{10}$. Sintering Method. A mixture of CuO (3.82 g), Na_2CO_3 (2.54 g), K_2CO_3 (3.32 g), and SiO_2 (11.5 g) (a 2:1:1:8 mole ratio mixture) in a platinum crucible was heated in a muffle furnace to 725 °C over ~1 h, held at this temperature for 1 day, heated to 765 °C over ~1 h, and held at this temperature for 6 days. The product, a hard, porous, blue solid with black impurities dispersed throughout it (18.8 g), was carefully broken out of the crucible (17.3 g).

This material was crushed with a diamond mortar to a powder which was almost all <100 mesh. The very small fraction of it which was >100 mesh was rejected. A mixture of some (3.0 g) of the

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(1) The name is sometimes alternatively given as lithidionite. The name litidionite is employed here because it has been used in the most recent edition of Fleischer's glossary[2] and because it is being used by Chemical Abstracts Service.[3]

(2) Fleischer, M. "Glossary of Mineral Species"; Mineralogical Record: Tucson, AZ, 1980.

(3) Cipollo, Dennis, private communication, Chemical Abstracts Service.

(4) Yada, K. *Acta Crystallogr.* **1967**, *23*, 704.

(5) Natural silicates commonly have variable compositions and the formulas given for them are thus of necessity generally idealized.

(6) Zussman, J. In "Asbestos, Properties, Applications, and Hazards"; Michaels, L., Chissick, S. S., Ed.; Wiley: New York, 1979; Vol. I, Chapter 2.

(7) Yoshinaga, N.; Aomine, S. *Soil Sci. Plant Nutr.* (*Tokyo*) **1962**, *8*, 6.

(8) Cradwick, P. D. G.; Farmer, V. C.; Russell, J. D.; Masson, C. R.; Wada, K.; Yoshinaga, N. *Nature* (*London*), *Phys. Sci.* **1972**, *240*, 187.

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(10) Belov, N. V. *Mineral. Sb.* (*Lvov*) **1969**, *23*, 115.

(11) The ions in bavenite can alternatively be viewed as belonging to the band group.[12]

(12) Liebau, F. *Am. Mineral.* **1978**, *63*, 918.

(13) Martin Pozas, J. M.; Rossi, G.; Tazzoli, V. *Am. Mineral.* **1975**, *60*, 471.

(14) Golovachev, V. P.; Drozdov, Yu. N.; Kuz'min, E. A.; Belov, N. V. *Sov. Phys.—Dokl.* (*Engl. Transl.*) **1971**, *15*, 902; *Dokl. Akad. Nauk SSSR* **1970**, *194*, 818.

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(19) Chiragov, M. I.; Mamedov, Kh. S.; Belov, N. V. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* (*Engl. Transl.*) **1969**, *185*, 96; *Dokl. Akad. Nauk SSSR* **1969**, *185*, 672.

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(22) Gittens, J.; Bown, M. G.; Sturman, D. *Can. Mineral.* **1976**, *14*, 120.

(23) Flink, G. *Medd. Groenl.* **1901**, *24*, 154.

(24) Shaller, W. T. *Am. Mineral.* **1950**, *35*, 911.

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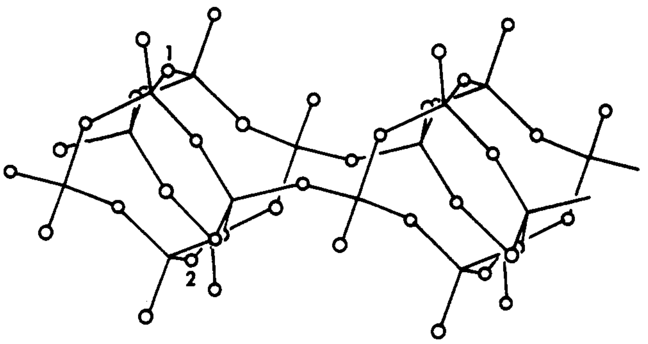

Figure 1. ORTEP drawing of the tube ion in litidionite made with data gathered by Martin Pozas, Rossi, and Tazzoli.[13] The junctions indicate silicon atoms and the open circles oxygen atoms. The O_1–O_2 distance is 4.85 Å.

remaining powder and distilled water buffered to a pH of 5 with potassium acid phthalate and sodium hydroxide (~200 mL) was refluxed with stirring for ~10 min and allowed to stand for ~4 min. The portion which settled out was isolated by decantation. This partially purified material was further purified by a succession of five like decantation steps. The resulting solid was recovered by filtration, washed with water and acetone, and dried (1.8 g). The product, a blue powder in which was interspersed a small amount of a dark powder, gave the expected powder X-ray diffraction lines[13,26] and three impurity lines.

The use of water buffered to a pH of 4 with potassium acid phthalate in the purification procedure led to a material grossly contaminated with decomposition products.

Modified Sintering Method. A mixture of CuO (1.27 g), Na_2CO_3 (0.848 g), K_2CO_3 (1.106 g), SiO_2 (3.85 g), and $Na_2B_4O_7 \cdot 10H_2O$ (0.707 g) (a 2:1:1:8 mole ratio mixture with 10% by weight of borax) was prepared. This was placed in a platinum crucible and heated to 675 °C over ~1 h, held at this temperature for 1 day, heated to 725 °C over ~1 h, held at this temperature for 1 day, heated to 760 °C over ~1 h, and held at this temperature for 5 days. The product, a hard, porous, blue solid with a shiny surface and black particles dispersed throughout (6.67 g), was carefully broken out of the crucible (5.02 g).

This solid was crushed to a powder that was virtually all <100 mesh. The few particles >100 mesh were rejected. A portion (2.00 g) of the rest was purified with a decantation process like that described above (12 cycles). The product, a blue powder in which was interspersed a small amount of a dark powder, gave the expected powder X-ray diffraction lines and one low-intensity impurity line (0.92 g).

Because of the excess of sodium in the reaction mixture, this product could have contained $Na_2CuSi_4O_{10}$. However, the X-ray data did not give evidence for its presence.[15,29,32]

Devitrification Method. A 2:1:1:8 mole ratio mixture of CuO, Na_2CO_3, K_2CO_3, and SiO_2 was heated in a platinum crucible to ~1200 °C. Part of the resulting glass was poured on a steel marver and flattened into a disk (1.31 g). This was placed on a bed of $NaKCuSi_4O_{10}$ (6 mg, <100 mesh), which was supported by a fused silica plate and heated at 765 °C for 12 days. The product, a disk approximately the size of the original disk, was gently pried from the silica plate (1.33 g). It was composed mainly of a mass of blue needlelike crystals oriented approximately perpendicularly to its surfaces. Along with these were a small amount of a gray material, a small silica shard, much of the powdered $NaKCuSi_4O_{10}$, and some blue glass. The gray material was present as a thin layer on the top and sides of the disk while the blue glass occurred between the crystals. A powder of a portion of the disk gave the expected diffraction lines and two impurity lines.

As is to be expected, the time required for substantial devitrification of the glass employed under the general conditions used is variable. In an experiment which was similar to that described except for the use of a thicker disk of glass, 14 days were insufficient but 28 days were sufficient.

Instrumentation. The X-ray data were collected with a General Electric XRD-5 spectrometer using cobalt radiation.

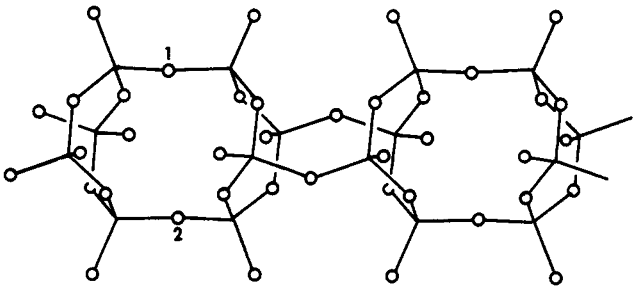

Figure 2. ORTEP drawing of the tube ion in narsarsukite based on data gathered by Peacor and Buerger.[36] The O_1–O_2 distance is 4.32 Å.

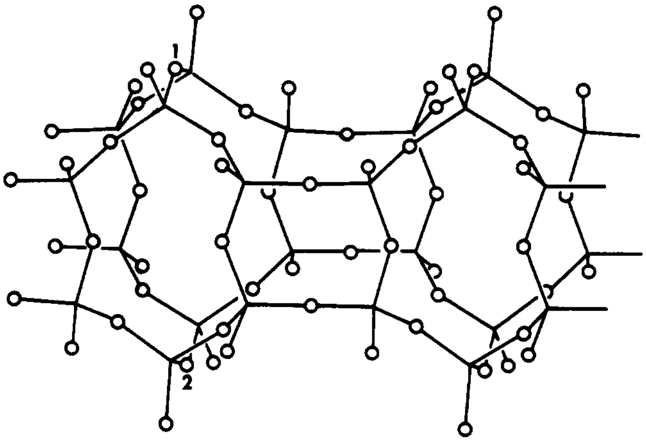

Figure 3. ORTEP drawing of the tube ion in miserite made with data gathered by Scott.[18] The O_1–O_2 distance is 7.53 Å.

Discussion

Synthetic Work. The two sintering routes described for the synthesis of litidionite are parallel to the two routes reported by Pabst for making the chemically and structurally related silicate cuprorivaite (Egyptian blue), $CaCuSi_4O_{10}$.[33,34] The devitrification route is probably parallel to the route by which natural litidionite is formed since natural litidionite occurs in association with a blue glass.[35]

Both the nonborax-sintering route and the devitrification route provide satisfactory methods for making the compound. The borax-sintering route is less satisfactory because it is experimentally more cumbersome and may give a product which is less pure.

Structural Considerations. As already indicated fenaksite, agrellite, $Na_2CuSi_4O_{10}$, narsarsukite, miserite, and probably canasite contain, like lititonite, tube silicate ions.[13–19] The first three contain ions that are the same as that in litidionite while the fourth contains a different type of ion (Figure 2). Still another is found in miserite (Figure 3) and probably also in canasite.

Each of these three types of ions is structurally related to other silicate ions. Thus, as pointed out earlier,[36] the ion in narsarsukite is related to a well-known sheet ion found in, for example, kaolinite, $Al_2Si_2O_5(OH)_4$.[37]

The basic relationship between these two ions is the same as that between their parent latticeworks. This relationship arises as is evident (Figure 4) because the pattern of the latticework tube taken circumferentially from a lengthwise line on its surface is the same as that in a strip of the latticework sheet.[38,39]

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(34) Mazzi, F.; Pabst, A. *Am. Mineral.* **1962**, *47*, 409.

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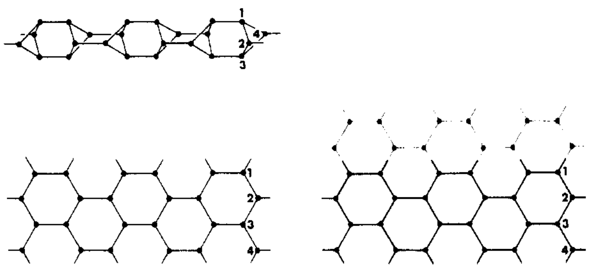

Figure 4. Parent latticework of the narsarsukite tube, this latticework opened along a lengthwise line and flattened, and the parent latticework of the kaolinite sheet with a strip emphasized that is the same as the opened and flattened tube latticework. The filled circles represent pendent units pointing outward in the case of the tube and upward in the case of the latticeworks. Like junctions have like numbers.

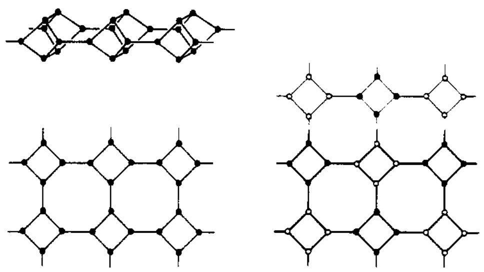

Figure 5. Parent latticework of the litidionite tube, this latticework opened, and the parent latticework of the apophyllite sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units. The filled circles represent pendent units pointing outward or upward and the open circles pendent units pointing downward.

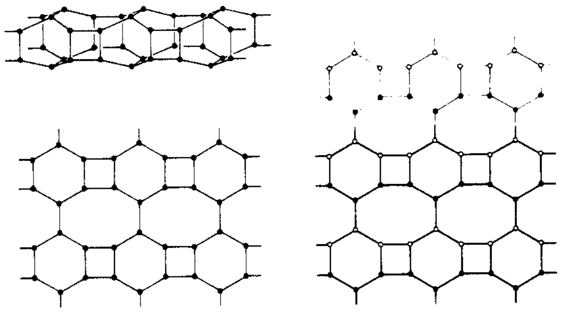

Figure 6. Parent latticework of the miserite tube, this latticework opened, and the parent latticework of the dalyite sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units.

Similarly but not quite so directly, the ion in litidionite is related to a less common ion found in such silicates as apophyllite, $KCa_4Si_8O_{20}F\cdot8H_2O$,[40] and cuprorivaite.[33] Here, again making reference to the parent latticeworks, the arrangement of the latticework tube is like that of a strip of the latticework sheet except that all the pendent units project from one surface (Figure 5). In the same manner the parent latticework of the ion in miserite is related to that of the ion in dalyite, $(K,Na)_2ZrSi_6O_{15}$[41] (Figure 6).[42]

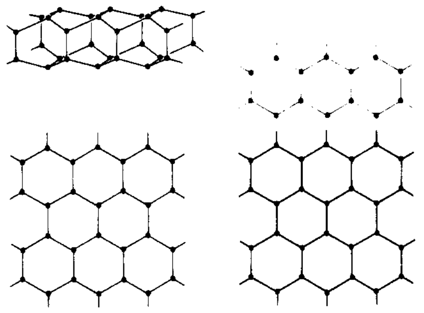

Figure 7. Second latticework tube related to the parent latticework of the kaolinite sheet, this latticework opened, and the kaolinite latticework sheet with a strip emphasized that is the same as the opened-tube latticework.

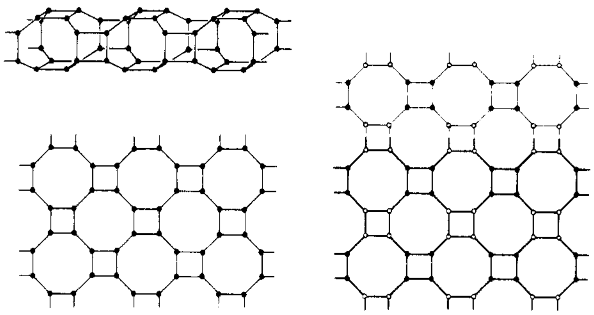

Figure 8. Second latticework tube related to the parent latticework of the apophyllite sheet, this latticework opened, and the apophyllite latticework sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units.

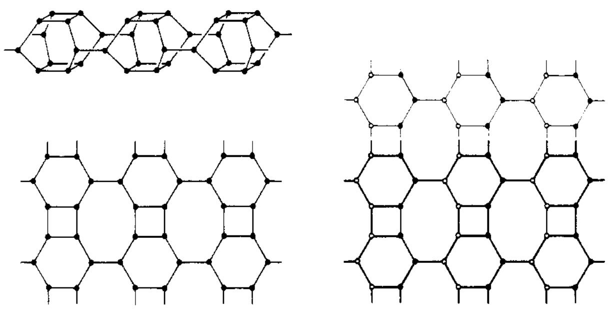

Figure 9. Second latticework tube related to the parent latticework of the dalyite sheet, this latticework opened, and the dalyite latticework sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units.

All three of these latticework tubes are similar in that each is achiral and has a shortest circumferential circuit in which the repeat pattern occurs twice. However, in the first tube the shortest circuit does not incorporate a sequence of in-line links (i.e., links whose counterparts in the corresponding strip are a straight line). In the second and third tubes, in contrast, the shortest circuits do incorporate unbroken in-line sequences of links. Similarly, in the first tube no links in the circuit are parallel to a plane perpendicular to the tube axis while in the second and third tubes links in the circuits are parallel to planes perpendicular to the tube axes.

Additional latticework tubes associated with the kaolinite, apophyllite, and dalyite latticeworks are shown in Figures 7–9 (a variant of the third tube is associated with the dalyite

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(38) For clarity the orientations of the tubes in Figures 2 and 4 are matched.

(39) The latticework tubes which are the true counterparts of the latticework sheets are, of course, those in which the links that are not parallel to the tube axes are curved. Here the discussion is not based on such tubes but rather on the corresponding tubes having appropriately shorter straight links in place of the curved links. The variations in the lengths of the links are not taken into account. This is acceptable because it appears, on the basis of the tubes examined, that often variants of these straight-link tubes have links of equal lengths (for example, a variant of the straight-link narsarsukite latticework tube has links with equal lengths). Further, the silicon–silicon distances in the Si–O–Si system is variable because the Si–O–Si angle is variable.

(40) Taylor, W. H.; Náray-Szabó, St. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1931**, *77*, 146.

(41) Fleet, S. G. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1965**, *121*, 349.

(42) Again for clarity the orientations of the tubes in Figures 1 and 5 and 3 and 6 are matched.

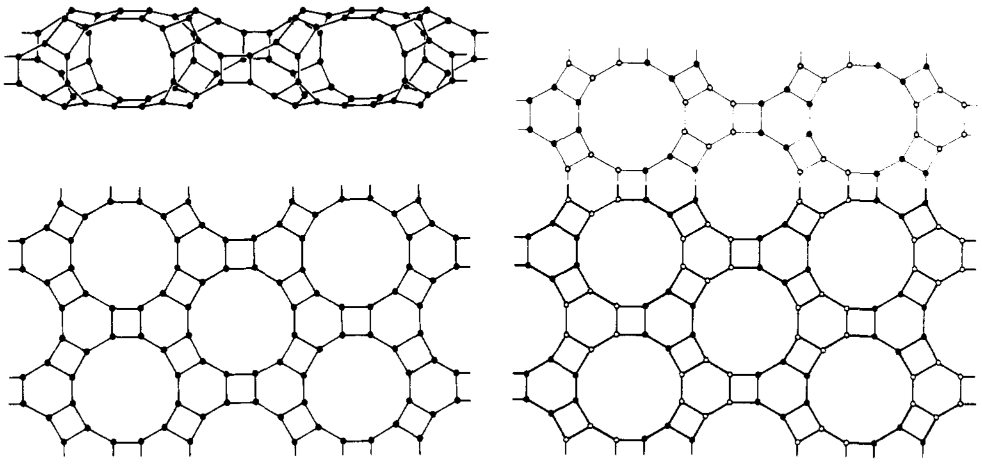

Figure 10. Latticework tube related to the parent latticework of the manganpyrosmalite sheet, this latticework opened, and the manganpyrosmalite latticework sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units.

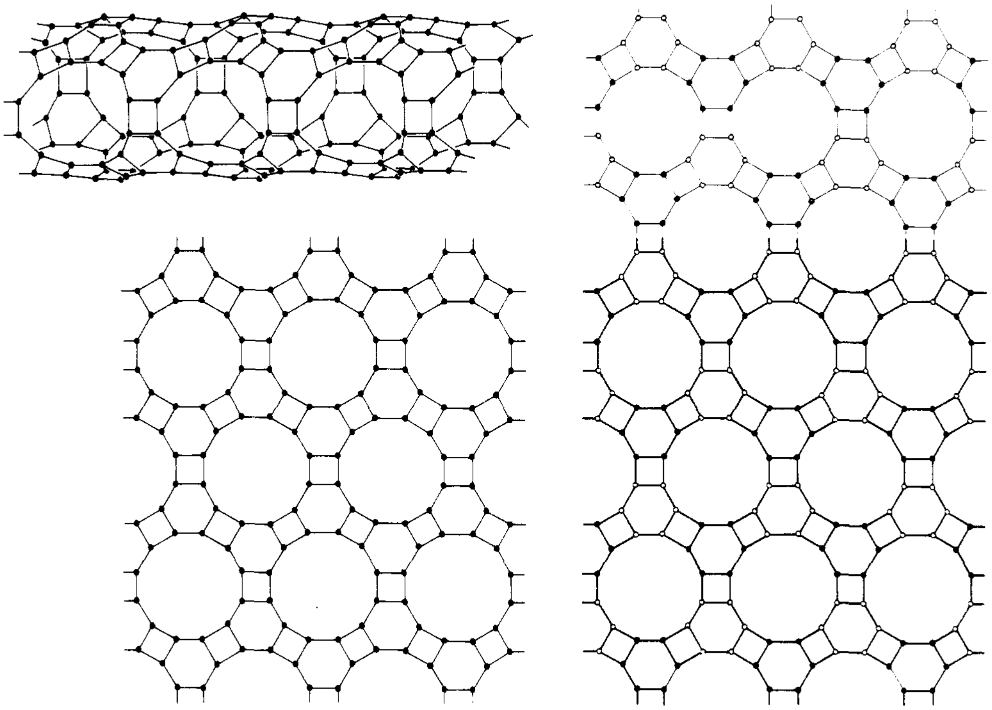

Figure 11. Second latticework tube related to the parent latticework of the manganpyrosmalite sheet, this latticework opened, and the manganpyrosmalite latticework sheet with a strip emphasized that is the same as the opened-tube latticework except for the arrangement of the pendent units.

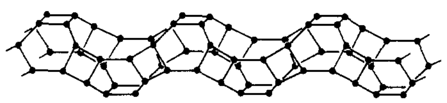

Figure 12. Latticework tube related to the larger of the two latticework tubes associated with the manganpyrosmalite latticework sheet.

Figure 13. Chiral latticework tube related to the apophyllite latticework sheet. A part of a series of links following a generally helical path is emphasized.

latticework when arranged so as to outline squares and regular octagons). Each of these particular latticework tubes, like the first three latticework tubes, is achiral. Further, like the second and third of these tubes, each has a shortest circuit which contains two repeat patterns, incorporates an unbroken in-line sequence of links, and includes links that are parallel to a plane perpendicular to the tube axis.

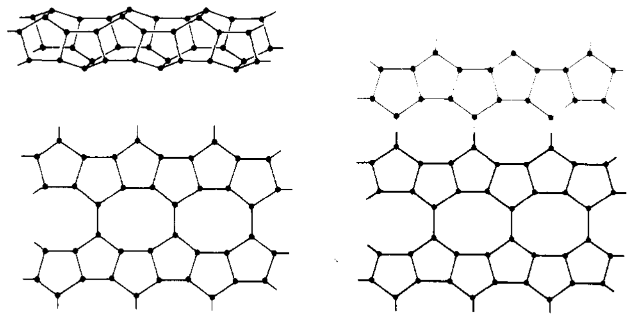

Figure 14. Latticework tube related to a pentagon-octagon latticework, this latticework opened, and the pentagon-octagon latticework with a strip emphasized that is the same as the opened-tube latticework.

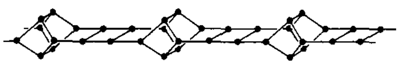

Figure 15. Latticework drum-ladder structure related to the 12_2:4,6,12 latticework tube.

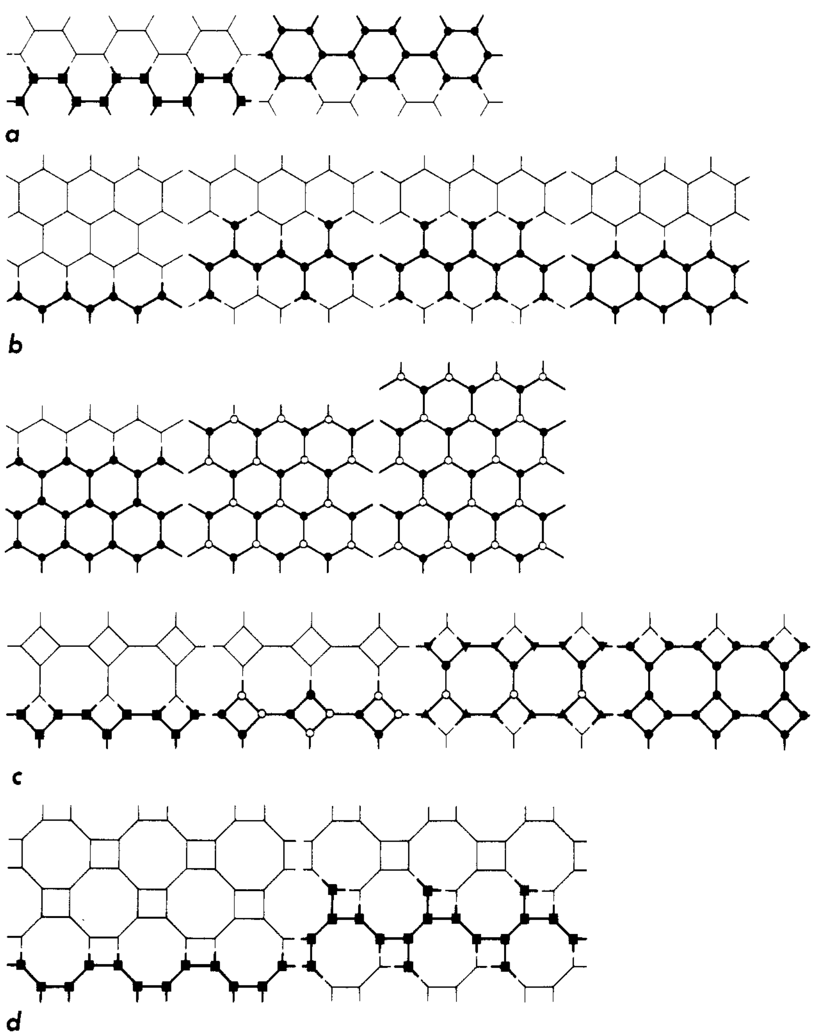

Figure 16. Relationships between known and potential silicate tubes and known silicate linear structures. The frameworks are those of strips corresponding to the tubes. Superimposed on these are the latticeworks of the linear systems. These are altered, as necessary, by minor or significant amounts. The latticework–framework pairs shown are (a) the diopside– and howieite–narsarsukite pairs, (b) the diopside–, aenigmatite–, astrophyllite–, tremolite–, jimthompsonite–, $Ba_5Si_8O_{21}$–, and $Ba_6Si_{10}O_{26}$–8_2:6 pairs, (c) the diopside–, vlasovite–, xonotlite–, and tinaksite–litidionite pairs, and (d) the diopside– and aenigmatite–8_2:4,8 pairs. In those cases where the latticeworks are substantially unaltered, the directions of the pendent units are indicated: short lines, filled circles, and open circles representing respectively units pointing sideways, upward, and downward; and triangle-short line combinations representing pairs of units pointing at an angle. In the remaining cases only the presence of the pendent units is indicated: square-short line combinations representing groups of two or three units.

Two latticework tubes associated with the latticework sheet corresponding to the ion in yet another sheet silicate manganpyrosmalite, $(Mn,Fe)_8Si_6O_{15}(OH,Cl)_{10}$,[43] are shown in Figures 10 and 11.[44] These tubes too are achiral and have shortest circuits of the same nature as those in all but the first tube.

Many additional simple latticework tubes are also associated with the kaolinite, apophyllite, dalyite, and manganpyrosmalite latticework sheets. An example is the tube which is like the larger of the two tubes associated with the manganpyrosmalite sheet except for having a shortest circuit with one repeat (Figure 12). Another is the tube which is like the litidionite latticework tube except for having a shortest circuit with three repeats.

Not surprisingly many of these latticework tubes are chiral. A tube of this type associated with the apophyllite latticework sheet is shown in Figure 13. This tube, as is seen, has a shortest circuit which contains one repeat pattern, does not incorporate an unbroken in-line sequence of links, and does not include links parallel to a plane perpendicular to the tube axis.[45]

Still more latticework tubes similar to those already discussed exist. These are associated with additional latticework sheets.[47] Such a tube is shown in Figure 14.

Since there are so many closely related latticework tubes a simple systematic method for describing them is needed. This need can be met by utilizing descriptors containing the following elements: a c if the tube is chiral, a number giving a number of links in the shortest circuit, a subscript number giving the number of repeats in the circuit, and one or more numbers giving the number of numbers of links in the shortest

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(43) Takéuchi, Y.; Kawada, I.; Irmaziri, S.; Sadanaga, R. *Mineral. J.* **1969**, *5*, 450. Takéuchi, Y. private communication.

(44) As examination shows, the latticework tubes in Figures 10 and 4 and 11 and 7 are close structural analogues.

(45) The kaolinite, apophyllite, dalyite, and manganpyrosmalite parent latticework sheets are, as is apparent, based on three-connected networks. It is of interest to note that the first of these latticeworks is based on the only regular three-connected network and that the second and fourth are based on two of the three semiregular three-connected networks.[46] It is also of interest that the dalyite parent latticework can be derived formally from the kaolinite parent latticework by appropriate insertion of sets of links arranged in U's and the apophyllite parent latticework similarly can be derived from the dalyite parent latticework.

(46) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford: New York, 1975; Chapter 3.

(47) These latticework sheets are also based, as they must be, on three-connected networks.

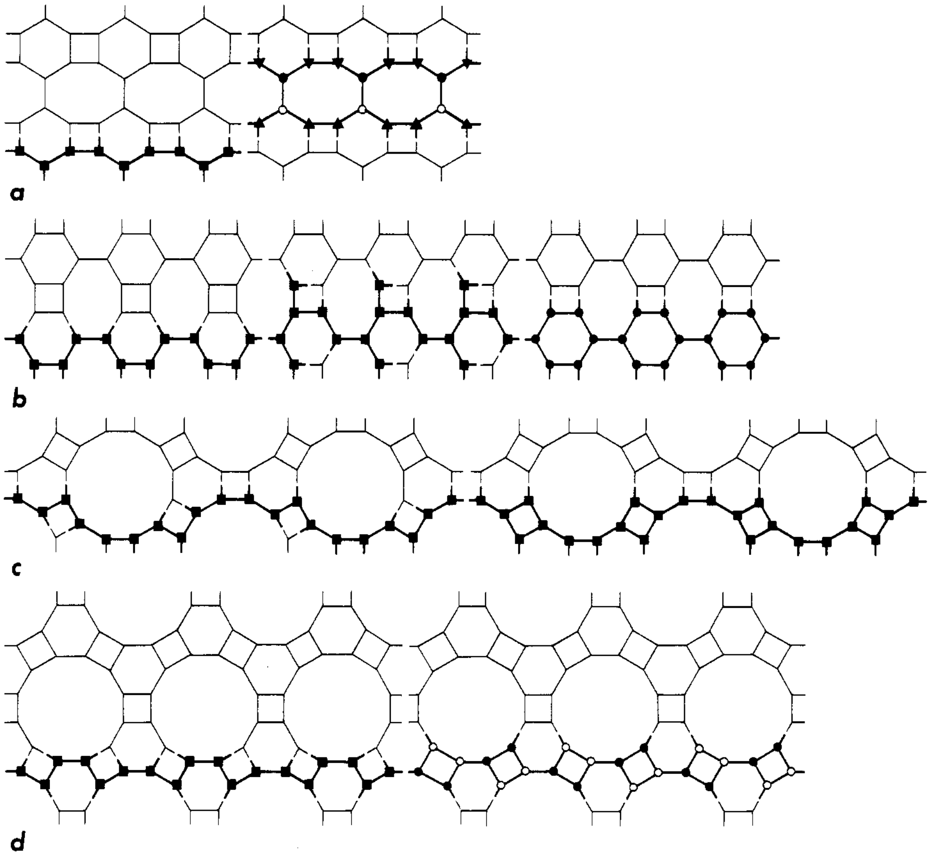

Figure 17. Additional relationships between known and potential silicate tubes and known silicate linear structures. The latticework–framework pairs shown are (a) the diopside– and xonotlite–miserite pairs, (b) the diopside– aenigmatite–, and howieite–6_2:4,6,8 pairs, (c) the diopside– and nordite–12_2:4,6,12 pairs, and (d) the diopside– and vlasovite–20_2:4,6,12 pairs (for economy only half the 12_2:4,6,12 and 20_2:4,6,12 frameworks are shown).

circuit or circuits in the surface of the tube. Thus with the use of this system the litidionite tube is the 6_2:4,8 tube.

In connection with the lattice work tubes discussed, it is interesting to note that (with use of the system just outlined) the 8_2:4,8 tube (Figure 8) and the 10_1:4,6,12 tube (Figure 12) are isomers. It is also interesting to note that half the latticework strip associated with the 12_2:4,6,12 tube (Figure 10) has a drum-ladder counterpart (Figure 15). Obviously this is just one of a family of such latticeworks. So far no silicate based on a latticework of this type nor of the analogous chain-cage type is known.

As might be expected, the known and potential silicate tubes have significant relationships with not just silicate sheets but also with other types of silicate structures as well. One of these is the linear or chain-band type.

Among the silicates that contain chains or bands with which the eight known and the potential silicate tubes discussed first have significant relationships are the following: diopside, $MgCaSi_2O_6$;[48] howieite, $Na(Fe^{2+},Mg,Fe^{3+},Al)_{12}(Si_6O_{17})_2(O,OH)_{10}$;[49] aenigmatite, $Na_2Fe_5TiSi_6O_{20}$;[50] astrophyllite, $(K,Na)_3(Fe,Mn)_7Ti_2Si_8(O,OH)_{31}$;[51] tremolite, $Mg_5Ca_2Si_8O_{22}(OH,F)_2$;[52] jimthompsonite, $(Mg,Fe)_5Si_6O_{16}(OH)_2$;[53] synthetic $Ba_5Si_8O_{21}$;[54] synthetic $Ba_6Si_{10}O_{26}$;[54] vlasovite, $Na_2ZrSi_4O_{11}$;[55] xonotlite, $Ca_6Si_6O_{17}(OH)_2$;[56] tinaksite, $K_2NaCa_2TiSi_7O_{19}(OH)$;[57] nordite, $Na_2(Na,Mn)(Ca,Sr)RE(Zn,Mg,Fe,Mn)Si_6O_{17}$.[58] The nature of some of these relationships is indicated in Figures 16 and 17. Again the relationships are complicated in some cases because of the positioning of the pendent oxygens.[59,60,62]

As is obvious, the known silicate tubes and the potential small to moderate sized silicate tubes have (assuming reasonable bond parameters for the latter) diameters covering a wide range. The lower end of this range is ~4 Å (Figures 1–3).[63]

With past experience in similar situations as a guide, it appears highly likely that silicate tubes of the narsarsukite,

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(48) Warren, B.; Bragg, W. L. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1928**, *69*, 168.

(49) Wenk, H. R. *Am. Mineral.* **1974**, *59*, 86.

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(55) Voronkov, A. A.; Pyatenko, Yu. A. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1962**, *6*, 755; *Kristallografiya* **1961**, *6*, 937.

(56) Mamedov, Kh. S.; Belov, N. V. *Zap. Vses. Mineral. Ova.* **1956**, *85*, 13.

(57) Petrunina, A. A.; Ilyukhin, V. V.; Belov, N. V. *Sov. Phys.—Dokl. (Engl. Transl.)* **1971**, *16*, 338; *Dokl. Akad. Nauk SSSR* **1971**, *198*, 575.

(58) Bakakin, V. V.; Belov, N. V.; Borisov, S. V.; Solovyeva, L. P. *Am. Mineral.* **1970**, *55*, 1167.

(59) Some of these tube-chain and tube-band relationships have been discussed before, e.g., the litidionite–vlasovite,[13] fenaksite–vlasovite,[14] $Na_2CuSi_4O_{10}$–vlasovite,[28] agrellite–vlasovite,[16] miserite–wollastonite (diopside),[18] miserite–xonotlite,[18] canasite–wollastonite (diopside),[19] and canasite–xonotlite[19] relationships (in the case of the miserite–xonotlite relationship the dissimilarities are focused on).

(60) As is clear, a close formal relationship exists between the chain in diopside and the bands in tremolite, jimthompsonite, and the synthetic barium silicates. It is thus interesting to note that the tremolite-type band in nephrite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH,F)_2$, is occasionally replaced by a triple-strand band.[61]

(61) Hutchison, J. L.; Jefferson, D. A.; Mallison, L. G.; Thomas, J. M. *Mater. Res. Bull.* **1976**, *11*, 1557.

(62) A real relationship may exist between the band in howieite and its counterpart sheet since it has been suggested that the band is formed from the sheet by a shearing process.[49]

(63) It should not be assumed, of course, that sizable channels or even any channels will exist in silicates having moderate sized tubes since the tubes may contain ions (as does the tube in miserite) or may not be fully extended (or both).

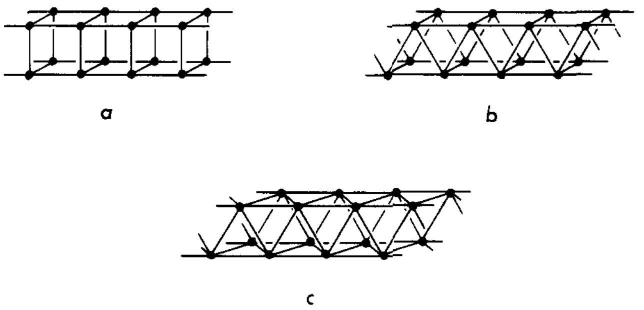

Figure 18. Tubes with a single-link members running lengthwise and circumferentially: (a) a tube with four units at each junction, (b) a tube with five units at each junction, and (c) a tube with six units at each junction.

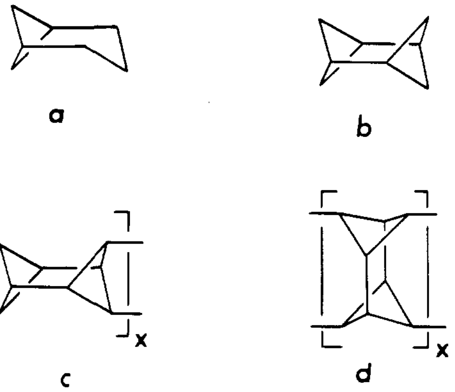

Figure 19. The structures of (a) norpinane, (b) tricyclo[3.1.1.1^{2,4}]-octane, (c) the hypothetical narsarsukite-type polymer, and (d) the hypothetical litidionite-type polymer.

litidionite, and miserite types will be found in silicates other than those in which they are now known. Since the litidionite tube has been found in several silicates and since the relationships between it and several linear silicates are strong, it is particularly likely that this tube will be found in other silicates.

It also appears likely that new types of silicate tubes will be found soon. Among the most likely to be found are those having the 8_2:6, 8_2:4,8, and 6_2:4,6,8 latticework tubes as parents since these latticework tubes are like those which are parents of the litidionite and miserite tubes. The probability of finding the silicate tube whose parent is the 8_2:6 tube is further enhanced because of the close relationships that exist between it and known silicate bands.

As is evident latticework tubes of the types described cannot simultaneously have continuous single-link members running lengthwise and circumferentially. Tubes of this type are, however, found among those having four, five, and six members radiating from a junction (Figure 18).

Finally, it is probable that in some cases organic tubes having carbon or carbon-heteratom frameworks like those discussed can be made. Thus, since norpinane can be made,[64] it seems likely that tricyclo[3.1.1.1^{2,4}]octane can be made and, hence, that narsarsukite-type and perhaps litidionite-type tubes can be made (Figure 19).[65] Such polymeric systems should have very interesting properties.

Acknowledgment. We wish to thank Dr. Kenneth Wynne and Dr. Kerro Knox for helpful discussions. We also gratefully acknowledge support of this work by the Dow-Corning Corp., the B. F. Goodrich Corp., and the Office of Naval Research.

Registry No. Litidionite, 12417-65-1.

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(65) The litidionite-type tube having a carbon framework would be strained to an appreciable extent.

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Theoretical Study on Dinitrogen Complexes. Position of the Third Protonation and the Reduction Mechanism

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Received September 9, 1981

This paper concerns itself with the position of the third protonation of the dinitrogen ligand and its reduction mechanism. It is considered that two kinds of isomers, $NHNH_2$ and N_2H_3 complexes, give N_2H_4 and NH_3 as reduction products, respectively. Though the N–N bond is weakened by the third protonation at the terminal nitrogen atom of the N_2H_2 complex, it does not lead to cleavage of the bond. On the other hand, it is calculated that $NHNH_2$ is released from the $NHNH_2$ complex by attack at the nitrogen atom attached to Cr. $NHNH_2^+$ decomposes to give NHNH and H^+, and then, two molecules of NHNH react to form N_2 and N_2H_4.

It has been a few years since the N_2 ligand in dinitrogen complexes of Mo and W was reduced to NH_3 and N_2H_4.[1] Complexes attached by one or two protons are considered to be intermediates of the reduction.[2] The features of protonation of the dinitrogen ligand are (1) the weakening of the N–N bond and (2) the reinforcement of the M–N one.[3] This trend was discussed on the basis of results of ab initio calculations of model complexes and the orbital-mixing rule.[4] In

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