THE STUFFED DERIVATIVES OF THE SILICA STRUCTURES

M. J. Buerger,

Massachusetts Institute of Technology, Cambridge, Massachusetts.

Abstract

A *derivative structure* is one derived from a simpler *basic structure* by generalization. This can occur either by distortion of the simpler structure, or by substitutions for its atoms by others of different chemical species. When the substitute atoms have smaller valences than those for which they substitute, this must be compensated by addition of other atoms which can be described as stuffing atoms. Only such atoms as can be accommodated in the available voids of the structure are acceptable stuffing atoms.

This paper treats of the stuffed derivatives of quartz, tridymite, and cristobalite.

Quartz has voids of limited sizes. These are too small for K or Na, but large enough for Li, Be, or B. Eucryptite, $LiAlSiO_4$, and $LiAlSi_2O_6$ are known derivatives of quartz.

Both tridymite and cristobalite have voids large enough to house Na, K, or Ca. The best known derivatives of tridymite are nepheline, $KNa_3Al_4Si_4O_{16}$, and the several forms of $KAlSiO_4$. The compounds $K_2MgSi_3O_8$, $K_2FeSi_3O_8$, and possibly $K_2Mg_5Si_{12}O_{10}$, appear to be derivatives of tridymite in which Mg substitutes for Si.

The cristobalite derivatives include carnegieite, $NaAlSiO_4$, and Na_2CaSiO_4. It seems likely that Na_2MgSiO_4 and Na_2BeSiO_4 may also assume tridymite-like structures.

Non-silicate derivatives of silica are briefly discussed.

Background

To appreciate some of the features of the stuffed derivatives of the silica structures it is necessary to understand the technical crystallographic meaning of "derivative," and some of the characteristics of the structures of the various forms of pure silica.

Derivative Structures. There exists a class of crystal structures which are derived from others by generalization. Such a derived structure is known as a *derivative structure*,[1] and it is derived by generalization of a *basic structure.* The symmetry of the derivative structures is a subgroup of the symmetry of the basic structure. Thus, in passing from the basic to the derivative structure there is a loss of symmetry in a given volume. This can be caused physically (*a*) by distortion of the basic structure, giving rise to a *distortion structure*, or (*b*) by substitution of different atoms for equivalent atoms in the basic structure, giving rise to a *substitution structure.*

Relations among the Structures of Pure Silica. Pure silica exists in three essentially different kinds of structures. The structures can be readily described in terms of their common structural unit, namely, a cluster of four oxygen atoms tetrahedrally surrounding a silicon atom. This unit is referred to briefly as a tetrahedron. The three kinds of silica comprise

---

[1] Buerger, M. J., Derivative crystal structures: *J. Chem. Phys.*, **15**, 1–16 (1947).

three different ways of linking the tetrahedra together by joining them vertex to vertex. Each vertex of a tetrahedron which is joined causes the oxygen of that vertex to be shared between two tetrahedra. When this occurs, only half of the shared oxygen may be said to belong to each of the neighboring tetrahedra. All three forms of silica are characterized by the sharing of all four vertices of all tetrahedra. The formula of the tetrahedron is therefore varied from the formula SiO_4 (for an isolated tetrahedron) to $SiO_{4/2} = SiO_2$ for the silica structures. The particular kind of linking is such that the tetrahedra are strung together in space networks in all three silica structures.

The three structural linkages correspond with the minerals cristobalite, tridymite and quartz. The idealized and most symmetrical linkage of tetrahedra in each of these arrangements is a high-temperature form. Each of these can be distorted to form a low-temperature form. The low-temperature forms are accordingly derivative structures, specifically distortion structures. In tridymite there are two distorted forms, known as middle-tridymite and low-tridymite. The natures of the distortions in these last two structures have not been determined in detail. Barth[2] has also examined the structure of high-cristobalite below its range of true stability (i.e., in the region of stability of high-tridymite) and found it somewhat distorted from the ideal structure[3,4]. Thus, the unstable structures may be derivative structures by distortion.

Chemical Basis of Stuffing. If, during the formation of a silica structure, a certain porportion of the Si^{++++} atoms is replaced by Al^{+++} atoms (which can also assume a coordination number four with respect to oxygen) the total valence of the metals in the structure is reduced in proportion to the number of substitutions. This loss of valence of the metals can be counterbalanced by addition of other metal atoms to the structure. In fact, if an Al^{+++} substitutes for a Si^{++++}, the field caused by the deficiency of positive charge forms a negatively charged site which attracts positive ions. The field is locally neutralized when the charge on the attracted ion just equals that of the average deficiency of the region. Taking coordination into account, the alkali and alkaline earth ions neatly perform the function of neutralizers. Naturally, these extra atoms must find space accommodation in the structure.

A list of the known stuffed derivatives of the silica structures is given in Table 1.

[2] Barth, Tom F. W., The cristobalite structures. I. High cristobalite: *Am. Jour. Sci.*, **23**, 350–356 (1932).

[3] Nieuwenkamp, W., Die Kristallstruktur des Tief-Cristobalits SiO_2: *Zeit. Krist.*, **A 92**, 82–88 (1935).

[4] Nieuwenkamp, W., Über die Struktur von Hoch-Cristobalit: *Zeit. Krist.*, **A 96**, 454–458 (1937).
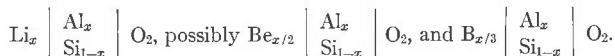
TABLE 1. STUFFED DERIVATIVES OF THE SILICA STRUCTURES

| Basic Structure	Derivative Structure	Space Group
High quartz		$C6_32$
	(low-quartz	$C3_12$)
	LiAlSiO$_4$ high eucryptite	$\begin{cases} C6_32 \text{ ?} \\ \text{or} \\ C2 \text{ ?} \end{cases}$
High tridymite		$C\dfrac{6_3}{m}\dfrac{2}{m}\dfrac{2}{c}$ $(C6/mmc)$
	BaAl$_2$O$_4$ SrAl$_2$O$_4$ BaFe$_2$O$_4$ SrFe$_2$O$_4$ PbFe$_2$O$_4$	$C6_32$
	KLiSO$_4$ KAlSiO$_4$ (kalsilite)	$C6_32$
	KAlSiO$_4$ (kaliophilite)	$C6_32$?
	KAlSiO$_4$ (orthorhombic)	?
	K$_2$MgSi$_3$O$_8$	?
	K$_2$FeSi$_3$O$_8$	?
	K$_2$Mg$_5$Si$_{12}$O$_{30}$	?
	KNa$_3$Al$_4$Si$_4$O$_{16}$ (nepheline)	$C6$
High cristobalite		$F\dfrac{4_1}{d}\bar{3}\dfrac{2}{m}$ $(Fd3m)$
	Barth's high cristobalite Barth's NaAlSiO$_4$, (high-carnegieite) Barth's NaCaSiO$_4$ Barth's Na$_2$Al$_2$O$_4$ Barth's K$_2$Al$_2$O$_4$ Barth's K$_2$Fe$_2$O$_4$ Barth's Rb$_2$Fe$_2$O$_4$ Barth's PbFe$_2$O$_4$	$P2_13$

QUARTZ-LIKE STRUCTURES

The structure of quartz is so tight that very limited space exists for the housing of extra stuffing atoms. Li$^+$, and presumably Be^{++} and B^{+++} are small enough to fit into the interstitial spaces of the quartz structure.

It is known that Li^+ can be drawn through the interstices of quartz at high temperatures with the aid of an electric field, but the larger alkalis Na^+ and K^+ cannot.[5] In accordance with this one might expect crystals of the type

$$Li_x \left| \begin{array}{c} Al_x \\ Si_{1-x} \end{array} \right| O_2, \text{ possibly } Be_{x/2} \left| \begin{array}{c} Al_x \\ Si_{1-x} \end{array} \right| O_2, \text{ and } B_{x/3} \left| \begin{array}{c} Al_x \\ Si_{1-x} \end{array} \right| O_2.$$

Conceivably similar stuffed structures could be based upon the quartz-like GeO_2 structure.

Actually lithium is known to stuff the quartz structure. During the war Winkler[6] incidentally synthesized eucryptite,

$$Li_{1/2} \left| \begin{array}{c} Al_{1/2} \\ Si_{1/2} \end{array} \right| O_2 = \tfrac{1}{2} LiAlSiO_4$$
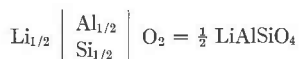
while preparing artificial nepheline. He later studied the structure of this material,[7] chiefly with the aid of powder photographs. He concluded that it had a high-quartz type structure in which Al atoms substitute for half the Si atoms of the quartz structure in alternate layers along the c axis. The Li atoms are in the interstitial space on the level where the substitution takes place, surrounded by four oxygen atoms. This arrangement has a very satisfactory Pauling electrostatic bond structure. The oxygens surrounding the Li are shared by one Si and one Al, so that they receive electrostatic bonds of strength $1\tfrac{3}{4}$ from this source. The tetrahedrally coordinated Li atoms contribute the remaining $\tfrac{1}{4}$.

Crystals similar to those described by Winkler were prepared in the Washken Laboratory[8] following Winkler's directions.[6] Before the appearance of Winkler's structure determination, the crystals were independently recognized as being of the quartz-type because of their habit (which resembles the high-quartz phenocrysts of quartz porphyries) and because their x-ray powder patterns and rotating crystal patterns resemble the quartz patterns.[8] An x-ray examination by Buerger[8,9] by powder, rotating-crystal, and precession methods revealed not only a doubled c axis discovered by Winkler, but a doubled a axis as well. In this respect,

[5] Harris, P. H., and Waring, C. E., Diffusion of lithium ions through quartz in an electric field: *J. Phys. Chem.*, **41**, 1077–1085 (1937).

[6] Winkler, Helmut G. F., On the synthesis of nepheline: *Am. Mineral.*, **32**, 131–136 (1947).

[7] Winkler, Helmut G. F., Synthese und Kristallstruktur des Eukryptits, LiAlSiO₄: *Acta Cryst.*, **1**, 27–34 (1948).

[8] Washken, Edward, Investigation of nepheline and related substances with particular emphasis on growing crystals for piezoelectric measurements. Contract **No. 2 36-039 sc-32333**. Quarterly interim report to the *U. S. Signal Corps*, No. **15** (15 April, 1948).

[9] Buerger, M. J., Crystals based on the silica structures: *Am. Mineral.*, **33**, 751–752 (1948).

and in respect to the appearance of reflections $000l$ in all orders (Buerger, but not Winkler), the results differ from Winkler's results, and suggest a monoclinic symmetry. Comparison of the Winkler and Buerger data are summarized in Table 2.

TABLE 2

	Low Quartz	High Quartz	Eucryptite	
			Winkler[7]	Buerger[8,9]
a	4.913 Å	5.02	5.27	2×5.275
c	5.404	5.48	2×5.625	2×5.61
c/a	1.10	1.09	2×1.067	1.064
cell content	$3 \, SiO_2$	$3 \, SiO_2$	$3 \, LiAlSiO_4$	$6 \, LiAlSiO_4$
space group	$C3_12$	$C6_22$	$C6_22$	$P2$ probably
density	2.649	2.518 at 600° C.	2.352 actual 2.305 x-ray	2.305 actual 2.30 x-ray

It is difficult to understand the divergence of Winkler's and Buerger's data. Winkler's structure is so obvious that one would not ordinarily doubt it. On the other hand, Buerger's data were obtained by the more powerful rotating-crystal and precession methods. Unfortunately only one crystal was so examined. The investigation should be repeated on other crystals for checking purposes.

It is possible that various degrees of disorder or deviation in formula can occur in eucryptite which would reconcile Winkler's and Buerger's data. Roy and others[10,11] have investigated the system eucryptite-silica. They have shown that a considerable range of composition can occur in eucryptite.

Gruner[12] has also given a brief statement that a form of

$$LiAlSi_2O_6 = 3 \, Li_{1/3} \left| \begin{array}{c} Al_{1/3} \\ Si_{2/3} \end{array} \right| O_2$$
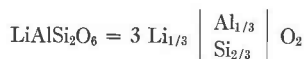
(which is the same composition as that of the mineral spodumene) has a structure which is a derivative of the quartz structure.

OPEN STRUCTURES WITH LIMITED STUFFING

Cristobalite and tridymite occur as minerals under circumstances which rule out their formation as stable structures of silica. Long ago it

[10] Roy, Rustom, and Osborn, E. F., The system lithium metasilicate-spodumene-silica: *J. Am. Chem. Soc.* **71**, 2086–2095 (1949).

[11] Roy, Rustom, Roy, Della M., and Osborn, E. F., Compositional and stability relations among the lithium aluminosilicates: eucryptite, spodumene, and petalite. *J. Am. Ceram. Soc.*, **33**, 152–159 (1950).

[12] Gruner, J. W., Progress in the silicate structures: *Am. Mineral.*, **33**, 679–691 (1948).

was pointed out[13] that the available analyses of such natural tridymite and cristobalite always contain small amounts of elements other than silicon and oxygen, including some large atoms of the alkali and alkaline earth groups. Evidently the large atoms can be housed in the interstitial spaces of the more open structures of tridymite and cristobalite, but cannot be accommodated in the structure of quartz. Conversely, a crystal which grows in such a way that it includes the elements shown by the analyses cannot have the quartz structure, but could only have the tridymite or cristobalite structures. The presence of the additional elements extends the temperature ranges of the open structures downward at the expense of the range of the tighter quartz structure.

More recently a specific case[14] of this was examined in the Mineralogical Laboratory of the Massachusetts Institute of Technology. The tridymite from Las Plumas County, California, was found to be based upon one of the orthorhombic space groups $F222$, Fmm, or $Fmmm$, with a comparatively large cell of dimensions

$$a = 9.91 \text{ Å}$$
$$b = 17.18$$
$$c = 81.57$$

Chemical and spectroscopic examination showed a small content of non-silica elements, the formula being approximately $NaCaAl_3Si_{15}O_{36}$.

Pure silica tridymite has transformations at 117° C. and 163° C. The Las Plumas tridymite has only one inversion at 127° C., directly from the low form to a high form which gives the x-ray reflections of the ordinary high-tridymite cell, plus some additional reflections whose characteristics vary non-reversibly with time. There is no middle tridymite form in this material.

The tridymite from San Cristobal, Mexico, has the same a and b axes as the Las Plumas material, but has only half as long a c axis. It inverts from the low form to the high form in two stages, but not at 117° C. and 163° C. as in pure silica tridymite. The inversion points occur at 121° C. and 135° C. The variation in inversion temperature must be a function of impurity with respect to pure silica as standard. The range of stability of middle tridymite would appear to become narrower with increasing impurity.

Barth and Kvalheim[15] subsequently but independently discovered the

[13] Buerger, M. J., The silica framework crystals and their stability fields: *Zeit. Krist.*, **A 90**, 186–192 (1935).

[14] Buerger, M. J., and Lukesh, Joseph, The tridymite problem: *Science*, **95**, 20–21 (1942).

[15] Barth, Tom F. W., and Kvalheim, Aslak, Christensenite, a solid solution of nepheline in tridymite: *Norske Videnskaps Akademi i Oslo*, No. **22** (1944).

same situation in natural tridymite from Deception Island in the Antarctic Archipelago. This tridymite has greater refractive indices than pure tridymite by about 0.01. The Deception Island tridymite inverts directly from the low form to the high form at about 135° C., with some variation between samples, but always between 130° C. and 140° C. Spectroscopic analyses showed that this material has a composition lying between that of silica and nepheline, specifically about 5% nepheline, 95% silica, i.e.

$$\frac{NaAlSiO_4}{SiSiO_4} = \frac{5}{95}$$

This suggests a formula approximately $NaAlSi_{49}O_{100}$.

Tuttle[16] has recently discovered small variations in the high-low transformation of quartz near 573° C., which may be attributed to small amounts of impurity.

The evidence presented in this section makes it plain that tridymite has been formed in nature, presumably by hydrothermal synthesis, which has small amounts of Al replacing Si atoms of the pure silica structure, and also small amounts of alkali or alkaline earth atoms. The latter are doubtless present in the large interstitial spaces of the tridymite structure and are responsible for the assumption of the tridymite structure by this group of atoms rather than the tighter quartz structure, which would be the stable form of pure silica under the conditions of formation.

STUFFED DERIVATIVES OF TRIDYMITE

The most important derivatives of tridymite have compositions in the range $NaAlSiO_4$-$KAlSiO_4$. The relations between the various species of these crystals are by no means entirely clear.

Nepheline. Schiebold[17] first suggested that nepheline has a tridymite-like structure, with half the Si atoms replaced by Al, and with Na in the interstices to balance the valence. This structure was merely a suggestion and was not supported by an intensity study. Buerger, Klein, and Hamburger[18] made a detailed x-ray investigation of nepheline and were led to a structure essentially the same as the structure suggested by Schiebold. This distribution of atoms of this structure with respect to the symmetry elements is such that the alkalis are clearly separated into two

---

[16] Tuttle, O. F., The variable inversion temperature of quartz as a possible geological thermometer: *Am. Mineral.*, **34**, 723–730 (1949).

[17] Schiebold, E., Zur Struktur von Nephelin und Analcim: *Naturwiss.*, **18**, 705–706 (1930).

[18] Buerger, M. J., Klein, Gilbert, and Hamburger, Gabrielle, The structure of nepheline: *Am. Mineral.*, **32**, 197 (1947).

categories, so that the formula of nepheline is $A' A_3'' Al_4Si_4O_{16}$. The structure is based upon a tridymite structure somewhat collapsed by a rotational distortion of the silica framework. The type of collapse is such that the void in which A' is situated is large while that within which A'' is situated is smaller. Since analyses of natural nepheline[19] show the presence of both potassium and sodium in a ratio which ranges in the neighborhood of 1:3, it is obvious that the natural formula for nepheline is not simple $NaAlSiO_4$, but rather $KNa_3Al_4Si_4O_{16}$.

The structure of nepheline is being refined by Theo Hahn and M. J. Buerger. A detailed account of the structure determination is expected shortly.

On the basis of this rational formula, Washken and Buerger[20] synthesized "rational" nepheline. This proved to crystallize directly from the melt, in contrast with the arbitrarily pure composition $NaNa_3Al_4Si_4O_{16} = 4\ NaAlSiO_4$, which, when crystallized from the melt, assumes the carnegieite form, which has a stuffed cristobalite structure.[31] This clearly shows that results of phase diagram investigations which include a nepheline phase should not necessarily be applied to all compositions having the nepheline structure.

Generally speaking, phase diagram results obtained in the melt-crystal region should not be regarded as fixing the natures of the phase fields involving crystalline phases at lower temperatures. This became obvious[21] when it was found that, although the plagioclase crystals are the classical examples of complete solid solutions at high temperatures as they precipitate from the melt, they certainly do not form complete solid solutions at low temperatures. The same is doubtless true in the system $NaAlSiO_4$-$KAlSiO_4$. Thus, Bowen[22] found a complete series of solid solutions in this system between "nepheline" and "kaliophilite." But it does not follow that the phases stable at low temperatures form this complete series of solid solutions. Incidentally, Bowen's diagram shows an interesting singularity even at high temperatures at about the ideal nepheline composition $KNa_3Al_4Si_4O_{16}$.

Recently Wyart has synthesized nepheline hydrothermally.[23] The raw

[19] Banister, F. A., and Hey, M. H., A chemical, optical, and x-ray study of nepheline and kaliophilite: *Mineral. Mag.*, **22**, 569–608 (1931).

[20] Washken, Edward, and Buerger, M. J., The effect of potassium on the nepheline-carnegieite transformation: *Am. Mineral.*, **35**, 290–291 (1950).

[21] Buerger, M. J., The role of temperature in mineralogy: *Am. Mineral.*, **33**, 101–121 (1948), especially pages 118–121.

[22] Bowen, N. L., The sodium-potassium nephelites: *Am. Jour. Sci.*, **43**, 115–132 (1917).

[23] Wyart, Jean, and Michel-Lévy, Mireille, Cristallisation du mélange $N_xK_{1-x}AlSiO_4$ en présence d'eau sous pression (formation de nepheline, kalsilite, hydrocancrinite, hydrosodalite, mica): *Compte Rend.*, **229**, 131–133 (1949).

materials were NaOH, KOH, Al_2O_3, and SiO_2, which were placed in closed red copper tubes and heated in a small autoclave. Nepheline prisms up to .080 mm. long were obtained at 415° C. which had a composition $Na_{1-x}K_xAlSiO_4$, where x is in the neighborhood of 0.2–0.3. Note that this composition corresponds with that deduced from the crystal structure analysis carried out in the Mineralogical Laboratory of the Massachusetts Institute of Technology.

The Forms of $KAlSiO_4$. The compound $KAlSiO_4$ appears to occur in three modifications, two hexagonal and one orthorhombic. The two hexagonal forms correspond to the minerals kaliophilite and kalsilite.[24] Some characteristic properties of these forms are shown in Table 3. Some data for high tridymite and nepheline are added for comparison.

TABLE 3

	Space Group	Cell Edges			Refractive Indices		Specific Gravity
		a	$a\sqrt{3}$, or b	c	ω (or γ)	ϵ (or α)	
Kaliophilite	$C\,6_32$?	26.9	46.7	8.55	1.530	1.526	2.606
Kalsilite	$C\,6_32$	5.17	8.96	8.67	1.542	1.537	2.59
Ortho $KAlSiO_4$	?	9.00	15.68	8.53	1.536	1.528	2.60
Tridymite	$C\,\dfrac{6}{m}\dfrac{2}{m}\dfrac{2}{c}$	5.03	8.70	8.22			
Nepheline	$C\,6_3$	9.99	17.3	8.39	1.544	1.539	2.65

It will be observed that kalsilite has a cell approximately the same as that of high-tridymite. Claringbull and Bannister[25] have shown that this mineral has indeed a structure which is a very simple derivative of the high-tridymite structure. Half the silicon atoms are replaced by aluminum atoms and the large interstices of this $(AlSiO_2)^{-1}$ net house the K^+ ions. The structure is very similar to that of the $BaAl_2O_4$ structure discussed in Appendix I.

The structure of the mineral kaliophilite is unknown. Bannister and Hey[19] have pointed out that the axes of kaliophilite are closely related to those of tridymite. These minerals have the same c axis length and the kaliophilite a axis is about $3\sqrt{3}$ times the a axis of high tridymite, i.e., about 3 times the long diagonal of the tridymite hexagonal unit cell. This

[24] Bannister, F. A., and Hey, Max H., Kalsilite, a polymorph of $KAlSiO_3$, from Uganda: *Mineral. Mag.*, **26**, 218–224 (1942).

[25] Claringbull, C. F., and Bannister, F. A., The crystal structure of kalsilite: *Acta Cryst.*, **1**, 42 (1948).

close geometrical relation, the relation between chemical formulae and the similarity in densities and refractive indices of kaliophilite and nepheline make it very probable that kaliophilite has a structure which is a derivative of that of high-tridymite.

Lukesh and Buerger[26] determined the space group of kaliophilite as $C6_32$ on the assumption that the material which they had was a single crystal. Although this material was as good as it was possible to obtain, there is a strong possibility that the material was twinned, in which case the symmetry may be lower than $C6_32$. For example, kaliophilite could actually be orthorhombic.

The structure of orthorhombic $KAlSiO_4$ is unknown. Table 3 shows that its *a* axis is about equal to the cell diagonal of kalsilite, its *b* axis is twice the *a* axis of kalsilite, and the *c* axes of the two crystals are about the same. From this relation and the similar refractive indices it is likely that the structure of kalsilite is also a derivative of that of high-tridymite.

The stability relations between these three forms of $KAlSiO_4$ have been investigated by Rigby and Richardson.[27] Their experimentation with melts suggests that kaliophilite is a low-temperature form and that the orthorhombic form is a high-temperature one. The inversion boundary between them is in the neighborhood of 900° C. Kalsilite requires a small percentage (1.5–5%) of Na_2O to form. Depending on the Na content, kalsilite inverts to the orthorhombic form at temperatures from 1300° C. to 1500° C. Schaierer[28] confirmed that the high-temperature form of $KAlSiO_4$ is the orthorhombic modification. This can accept considerable Na in place of K. Wyart[29] synthesized kalsilite hydrothermally at temperatures up to 500° C. This was accomplished in the absence of soda, using silica, amorphous alumina, and a solution containing potassium.

It will be noted in passing that Bowen's conclusions[22] regarding the continuous series of solid solutions between nepheline and kaliophilite appear to be in error. Nepheline has a cell which is different from that of any of the three forms of $KAlSiO_4$. This emphasizes the danger of extrapolating data which determine liquidus curves into the field of the lower-temperature crystalline phases.

Tridymite-Like Potassium Magnesium Silicates. Roedder[30] has dis-

[26] Lukesh, Joseph S., and Buerger, M. J., The unit cell and space group of kaliophilite: *Am. Mineral.*, **27**, 226–227 (1942).
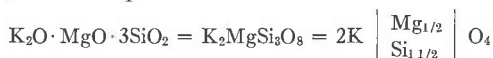
[27] Rigby, G. R., and Richardson, H. M., The occurrence of artificial kalsilite and allied potassium aluminum silicates in blast-furnace linings: *Mineral. Mag.*, **28**, 75–87 (1947).

[28] Schairer, J. F., The alkali-feldspar join in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2: *Jour. Geol.*, **58**, 512–517 (1950).
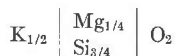
[29] Wyart, Jean, Synthése de la kalsilite et de l'orthose: *Compte Rend.*, **225**, 944–946 (1947).

[30] Roedder, Edwin Woods, The system K_2O—MgO—SiO_2: *Am. J. Sci.*, **249**, 81–130, and 224–248 (1951),

covered at least one tridymite-like compound in investigating the system $K_2O\text{-}MgO\text{-}SiO_2$. The compound
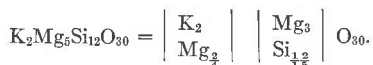
$$K_2O \cdot MgO \cdot 3SiO_2 = K_2MgSi_3O_8 = 2K \left| \begin{array}{c} Mg_{1/2} \\ Si_{1\,1/2} \end{array} \right| O_4$$

can also be written

$$K_{1/2} \left| \begin{array}{c} Mg_{1/4} \\ Si_{3/4} \end{array} \right| O_2$$

to bring out its relation to the SiO_2 formula. This occurs in two forms designated α and β. The α form is obtained directly from melts, has a hexagonal outline and a uniaxial interference figure. Nevertheless the platelets bear certain groves which suggest twinning of a less symmetrical structure than hexagonal. The powder pattern is very similar to that of kalsilite. The structure, therefore, is undoubtedly that of a stuffed tridymite-like kalsilite in which, curiously enough, the comparatively large Mg atom substitutes for $\frac{1}{4}$ of the Si atoms in the network. This phase tends to invert spontaneously but slowly to a fibrous form which has been designated β.

Later Roedder[30a] discovered the compound $K_2O \cdot FeO \cdot 3SiO_2 = K_2FeSi_3O_8$ in the system $K_2O\text{-}FeO\text{-}SiO_2$. This melts congruently near $900°$ C. Its mean refractive index is about 1.575 with a birefringence of 0.01. Some of the individual crystals are definitely uniaxial negative, and powder photographs are nearly identical with those of the magnesium analog. The formula can therefore be interpreted as tridymite-like, or as

$$K_{1/2} \left| \begin{array}{c} Fe_{1/4} \\ Si_{3/4} \end{array} \right| O_2.$$
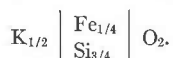
Roedder[30] also encountered a phase having the composition $K_2O \cdot 5MgO \cdot 12SiO_2 = K_2Mg_5Si_{12}O_{30}$ which crystallizes in thin hexagonal plates having uniaxial optical properties with $\omega = 1.543$, $\epsilon = 1.550$. These properties suggest a tridymite-like structure. If so, the structure can be fitted to a silica-like formula as follows:

$$K_2Mg_5Si_{12}O_{30} = \left| \begin{array}{c} K_2 \\ Mg_{\frac{3}{4}} \end{array} \right| \; \left| \begin{array}{c} Mg_3 \\ Si_{\frac{12}{15}} \end{array} \right| O_{30}.$$

STUFFED DERIVATIVES OF CRISTOBALITE

Barth and Posnjak[31-33] have shown that two silicates have structures

[30a] Roedder, Edwin, A reconnaissance of liquidus relations in the system $K_2O \cdot 2SiO_2$—FeO—SiO₂: *Am. Jour. Sci.*, 435–456 (1952).

[31] Barth, Tom F. W., and Posnjak, E., Silicate structures of the cristobalite type I. The crystal structure of carnegieite (NaAlSiO₄): *Zeit. Krist.*, **81**, 135–141 (1932).

[32] Barth, Tom F. W., and Posnjak, E., Silicate structures of the cristobalite type II. The crystal structure of Na₂CaSiO₄: *Zeit. Krist.*, **81**, 370–375 (1932).

[33] Barth, Tom F. W., and Posnjak, E., Silicate structures of the cristobalite type III. Structural relationships of high-cristobalite, α-carnegietie and Na₂CaSiO₄: *Zeit. Krist.*, **81**, 376–385 (1932).

which are stuffed derivatives of cristobalite. These are the high-carne-gieite form of $NaAlSiO_4$, and Na_2CaSiO_4.

Carnegieite. Bowen and Grieg's early investigation[34] of the phases of $NaAlSiO_4$ showed that, whereas nepheline is the stable form below 1248° C., the form stable just above this temperature is an isometric form known as carnegieite. Nepheline and carnegieite are separated by a sluggish transformation. If the form of carnegieite stable just above this transformation point is cooled past 1248° C. and not allowed time to invert, it suffers another rapid and reversible transformation at 690° C. to a birefringent form. The forms above and below this rapid inversion may be designated high- and low-carnegieite respectively.

Barth and Posnjak[31] investigated the structure of high-carnegieite by the powder method and found it to be a stuffed derivative of cristobalite in which a network of composition $(AlSiO_4)^{-1}$ assumes the structural role of the pure silica network of cristobalite, and in which Na^+ ions occupy half the voids in the network.

Barth and Posnjak's structure[31] has the symmetry $P2_13$, which is a derivative symmetry of that of high-cristobalite,

$$Fd3m = F\frac{4_1}{d} \ 3 \ \frac{2}{m} \cdot$$

Unfortunately, these investigators determined this structure from x-ray diffraction data secured at about 750° C. Although this temperature is above that of the inversion to low-carnegieite, it is below that of the nepheline inversion, 1248° C. The crystals were therefore unstable and in a condition known as a stranded phase [13,35]. The symmetry $P2_13$ is doubtless correct for this condition, but the writer believes that the structure would have a higher symmetry if examined in its true stability range above 1248° C. This is essentially the same comment which was made above in connection with the relation between Barth's[2] unsymmetrical high-cristobalite structure as compared with Nieuwenkamp's symmetrical one.

Na_2CaSiO_4. Barth and Posnjak[32,33] also investigated the structure of the artificial compound Na_2CaSiO_4 and found it to be a derivative of the high-cristobalite structure. The silica network is replaced by one of composition $(CaSiO_4)^{-2}$ and the 2 Na^+ ions completely fill the larger voids of the network. The structure is substantially the same as that of carnegieite except that the replacement Ca^{2+} for Al^{3+} in the network increases the negative charge on the net so that two Na^+ ions are required for neutralization.

---

[34] Bowen, N. L., and Greig, J. W., The crystalline modifications of $NaAlSiO_4$: *Am. J. Sci.*, 10, 204–212 (1925).

[35] Buerger, M. J., The general rôle of composition in polymorphism: *Proc. Nat. Acad. Sci.*, 22, 685–689 (1936).

In this network the Ca^{2+} ions have four coordination, which is unusual, because the large radius of Ca^{2+} ordinarily requires a coordination of six to nine oxygen atoms. The tetrahedral coordination could be more reasonably expected for the two smaller alkaline earth ions Mg^{2+} and Be^{2+}. For this reason the writer believes it likely that the compounds Na_2MgSiO_4 and Na_2BeSiO_4 may also assume this structure.

APPENDIX I
Nonsilicates with Silica-Like Structures

There are a number of compounds which contain no silica and which, therefore, could not possibly be termed stuffed derivatives of the silica structures in the strict sense, but which nevertheless have structures which are similar to such structures. These are chiefly aluminates and ferrates of tridymite and cristobalite types.

Tridymite-Like Nonsilicates

Barium-Aluminate-Type Structures. The structure of $BaAl_2O_4$ was established by Wallmark and Westgren.[36] They heated mixtures of various proportions of BaO and Al_2O_4 in platinum crucibles over a gas flame and examined the reaction products by the x-ray powder method. They deduced a hexagonal structure which has Al and O atoms arranged as the Si and O atoms in the high-cristobalite structure, with the Ba atoms in the interstitial spaces. Similar structures were found for $SrAl_2O_4$, $BaFe_2O_4$ $SrFe_2O_4$ and $PbFe_2O_4$. These structures are essentially the same as that of hexagonal $KAlSiO_4$, kalsilite.

All these structures are open to the objection that they were investigated by the comparatively weak powder method which is very insensitive to symmetry. Though the general features of the structures are doubtless correct, there remains a chance that they may, in fact, be less symmetrical.

Potassium-Lithium-Sulfate-Type Structures. The structure of $KLiSO_4$ was analyzed many years ago by Bradley[37], who used powder and spectrometer methods. The structure is of the general tridymite type. Li and S atoms substitute for Si, and K^+ fills the large voids in the $(LiSO_4)^{-1}$ network. This structure is exactly isotypic with the kalsilite form of $KAlSiO_4$.

Cristobalite-Like Nonsilicates

Barth[38] studied the compounds $K_2Al_2O_4$, $K_2Fe_2O_4$ and $Na_2Al_2O_4$ and

[36] Wallmark, Signe, and Westgren, A., X-ray analysis of barium aluminates: *Arkiv. för Kemi. Min. och Geol.*, **1213**, No. 35 (1937).

[37] Bradley, A. J., The crystal structure of lithium potassium sulfate: *Phil. Mag.*, **49**, 1225–1237 (1935).

[38] Barth, Tom F. W., Non-silicates with cristobalite-like structure: *J. Chem. Phys.*, **3**, 323–325 (1935).

found them all to have powder photographs similar to those of the cristo-balite derivatives such as Na_2CaSiO_4. Barth also pointed out that from the data provided by Hilpert and Lindner,[39] it could be deduced that $Rb_2Fe_2O_4$ and $PbFe_2O_4$ also have similar structures.

APPENDIX II

Tridymite Versus Cristobalite Structures

It is interesting to compare lists of compounds having the tridymite and cristobalite structures. Such lists are shown in Table 4. From this it is evident that, except for $PbFe_2O_4$ and high-$NaAlSiO_4$, all compounds with a single stuffing atom assume a tridymite-like structure, while those with two stuffing atoms assume cristobalite-like structures.

TABLE 4. COMPOUNDS ASSUMING TRIDYMITE-LIKE AND CRISTOBALITE-LIKE STRUCTURES

Tridymite-Like Structures	Cristobalite-Like Structures
$K \left\| \begin{matrix} Li \\ S \end{matrix} \right\| O_2$	
$Rb \left\| \begin{matrix} Li \\ S \end{matrix} \right\| O_2$	
low-$Na \left\| \begin{matrix} Al \\ Si \end{matrix} \right\| O_2$	high-$Na \left\| \begin{matrix} Al \\ Si \end{matrix} \right\| O_2$
$K \left\| \begin{matrix} Al \\ Si \end{matrix} \right\| O_2$	$Na_2 \left\| \begin{matrix} Ca \\ Si \end{matrix} \right\| O_2$
Ba Al_2O_4 Sr Al_2O_4 Pb Al_2O_4	$Na_2Al_2O_4$ $K_2Al_2O_4$
Ba Fe_2O_4 Sr Fe_2O_4 Pb Fe_2O_4	$K_2Fe_2O_4$ $Rb_2Fe_2O_4$ Pb Fe_2O_4

This observation can be rationalized. With one void stuffed, a collapse of the network is permitted provided that the network is the hexagonal tridymite network. Such a collapse, which consists of a rotation of tetra-hedra about the hexagonal axis, is such as to offer better coordination to the stuffing ions. On the other hand, with two voids stuffed, the net could collapse very little indeed. In such an event the hexagonal network is no

[39] Hilpert, S., and Lindner, A., Über Ferrite. 2. Metteilung: Gruppe der Alkali-, Erdalkali- und Bleiferrite: *Zeit. f. physik. Chemie*, **B22**, 395–405 (1933).

longer the favored one. The question is, why is the isometric (cristobalite) network assumed. It would appear that the greater symmetry of the isometric network makes it a more probable structure, and therefore one more likely to be assumed by the atoms in question. This is also the reason for the assumption of the more symmetrical network by the high-temperature forms such as high-cristobalite itself and high-carnegieite. Furthermore, in the higher temperature stuffed structures, the stuffing atoms doubtless flow through the voids of the network in interstitial disorder. The flow is easier in the more symmetrical network.

TABLE 5. TRIDYMITE-LIKE CRYSTALS WITH FRACTIONAL AMOUNTS OF STUFFING ATOMS

$K_{1/4}$ $Na_{3/4}$	Al_1 Si_1	O_2	ideal nepheline
$Na_{1/18}$ $Ca_{1/18}$	$Al_{1/6}$ $Si_{5/6}$	O_2	Las Plumas tridymite
$Na_{.2}$	$Al_{.2}$ $Si_{.98}$	O_2	christensenite
$K_{1/2}$	$Mg_{1/4}$ $Si_{3/4}$	O_2	
$K_{1/2}$	$Fe_{1/4}$ $Si_{3/4}$	O_2	compounds produced by Roedder[30,30a]
$K_{2/15}$ $Mg_{2/15}$	$Mg_{1/5}$ $Si_{4/5}$	O_2	

Table 5 lists some tridymite-like crystals discussed in the text in which the stuffing atoms occur in fractional amounts, based upon an SiO_2 formula. These compounds also comform to the discussion just given.