References and Notes

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A Clathrate Crystalline Form of Silica

Abstract. *The low-density cubic form of silica (impure), melanophlogite, has a clathrate-type structure that incorporates organic molecules, including long straight-chain hydrocarbons. The structure is analogous to that of the clathrate crystalline hydrates of composition* $6X \cdot 46H_2O$ *or* $8X \cdot 46H_2O$*. This is the first known example of a silicate framework structure with the pentagonal dodecahedron as a framework element.*

The structures of forms of ice (*1*) are of interest in relation to the polymorphs of silica because of the strong tendency for both SiO_2 and H_2O to form tetrahedrally linked framework structures. The structural analogy between ordinary ice (ice I) and tridymite is well known. Some of the better-characterized crystalline phases of H_2O and SiO_2, together with their densities relative to the corresponding forms ice I and tridymite, are compared in Table 1. The arrow symbol shows which pairs of polymorphs actually are structural analogs. The significance of the relationships in Table 1 will be discussed more fully elsewhere, but I wish to call attention here to an interesting comparison between the bottom pairs of entries in the table.

The low-density form of silica, melanophlogite, has been studied by Skinner and Appleman (*2*), who report the x-ray crystallographic data listed in Table 2. The least-dense ice-like phases available for structural comparison are the fully hydrogen-bonded crystalline hydrates (*3*, *4*), of which one type, the 12-Å gas hydrate of composition $6X \cdot 46H_2O$ (with X = CH_4, H_2S, CO_2, SO_2, . . .), is listed in Table 1. I wish to show that published x-ray data support the idea that melanophlogite is the structural analog of the 12-Å crystalline hydrate.

Structural data for a typical 12-Å hydrate (*5*), $6Cl_2 \cdot 46H_2O$, are shown in Table 2 for comparison with melanophlogite. Both are cubic, and the ratio of cell sizes 13.40/11.92 (= 1.13) is very close to the ratio 3.09/2.76 (= 1.12) between the Si—Si distances in β-tridymite and the H_2O—H_2O distances in ice I (Table 2). The space group reported (*2*) for melanophlogite, $P4_232$, is simply a subgroup of the space group of chlorine hydrate, $Pm3n$ (complete symbol $P4_2/m32/n$), obtained from the latter by dropping the mirror planes. Thus a tetrahedrally linked SiO_2 framework of the size and symmetry required for melanophlogite, with Si—Si distances close to the value 3.1 Å that occurs in the common polymorphs of silica, may be constructed. A degradation in symmetry, as from $Pm3n$ to $P4_232$, would not be unexpected; it is a familiar feature in silica polymorphs, represented by the nonquenchable high-low (β to α) transitions, in which slight structural distortions apparently improve the bond angles in the structure at the expense of some of the symmetry elements of the high-temperature forms (*6*).

The proposed hydrate-analog structure for melanophlogite indicates 46 units of SiO_2 per unit cell, instead of the 48 reported by Skinner and Appleman (*2*). The difference between these figures arises because Skinner and Appleman did not take into account the content of sulfur and organic compounds present in the melanophlogite crystals; they argued instead that "the organic pigment is mechanically included in the crystals and does not affect the crystal structure of melanophlogite." In view of the hydrate analog, the foreign constituents, which invariably make up 7.7 to 12 percent by weight of the crystals (*2*), are essential structural elements, playing the same stabilizing role in filling the large open cavities in the melanophlogite structure that the molecules CH_4, SO_2, H_2S, and others play in the 12-Å crystalline hydrates. Both structures are in this sense clathrates, and the somewhat variable content of the guest constituents in melanophlogite is accordingly understandable. If the unit cell contains 46 units of SiO_2 plus a guest contribution in proportion to the weight fraction of foreign constituents to SiO_2 reported in the analysis by Skinner and Appleman (*2*), the calculated density of melanophlogite is 2.06 g cm^{-3}; this value is in better agreement with the measured density 2.05 ± 0.013 g cm^{-3} than the value 1.99 calculated (*2*) on the basis of 48 units of SiO_2 per unit cell, with no foreign constituents.

Table 1. Partial list of H_2O and SiO_2 polymorphs.

H_2O				SiO_2		
Form	Cryst.	ρ/ρ_{ice}		Form	Cryst.	$\rho/\rho_{tridymite}$
Ice VII	cubic	1.82		stishovite	tetrag.	1.95
Ice V	monocl.	1.34		coesite	monocl.	1.33
Ice II	hex.	1.27		α-quartz	hex.	1.20
Ice III	tetrag.	1.24*	⟷	silica K	tetrag.	1.14
Ice Ic	cubic	1.00	⟷	β-cristobalite	cubic	1.00
Ice I	hex.	1.00	⟷	β-tridymite	hex.	1.00
$6X \cdot 46H_2O$	cubic	0.90†	←?→	melanophlogite	cubic	0.86†

* The symbol ⟷ designates pairs of structurally analogous polymorphs. † Framework density only. Hex, hexagonal; tetrag, tetragonal; mono, monoclinic.

The guest material in the analyzed sample (*2*) consists, per unit cell, of about 2 atoms of sulfur, 3 of carbon, 6 of oxygen, and 24 of hydrogen. The actual chemical form in which this material is incorporated into the crystals is not known, but spectroscopic measurements (*2*) indicate that abundant hydrocarbons are present, as well as H_2O and CO_2. There are conflicting indications whether the sulfur is present as H_2S, SO_2, SO_3, or perhaps bonded to the organic constituents. If the species present were SO_2, H_2O, and CH_4, there should be only 16 H atoms per unit cell, which is somewhat too few. The number of guest molecules per unit cell would be 7, one less than the number of polyhedral cavities available in the hydrate-analog clathrate structure (*5*, *7*). All of these molecules are small enough to fit easily into the six larger polyhedral cavities in the structure (tetrakaidecahedra, free diameter 5.8 to 6.8 Å, depending on degree of bending of the Si—O—Si linkage); and H_2O, CH_4, or H_2S could also fit easily into the two smaller cavities (pentagonal dodecahedra, free diameter 4.4 to 5.8 Å).

The spectroscopic evidence (*2*) suggests that hydrocarbons of various sizes are present, and the yellow to brown color of many of the crystals suggests incorporation of long-chain conjugated

Table 2. X-ray data for melanophlogite and chlorine hydrate.

Parameter	Melanophlogite	Chlorine hydrate
Space group	$P4_232$	$Pm3n$
Cell edge, *a*	13.40 Å	11.82 Å
Cell content, *Z*	48 $\mathrm{SiO_2}$	46 $\mathrm{H_2O}$
Density (obs.)	2.05 ± 0.013 g/cm³	1.23 to 1.29 g/cm³
Density (calc.)	1.99 g/cm³	1.26 g/cm³
Reference	(*2*)	(*5*)

systems, in which sulfur, if present, could have an auxochromatic effect (*8*). The tetrakaidecahedra in the hydrate-analog structure are connected in chains parallel to the crystal *a* axes (*7*), the connecting openings between cavities being hexagons of free diameter 1.7 to 2.7 Å (depending, again, on the degree of Si—O—Si bending). This opening is not large enough to allow straight-chain hydrocarbons to pass through freely (*9*), but it might be large enough to accommodate the "waist" at the center of the carbon-carbon bond, whose effective width is probably somewhat smaller than the 2.8 Å implied by the van der Waals radius of carbon, and it may be as small as 2.0 Å (*3*, p. 263). If so, the chains of tetrakaidecahedral cavities would permit long straight-chain hydrocarbons to be incorporated, and the structure could in this case accept a rather large content of organic guest material (about 20 carbon atoms per unit cell). These considerations, while somewhat speculative, are in harmony with the known chemistry of melanophlogite.

Rough atomic coordinates for the proposed melanophlogite structure are given in Table 3. They are derived directly from the 12-Å hydrate structure (*5*), with the oxygen atoms placed midway between the silicon atoms; the bending of the Si—O—Si linkages is ignored, although this is doubtless an important feature of the detailed structure. The atomic positions (Table 3) involve the mirror plane and *n*-glide plane of the chlorine hydrate structure; this implies extinction of x-ray reflections of type *hhl* with *l* odd. This is in agreement with Skinner and Appleman's x-ray powder data (*2*), in which no observed lines consisting only of reflections *hhl* with *l* odd were reported, the data thus strongly suggesting at least a pseudo-*n*-glide plane (*10*).

Table 3. Preliminary atomic parameters for melanophlogite (referred to space group $Pm3n$). X represents guest molecules in polyhedral cavities. In the calculation for Table 4, X is taken as $\frac{3}{8}\mathrm{O} + \frac{1}{4}\mathrm{S} + \frac{3}{8}\mathrm{C}$. *B* values, chosen on the basis of refined zeolite structures, are: 0.5Å² for Si; 2.0Å² for O; 3.0 for X.

Atom	Position	*x*	*y*	*z*
$\mathrm{Si_1}$	24 *k*	0	0.316	0.116
$\mathrm{Si_2}$	16 *i*	0.183	0.183	0.183
$\mathrm{Si_3}$	6 *c*	1/4	0	1/2
$\mathrm{O_1}$	48 *l*	0.091	0.246	0.150
$\mathrm{O_2}$	24 *k*	0	0.405	0.216
$\mathrm{O_3}$	12 *f*	0.310	0	0
$\mathrm{O_4}$	8 *e*	1/4	1/4	1/4
$\mathrm{X_1}$	6 *d*	1/4	1/2	0
$\mathrm{X_2}$	2 *a*	0	0	0

A test of the structure can be made by comparing predicted intensities of x-ray powder lines I_c, calculated from the coordinates in Table 3, with semiquantitative intensities I_o reported by Skinner and Appleman (*2*) (Table 4). Although the match is far from quantitative, the general pattern of agreement is fairly good, not only for the strong lines but also for the moderate and weak ones. In view of the sensitivity of the calculated intensities to the many unrefined atomic parameters (framework positions, thermal motions, and detailed guest-molecule distributions), and considering the only semiquantitative significance of the observed intensities, one can conclude that the extent of agreement between I_c and I_o in Table 4 supports the proposed basic structure for melanophlogite.

The clathrate structure provides a satisfying explanation for the peculiar and unique occurrence of melanophlogite (*2*), which has been found only in the Sicilian sulfur deposits localized in sulfur- and sulfate-rich zones in limestone saturated with liquid bituminous matter (*11*). Since the very open silica framework probably would not be stable if the polyhedral cavities were empty, a necessary condition for its formation is an abundance of the sulfur and organic compounds suitable as cavity fillings. The facts that sulfur is always present to the extent of two atoms per unit cell (or only slightly more) and that the sulfur is very firmly bound to the structure (*11*) suggest that the essential stabilization is achieved by a sulfur compound in the dodecahedral cavities. Some organic filling of the tetrakaidecahedra is probably also necessary for formation of the crystals initially, but it can be expelled, at least in part, without causing the crystals to invert (*2*).

The clathrate structure also gives an explanation of the remarkable optical properties of melanophlogite (*2, 11*), in particular the pattern of optical anisotropy. From a diagram of the proposed structure (*7*), it is seen that at any stage in the growth of a melanophlogite cube, each cube face will have incompleted chains of tetrakaidecahedra in the form of grooves in the surface. These grooves are natural lodging places for long-chain hydrocarbons in the nourishing fluid, hence such molecules will be incorporated preferentially or exclusively in orientations parallel to the locally growing cube face. This should confer uniaxial optical anisotropy with the optic symmetry axis perpendicular to the growing cube face and with greatest refractive index for the electric field vector parallel to this cube face, in agreement with observation (*11*). In principle there must also be some distortion of the cubic framework to tetragonal symmetry. The fact that this

Table 4. Calculated and observed x-ray powder line intensities for melanophlogite.

hkl	I_c*	I_o	*hkl*	I_c	I_o
110	8	30	711,551	0	
111	0		640	0	
200	19	30	720,641	3	5
210	145	80	721,633,552	4	10
211	41	60	642	2	5
220	2		722,544	0	
221	0		730	2	5
310	13	10	731,553	0	
311	0		650,643	10	20
222	84	70	732,651	2	10
320	15	50	800	1	
321	142	100	810,740,652	2	10
400	22	10	811,741,554	5	20
410,322	22	50	733	0	
411,330	16	40	820,644	1	5
331	0		821,742	1	
420	6	5	653	6	10
421	40	20	822,660	7	10
332	0	10	830,661	2	
422	0	10	831,750,743	4	10
430	0	5	751,555	0	
510,431	7	5	662	3	5
511,333	0		832,654	0	
520,432	16	30	752	0	
521	0		840	1	5
440	1	5	841,744,663	0	
522,441	0		910,833	0	
530,433	23	30	911,753	3	5
531	8	5	842	0	
600,442	5	20	920,760	0	
610	1		921,761,655	4	10
611,532	11	20	664	1	
620	0		922,850,843	3	
621,443	1		930,851,754	12	20
541	3	20	931	1	
533	0		852	0	
622	6		932,763	1	
630,542	2	10	844	4	5
631	6	20	940,665	1	
444	7	40	941,853,770	4	10
632	2	5	933,771,755	0	
710,550	1	10	1000,860	2	5

* Calculated intensities (I_c) are for the coordinates in Table 3. I_c is the square of the structure factor, multiplied by the powder line multiplicity and the Lorentz-polarization-Debye-Scherer correction factor $(1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)$, times an arbitrary scaling factor 1.7×10^{-6}, summed over the groups of coincident powder lines. Observed intensities (I_o) are semiquantitative, by Skinner and Appleman (*2*).

could not be detected by x-rays (*2*) reflects the slightness of the effect, as shown by the very weak birefringence, and it is a common situation in weakly birefringent cubic crystals. The permanent destruction of the birefringence on heating (*2*) must correspond, in this interpretation, to breaking of carbon-carbon bonds in the long-chain hydrocarbons.

It will be interesting to see whether the ideas advanced here are confirmed by a detailed single-crystal structural study, which is reported to be underway (*2*). Such a study is necessary to delineate detailed structural features such as Si—O—Si linkage bending, and distribution of guest molecules in the polyhedral cavities.

If the clathrate structure is correct, melanophlogite constitutes the first known example of a silica or tectosilicate framework in which the pentagonal dodecahedron occurs as a structural unit.

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6. D. Appleman, who kindly reviewed the manuscript, informs me that in work subsequent to the original paper (*2*) he has reached the conclusion that the space group of melanophlogite is in fact *Pm3n*, hence in complete agreement with that of chlorine hydrate. A symmetry degradation such as was implied by the earlier work thus seems now not to be a necessary feature of the melanophlogite structure.
7. A particularly helpful illustration of the 12-Å hydrate structure is given by L. Pauling, *College Chemistry* (Freeman, San Francisco, ed. 3, 1964), p. 461.
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10. This evidence was important originally in supporting the correctness of the proposed structure in spite of the different space group reported (*2*). We now know (*6*) that the *n*-glide extinction seems to be rigorously satisfied.
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12. Division of the Geological Sciences, contribution No. 1308. The ideas in this paper were first presented at a meeting of the Mineralogical Society of Southern California, 14 October 1963, in Pasadena. The calculations for Table 4 were carried out on the IBM 7094 by means of the CRYRM system designed by R. E. Marsh and his collaborators, whose help I gratefully acknowledge.

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Wisconsinan Age of the Titusville Till (formerly called "Inner Illinoian"), Northwestern Pennsylvania

Abstract. *Peat discovered below drift near Titusville, Pennsylvania, formerly called "inner Illinoian," has a carbon-14 age of 31,400 ± 2,100 years. The overlying drift, herein named Titusville Till, is therefore not Illinoian but is "late early Wisconsinan" or late Altonian of the Lake Michigan lobe classification.*

The correlation of glacial deposits in the Allegheny plateau in northeastern Ohio and northwestern Pennsylvania with those in other regions, especially with the type sections in the Mississippi valley, has been somewhat imprecise because organic material for C^{14} dating has been most elusive. The correlation and age assignment of the drift in the Grand River lobe outside the "Wisconsin" border in northwestern Pennsylvania are particularly uncertain. Peat, which by C^{14} assay is 31,400 ± 2,100 years old, has been discovered at Titusville, Pennsylvania, below drift called "Illinoian." For the first time this makes possible precise age assignment and provides a point of reference in the stratigraphic column for other tills at the surface and in the subsurface.

Beyond the Kent Till of Wisconsinan age in northwestern Pennsylvania (Fig. 1) a belt of older drift, mainly till, is from less than a mile (about 1 km) to 15 miles (24 km) wide. This drift was assigned an Illinoian age by Leverett (*1*); our studies during the years 1952 to 1957 showed that this older drift is of two ages, which we called "inner Illinoian" and "outer Illinoian" (*2*). Stratigraphic studies conducted in 1964, which were facilitated by deep new strip mines for coal and for limestone and by cuts for interstate highways, show that the "inner Illinoian" till extends westward beneath the Kent Till continuously to the Ohio-Pennsylvania state line and thence further west in Ohio. The color of this till, where it is oxidized, is so distinctly olive brown, in contrast to the yellow brown color of the Kent Till, that we have called it "olive till." At a few places beneath the Kent Till a truncated weathered zone on the "olive till" is preserved, which at some places consists of as much as 5 feet (1.5 m) of leached till with 1 foot or more of silty clay loam that is the preserved lower part of the B horizon of an ancient soil. At some deeper cuts, one to four tills are present below the "olive till," but which of these may be the '"outer Illinoian" is not yet determined.

Extensive bodies of gravel in the form of kames and kame terraces associated with the till called "inner Illinoian" are large enough to be commercial sources of sand and gravel and to be shown on a geologic map (*2*). Lewis C. Strawbridge operates a large gravel pit 0.5 mile (800 m) south of East Titusville, in the eastern part of the large kame terrace that extends for almost a mile on the south side of the valley of Pine Creek eastward from its junction with Oil Creek. In prospecting other parts of the deposit in the late spring of 1964, Strawbridge found at the base of the kame terrace, at the Venango-Crawford county line, 0.3 mile east of the SE corner of Titusville corporation, and 0.9 mile ENE of the famous Drake oil well, 1 foot of peat below 15 feet of gravel. The exploratory excavation was filled in, but shreds of peat are scattered on the surface and Strawbridge had saved a sample of compressed, silty, humic peat of about 100 cubic inches. The age of this peat is 31,400 ± 2,100 years (*3*). It is hoped that the existing gravel pit, the margin of which is now 0.25 mile to the E, will eventually be expanded so the peat may again be exposed, but this is some years in the future.

Till is associated with the gravel at several places in the terrace and is exposed at several places nearby. An extensive exposure of the till is in the south margin of a large gravel pit and in an adjacent deep cut (*4*) along Pennsylvania highway 8, Cherry Tree township, Venango County, about 1.6 miles S of the post office in Titusville, 1.2 miles SW of the Drake well, and 1.7 miles W of the Strawbridge pit. The till in the highway cut was described by Droste and Tharin (*5*), who made detailed analyses of the texture and clay minerals of the till in both unweathered and weathered zones. The till here is leached to a depth of 8.5 feet and oxidized to a depth of 16 feet.

We now propose to name this rock-stratigraphic unit the "Titusville Till." The type section is that already re-