MELANOPHLOGITE FROM MOUNT HAMILTON, SANTA CLARA COUNTY, CALIFORNIA

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Abstract

Melanophlogite, the rare polymorph of silica, occurs as sharp crystals lining fracture surfaces in a metamorphosed serpentine vein in the Franciscan formation 6 miles east of Mount Hamilton, Santa Clara County, California, the third recorded occurrence of this mineral. Associated minerals include quartz, cristobalite, dolomite, calcite, magnesite, and pyrite.

The mineral is cubic with $a = 13.404(5)$ Å and $V = 2408$ Å^3. The X–ray powder diffraction data is in excellent agreement with that of the Sicilian material.

Melanophlogite is colorless with an adamantine luster, $H = 6$–7. Fracture conchoidal with no cleavage. Density (calc.) $= 1.982$ g/cm^3; specific gravity (meas.) $= 1.990(10)$. Optically isotropic. Index of refraction varies from $1.436(2)$ for unexposed crystals to $1.423(2)$ for exposed crystals.

The crystals, measuring up to 5 mm along an edge, are simple cubes or multiple intergrowths. Modification of the cube edges by the tetrahexahedral form {210} is common. The six–fold pyramidal growth pattern and an unusual internal hopper–shaped structure are evident and reveal the growth regularity of the crystals.

Chemical analysis of unexposed crystals gives: SiO_2 96.18, C 0.84, H 0.79, O 2.24, sum 100.05 wt. % corresponding to 46 $SiO_2 \cdot C_{2.9}H_{22.7}O_{4.0}$. This material loses organic matter upon exposure to the atmosphere with a resultant zonal conversion to cristobalite. TGA shows 0.72 % weight loss below 800°C and 1.91 % above 800°C with major loss at 900° and 1000°C. RGA indicates only H_2O with a trace of CO_2 at 500°C. Structure stabilization is attributed to aliphatic hydrocarbons or their derivatives and possibly water in the polyhedral cavities of the clathrate structure.

Introduction

Melanophlogite, the rare polymorph of silica, has recently received considerable attention as a mineral species. The properties and character of this clathrate–type framework silicate have been investigated by Skinner and Appleman (1963), Appleman (1965), Kamb (1965), and Žák (1972). Guest molecules, both organic and inorganic in nature, occupy the large polyhedral cavities of the structure and are important in its formation and stabilization.

The classic occurrence of melanophlogite is in the sulfur deposits of Racalmuto and Lercara, Sicily where it occurs with cristobalite, quartz, sulfur, calcite, and celestite. A second world occurrence has been recently described by Žák (1967, 1968) from a metamorphosed Fe–

rhodochrosite horizon at Chvaletice, East Bohemia, associated with cristobalite, dolomite, rhodochrosite, pyrite, marcasite, and chalcedony.

In 1970 a third world occurrence of melanophlogite, consisting of large, well–crystallized samples on cristobalite, was discovered by the authors in a small metamorphosed serpentine vein east of Mount Hamilton, Santa Clara County, California. This paper presents the results of a study of the chemical and physical properties of melanophlogite from this interesting locality in relation to the unusual growth features and effects of weathering.

A type sample of melanophlogite from this locality has been deposited in the U. S. National Museum.

OCCURRENCE AND GEOLOGICAL SETTING

The melanophlogite locality is about 30 miles east of San Jose, California, in a roadcut on California Route 130. The exact locality is 6 miles east of Lick Observatory at Mount Hamilton and about 1/2 mile south of the Bayo Valley ranch in NE 1/4 sec. 6, T. 7 S., R. 4 E., Mount Diablo Meridian.

The area surrounding Mount Hamilton is essentially composed of Franciscan sandstones and shales of Jurassic age. The sediments are highly fractured and folded, often showing local intrusion by serpentine masses. Local metamorphism has altered portions of the serpentine to small silica–carbonate and eclogite bodies. The geological features of this area have been investigated by Crittenden (1951) and Bailey *et al.* (1964). A more detailed description of the area east of Mount Hamilton is given by Soliman (1965).

The contact zone exposed by the roadcut is located between the serpentine and a partially silicified arkosic sandstone. This zone has been subjected to several periods of hydrothermal activity and fracturing after its initial formation. These periods have produced a brecciated rock composed of rounded masses of silicified serpentine surrounded by quartz and dolomite seams. Small quantities of pyrite, magnesite, and calcite were the only accessory minerals noted in the seams.

After the breccia had developed it was again subjected to folding and transverse fracturing. Low–temperature and pressure silica–bearing solutions entered the fractures and formed cristobalite and melanophlogite along a limited section of the contact zone. These solutions were probably sulfur–free and low in organic content and were of an epigenetic origin. This is in contrast to the Sicilian melanophlogite that was characterized by Skinner and Appleman (1963) as having been precipitated from an organic medium of a syngenetic–diagenetic origin. Evidence

suggests that a complex paragenesis occurred at Mount Hamilton that is characterized by interchanging and overlapping periods of crystallization of cristobalite and melanophlogite. Žák (1972) describes the assemblage at Chvaletice as having formed under low temperature and pressure conditions of a metamorphic hydrothermal vein formation by Alpine paragenesis processes.

Morphology and Crystal Growth

Melanophlogite occurs as single crystals and multiple intergrowths of sharp cubes (Fig. 1) which range in size from 0.1 to 5 mm along an edge. The larger crystals often show contour–like growth lines on the surfaces and internal fracturing. Both single and intergrown crystals show pseudo hopper–shaped structures internally. Modification of the cube edges is a unique property of melanophlogite at this locality. Goniometric measurements of the interfacial angles (Table 1) shows conformity to the tetrahexahedral form {210}. Unequal development of these modified cube edges is common in contrast to the ideal shape (Figs. 2a, 2b). No explanation can be given for this
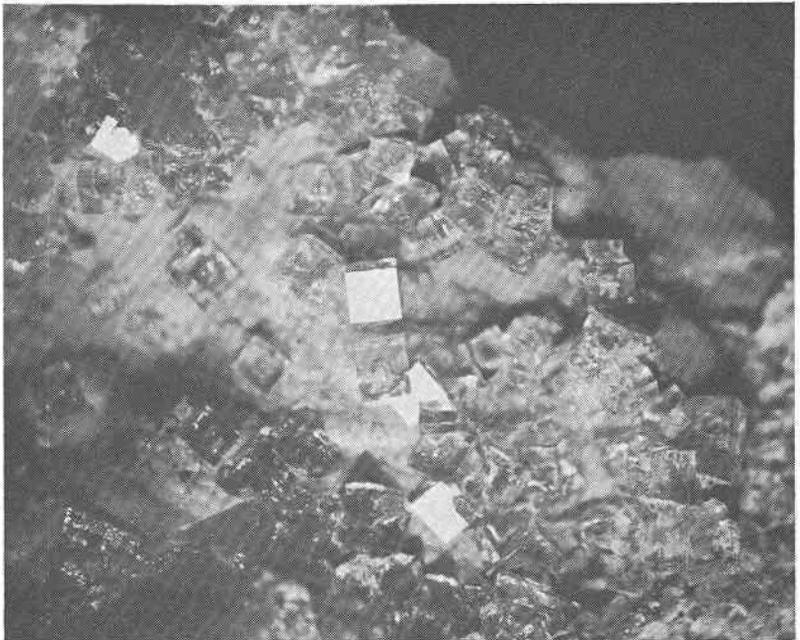

Fig. 1. Melanophlogite cubes, 1–3mm along an edge, with hopper-shaped structures on cristobalite.

TABLE 1. MELANOPHLOGITE ANGLE TABLE

	Forms	φ	ρ = A₃	A₁	A₂
a	100	———	0°00′	90°00′	90°00′
e	210	0°00′	23 33.5	90 00	53 25.5

modification tendency of melanophlogite. The crystals from Sicily and Chvaletice showed no positive indication of modification.

The internal features of the crystals can be divided into groups which reflect their growth habit. These are (1) single crystals which are clear and show excellent development of the six–fold pyramidal growth patterns described first by Bertrand (1880) and later by Skinner and Appleman (1963) on Sicilian material, and (2) crystals with pseudo hopper–shaped structures that display off–center variants in their growth pattern. There appears to be no relationship between these internal features and the development of the {210} crystal form.

This pseudo hopper–shaped structure consists of a void surrounding a pyramidal growth unit (Fig. 3b) and resembles a typical isometric hopper structure with the exception that the apex of the pyramid initiates near the (001) face rather than at the geometric center of the crystal. These pyramidal units often show unequal development; and preferential growth of one or more of these units, with the subsequent distortion of the remaining units, produces off–center variants whose pyramidal apices do not meet at the geometric center of the crystal. This unequal growth may so restrict the de-
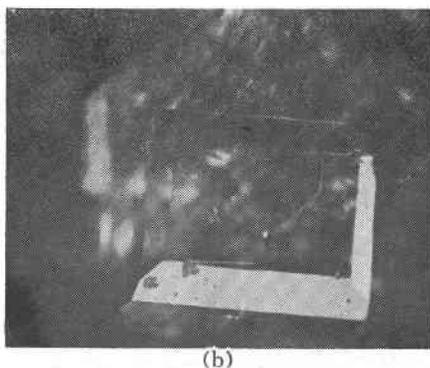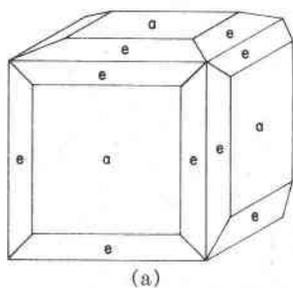

FIG. 2. Modification of melanophlogite cubes.
  (a) ideal cube modified by the {210} tetrahexahedron.
  (b) actual modified 2mm crystal showing typical unequal face development.
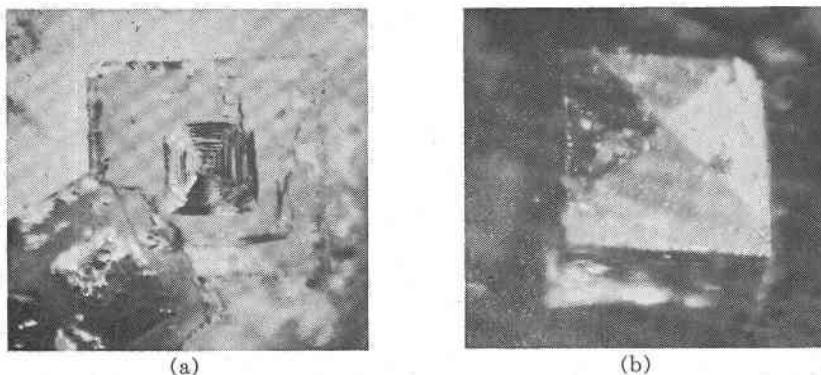
(a)   (b)

FIG. 3. Internal growth patterns of melanophlogite.
  (a) hopper–shaped internal growth in 1mm crystal.
  (b) six–fold pyramidal growth in 1mm crystal.

velopment of the opposite pyramidal units that they are often reduced to thin vestigial layers. A nucleation site near the surface of the silica solutions may account for this unusual growth condition.

PHYSICAL PROPERTIES

The crystals are colorless and transparent when unexposed but have a turbid white appearance when weathered. They have an adamantine luster, are quite brittle, and possess a conchoidal fracture with no cleavage. The Mohs hardness is between 6 and 7.

An examination of the samples during collecting indicated the possibility of variable chemical and optical properties. The samples were classified as (1) crystals with no visible effects of weathering from an unexposed section of the vein; (2) crystals that had been exposed to the atmosphere but were not visibly weathered; and (3) turbid white crystals that occurred as peripheral groups to type (2).

The specific gravity of type (1) crystals was determined on ten single crystals and several fragments on a Berman torsion balance using toluene as the immersion liquid. A total of 15 separate measurements were made and an average value of 1.990(10) obtained. This value compares favorably with that obtained by Žák (1968) of 2.005(5) on crystals of similar composition (Žák, 1972). The calculated density is 1.982 g/cm^3 based on 46 molecules of SiO_2 per unit cell (Kamb, 1965) plus the contribution of the guest molecules calculated from the chemical analysis. No significant differences in specific gravity were observed between the unexposed type and the two exposed types.

Single crystals of the three types were heated for 24 hours at 900°C in air and showed considerable variation in their reactions. The un-

exposed crystals, type (1), rapidly turned black and opaque within two hours while the altered crystals, type (2) either darkened moderately or remained clear after 24 hours heating, indicating a variable organic content. The turbid crystals, type (3), showed no visible darkening after 24 hours but became white and opaque. This opaqueness was determined to be the result of thermal fracturing of the crystals after the loss of essential stabilizing molecules. An X–ray powder pattern of this heated material corresponded to that of cristobalite plus a smaller fraction of melanophlogite. Complete conversion of type (3) was obtained after an additional 8 hours heating, while types (1) and (2) required an additional 24 hours at 1000°C to complete conversion.

Skinner and Appleman (1963) observed the conversion of melanophlogite to cristobalite after heating at 900° and 1000°C for a few days. From these observations it seems probable that the thermal energy required to convert melanophlogite to cristobalite is a function of the type and quantity of structure stabilizing molecules.

Under the polarizing microscope melanophlogite crystals (1–2 mm thick) are not visibly birefringent. Unexposed crystals, type (1), have an average index of 1.436(2) while the clear exposed crystals, type (2), have a lower average index of 1.423(2). This difference suggests a relation to the partial loss of the guest molecules and also confirms the absence of sulfur compounds in the structure. The refractive index of the turbid material, type (3), varies from 1.423(2) to 1.485(2). The population of crystal grains with this higher index is quite small (< 5 percent) and is related to a zonal transformation of melanophlogite to cristobalite under natural conditions of weathering. At this locality the melanophlogite has been exposed to the effects of weathering for approximately 30 years, and it appears that this period of time has been sufficient to effect a breakdown and loss of the guest molecules.

X–Ray Diffraction Data

Single crystals of the three types were carefully crushed to a fine powder and exposed for 12 hours using V–filtered CrK_α (2.29092 Å), K_{α_1} (2.28962 Å), and K_{α_2} (2.29351 Å) X–rays in a 114.59 mm diameter Debye-Scherrer camera on a GE XRD–5 unit. The powder data, computed with an internal standard of silicon, are given in Table 2 and were indexed to a cubic cell with no indication of a superstructure. The powder patterns were essentially identical except that type (3) showed several very weak lines which were attributed to cristobalite.

The peak intensities were read from the powder film with a Joyce

hkl	d(calc.)	d(obs.)	I/I₁	hkl	d(calc.)	d(obs.)	I/I₁
110	9.478	9.476	11	810,740,652	1.663	1.662	5
200	6.702	6.700	20	811,741,554	1.650	1.649	6
210	5.994	5.992	88	653	1.602	1.600	5
211	5.472	5.471	66	822,660	1.580	1.578	5
310	4.239	4.238	9	831,750,743	1.558	1.557	9
222	3.869	3.868	37	662	1.538	1.536	2
320	3.717	3.716	32	920,760	1.454	1.452	1
321	3.582	3.580	100	921,761,655	1.445	1.444	6
410	3.251	3.250	27	664	1.429	1.427	5
411,330	3.159	3.157	19	850,762	1.421	1.420	6
421	2.921	2.919	11	930,851,754	1.413	1.412	12
332	2.858	2.856	2	852	1.390	1.388	2
422	2.736	2.735	3	844	1.368	1.367	3
430	2.681	2.679	5	941,853,770	1.354	1.353	5
510,431	2.628	2.626	6	860, 10,0,0	1.340	1.340	3
520,432	2.489	2.488	13	764,861	1.334	1.334	5
440	2.370	2.371	9	862, 10,2,0	1.314	1.314	5
530,433	2.299	2.297	14	950,943	1.302	1.301	3
531	2.266	2.264	2	952, 10,3,1	1.278	1.277	1
600,442	2.234	2.233	8	870	1.261	1.261	4
611,532	2.174	2.174	7	871	1.255	1.256	<1
541	2.068	2.068	8	953	1.250	1.250	3
630,542	1.998	1.998	5	10,4,0	1.245	1.244	<1
631	1.976	1.976	2	10,4,2	1.224	1.223	2
444	1.935	1.935	9	962	1.219	1.218	3
632	1.915	1.915	3	873, 11,1,0	1.213	1.213	<1
710,550	1.896	1.896	2	10,4,3	1.199	1.199*	13
720,641	1.841	1.841	2	963	1.194	1.194*	9
721,633,552	1.824	1.824	6	880	1.185	1.185	<1
650,643	1.716	1.715	9	plus 7 lines to d = 1.150 Å			
732,651	1.702	1.699	3	*Denotes CrKα₁ lines			

Loebl microdensitometer and normalized with the strongest value set
at 100. Except for minor intensity differences and the absence of some
of the weaker lines, the data compare very well with the results ob-
tained by Skinner and Appleman (1963) on the Sicilian material.

The lattice consant was derived from the powder data using 34
data points between 2θ values of 84° and 158°. A lattice parameter
was calculated from each peak and these data were plotted as a func-
tion of the Nelson–Riley function (Barrett and Massalki, 1966) to
obtain the corrected values of the lattice parameter. The extrapolated

value of a was obtained by a least squares fit of the data. The experimental limits of each parameter were determined by the deviation of the experimental points from the calculated least squares curve. These calculations gave a unit cell value of 13.404(5) Å and a volume of 2408 Å^3.

The observed d are consistent with the extinction conditions of the type hhl with l odd (Nuffield, 1966) which conforms to the space group $Pm3n$ and is in agreement with the observed space group determined by Appleman (Kamb, 1965) on the Sicilian melanophlogite. However, without single crystal photographs, which would reveal the presence or absence of very weak reflections, positive distinction between the space groups $Pm3n$ and $P4_232$ cannot be made.

CRYSTAL CHEMISTRY

The impurity elements were determined by quantitative spectrographic analysis on a CEC direct–reading emission spectrograph by blending two samples with an internal standard composed of 21 elements. A similar analysis was made on the cristobalite associated with the melanophlogite. These results are tabulated in Table 3.

A complete chemical analysis of type (1) crystals was made to determine the constituents and their levels before work was begun on the remaining two types. A one gram sample was used in obtaining duplicate analyses on types (1) and (2), but only a single analysis of type (3) was made because of the limited amount of material available.

The evolution of H_2O was determined on duplicate samples in increments of 100° through 1000°C on a CEC moisture analyzer. The H_2O was considered to be both molecular and as OH derivatives of the organic molecules. A constant evolution of H_2O was recorded on type (1) crystals through 800°C of 0.08 weight percent per 100°C. The largest peak was observed at 900°C of 1.05 weight percent with a smaller peak at 1000°C of 0.83 weight percent. Proportionally smaller amounts of H_2O were recorded on types (2) and (3). The weight loss of each sample was nearly identical to the total water recorded indicating no appreciable volatiles in addition to H_2O. *TGA* of type (1) crystals showed 0.72 percent weight loss below 800°C and 1.91 percent above 800°C with the major loss at 900° and 1000°C, confirming that H_2O was the only volatile structural constituent besides small amounts of organic products.

Total carbon was determined by combustion using a Leco low-carbon analyzer. To distinguish between carbon present in the organic state and that possibly present as CO_2, a supplementary *TGA* was

TABLE 3.   SPECTROGRAPHIC ANALYSIS OF MELANOPHLOGITE AND OPAL
FROM MOUNT HAMILTON, CALIFORNIA.

Element	weight per cent	
	melanophlogite	opal
Si	Major	Major
Mg	0.0027	0.20
Al	0.011	0.06
Ca	< 0.003	0.47
Co	0.0078	<0.0001
Mn	0.0013	0.0011
Mo	0.0012	< 0.0007
Ni	0.0055	< 0.0007
Sn	0.0036	0.0013
V	0.010	< 0.003
B	< 0.0005	0.002
Na	0.0008	0.001
Cd	< 0.0002	< 0.0002
Cr	0.0004	0.0003
Cu	0.0011	0.0012
Fe	0.0024	0.003
Pb	< 0.0002	<0.0002
Ag	<0.0001	<0.0001
W	<0.0001	<0.0001
Zn	<0.002	<0.002
Sr	<0.0001	<0.0001

Elements not detected: Sb,Be,Bi,Au,Ce,Hg,In,K,Nb,Ta,Y,Th.

made which indicated only H_2O with a trace of CO_2 at 500°C. Sulphur was analyzed for on a Leco sulphur analyzer; however it was not detected at an analytical level greater than 0.01 weight percent. Hydrogen was determined as H_2O from the combustion of the carbon analysis to give a total hydrogen, and also by a continued analysis of the samples used for H_2O evolution. The remainder of the sample was analyzed for SiO_2 by standard wet methods. Comparative chemical data for melanophlogite are given in Table 4.

A formulation of the guest molecule content for type (1) crystals based on the unit cell content of 46 molecules of SiO_2 proposed by Kamb (1965) and a cell edge of 13.404 Å leads to 46 $SiO_2 \cdot C_{2.01}H_{22.69}O_{4.02}$ or approximately 46 $SiO_2 \cdot C_2H_{21}O_3 \cdot H_2O$ if the water below 800°C is considered to be molecular as suggested by the RGA and TGA. The two weathering stages of melanophlogite give formulas which reflect the breakdown and removal of the organic content and are respectively for type (2) 46 $SiO_2 \cdot C_{0.92}H_{9.12}O_{1.33}$ and for type (3) 46 $SiO_2 \cdot C_{0.18}H_{2.60}O_{0.61}$.

TABLE 4. CHEMICAL ANALYSES OF MELANOPHLOGITE.

Constituent	Weight per cent				
	This study			Žák (1972)	Skinner & Appleman (1963)
	type(1)	type(2)	type(3)		
SiO_2	96.18	98.45	99.4	94.6	92.4
C	0.84	0.39	0.08	0.9	1.2
H	0.79	0.32	0.09	0.6	0.81
O	2.24	0.76	0.36	2.6	3.40[a]
S	<0.01	<0.01	<0.01	0.1	2.3[a]
Total	100.05	99.92	99.93	98.8	100.11

[a]Recalculated from oxides.

The probable combinations of the guest elements are: C + H + O, H + O, and C + O and likely constitute aliphatic hydrocarbons or their derivatives and water. Small amounts of CO_2 may be present.

The Mount Hamilton melanophlogite shows close agreement with the unit cell edge of Skinner and Appleman (1963) although the guest element levels are different, in addition to the sulfur. The close similarity between the Mount Hamilton and Chvaletice guest element content is interesting in light of the symmetry difference. A comparison of the known properties of melanophlogite are presented in Table 5. Differences in the structure position and configuration of

TABLE 5. PHYSICAL AND CHEMICAL PROPERTIES OF MELANOPHLOGITE.

Parameter	This study	Žák (1972)	Skinner & Appleman (1963)
G.	1.990(10)	2.005	2.052(13)
n	1.436-1.423	1.457	1.467
Symmetry	cubic	tetragonal-pseudocubic	cubic
S.G.	Pm3n (?)	P4$_2$/nbc	Pm3n[a]
a (Å)	13.404(5)	26.82(3)	13.402(4)
c (Å)	—	13.37(2)	—
Z[c]	$46SiO_2 \cdot X$	$46SiO_2 \cdot X$	$46SiO_2 \cdot X$
X	type (1) $C_2H_{23}O_4$ (2) $CH_9O_{1.3}$ (3) $C_{.2}H_{2.6}O_{.6}$	$C_2H_{17}O_5S_{.1}$	$C_3H_{24}O_6S_2$[b]

[a]Appleman (Kamb, 1965).

[b]Calculated from chemical analysis.

[c]From Kamb (1965).

the guest molecules in the clathrate structure may account for the tendency to distort the cubic lattice. These and other problems concerning the growth and stabilization of melanophlogite must await identification of the guest molecules and their positions in the clathrate structure.

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