MELANOPHLOGITE, A CUBIC POLYMORPH OF SILICA[1]

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Abstract

Melanophlogite, found as single crystals and interlocking intergrowths on sulfur crystals from Agrigento (formerly Girghenti) and Palermo in Sicily, is a low temperature cubic polymorph of silica, space group $P4_232$, $a = 13.402 \pm 0.004$ Å, $Z = 48$ [SiO$_2$]. The index of refraction is 1.425 ± 0.002 and the calculated density 1.99 g/cc.

New chemical analysis reveals a [C+H+S] content of at least 6% in all samples. These elements are present in organic films trapped on the cube growth surfaces. The physically included organic matter is the brown pigmenting agent in melanophlogite, and is the material which turns black when heated, giving melanophlogite its name. The pigment is optically anisotropic, causing the cubic melanophlogite crystals to exhibit a weak birefringence. The optical anisotropy is destroyed on heating due to breakdown of the organic inclusions.

Introduction

Historical. Melanophlogite was first described and named as a new mineral by von Lasaulx (1876 a, b), although it is stated by Spezia (1892, p. 8) that G. Alessi had recorded a mineral apparently identical with melanophlogite as early as 1827. The compound recorded, but not named by Alessi, the specimen studied and described by von Lasaulx, and all specimens of melanophlogite subsequently studied and described by other workers, came from the Sicilian sulfur deposits, and in particular from those at Racalmuto in Agrigento Province[2] and at Lercara in Palermo Province. The name melanophlogite describes the fact that the mineral turns black when heated.

Von Lasaulx and succeeding workers realized that the composition of melanophlogite was essentially SiO$_2$. They were puzzled, however, by the presence of organic matter, sulfur and water up to a total of 12% in their analyses. It was suggested at an early date that the organic matter was a mechanically incorporated pigmenting agent, which caused the color zones in the melanophlogite crystals and gave the mineral its peculiar thermal properties. When heated, this organic material broke down, in part, to amorphous carbon and caused the mineral to turn black. The presence of the sulfur remained a problem.

Von Lasaulx described melanophlogite as a cubic form of silica with a hardness of about 6.5 to 7 and a specific gravity of 2.04 at 17.5° C. Because of the perfection of the cube form of some of his specimens, he

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] Girghenti, the old name for Agrigento, is used in all of the older literature of melanophlogite. The name was officially changed in 1927.

suggested that the mineral was pseudomorphous after fluorite or halite. Von Lasaulx (1879) later attempted to find melanophlogite at Agrigento and Palermo, but due to its scarcity was unable to do so. Brezina (1876) suggested, from the similar reported compositions, that melanophlogite resembled a sulfur-containing colloidal silica described from Greece.

Bertrand (1880) reported that the mineral exhibited anisotropic optical properties which could not possibly belong to a cubic compound. These observations were further elaborated by Spezia (1883) and by Friedel (1890).

Spezia (1883) made a detailed optical, thermal and chemical study of melanophlogite and added greatly to the available data. Later (1892), he repeated some of his previously published observations, and listed melanophlogite with quartz, chalcedony and opal as one of the forms of silica found in the Sicilian sulfur deposits.

Spezia's (1883) accurate descriptions of partly altered melanophlogite crystals and melanophlogite overgrowths on quartz and opal nucleii are the most careful and detailed ever published. His chemical studies demonstrated beyond doubt that the carbon reported in the chemical analyses was present as a physically incorporated pigment.

Pisani (1888) reported a chemical analysis of some colorless cubes of melanophlogite which reached a maximum size of 2 mm on an edge. He suggested that melanophlogite might be a compound of silica and sulfuric acid. Streng (1890, 1891) discussed the whole problem and suggested that sulfur was present in solid solution in the form of SiS_2.

Mallard (1890) observed that many specimens of melanophlogite are more or less altered to quartz and that the optical anisotropy disappeared when the mineral was heated to about 400° C.

Friedel (1890) visited Sicily, collected many specimens of melanophlogite and described their occurrence in the sulfur deposits near Agrigento. He was impressed by the unusual abundance of bitumen in the mines where the melanophlogite was found, and by the beautiful crystals of sulfur and calcite on which the melanophlogite crystals had formed. His excellent chemical analyses of melanophlogite were the most reliable made up to that time, largely because of the abundant material at his disposal. Friedel (1891) strongly rejected Streng's suggestion that sulfur was present as SiS_2. He observed the weak optical anisotropy mentioned by Bertrand and was struck by its regular, consistent nature from crystal to crystal. Friedel's goniometric measurements of the crystals led him to believe that melanophlogite was actually tetragonal, departing very slightly from cubic symmetry, and that this was the reason for the optical anisotropy.

Bombicci (1891) and Panebianco (1891) both questioned aspects of

Friedel's study and suggested that melanophlogite did not have a fixed chemical composition, but that SO₃ was present in a form analagous to water of crystallization in a series of different hydrates. Bombicci (1891) also suggested that the presence of quartz cores in some melanophlogite cubes indicated a process of "melanophlogitisation" of quartz rather than a "quartzification" of melanophlogite. Friedel (1892) presented convincing arguments against these suggestions.

Zambonini (1906) summarized much of the significant work on melanophlogite and confirmed the previously reported optical properties. He contributed the very significant observations that the birefringence was strongest in the most heavily pigmented zones and that the temperature at which the birefringence disappeared differed from zone to zone, being as low as 150° C. for the relatively colorless, and hence pigment-poor zones, but over 300° C. for some of the darker colored, more heavily pigmented zones. Zambonini also made detailed goniometric measurements but could not substantiate Friedel's (1890) observations and conclusion that melanophlogite was tetragonal. Zambonini showed that the crystals were irregularly distorted and the average of all observations indicated that melanophlogite was geometrically cubic. The weak anisotropic optical properties were clearly those of the incorporated organic pigment, hence were not to be entered as evidence in favor of a nonisometric symmetry.

Manzella (1918) analyzed several crystals of melanophlogite, and found that the sulfur content varied noticeably from sample to sample and was related to the amount of pigmenting material. He established that both the organic matter and the sulfur were part of the pigmenting material.

Von Gliszczynski and Stoicovici (1938) examined a number of specimens of supposed melanophlogite by x-ray diffraction. The only crystalline phase they could find in their samples was quartz. They studied the orientation of the quartz, relative to the cube, and suggested that melanophlogite was a quartz paramorph after high cristobalite. Their samples were regular cubes, with a turbid-white color which we have observed to be characteristic of altered material. In view of our observations, and of the statements of Friedel (1890) and others who have collected melanophlogite in situ concerning the widespread alteration of melanophlogite and the rarity of unaltered crystals, it is not altogether surprising that von Gliszczynski and Stoicovici unfortunately used altered crystals for their studies.

Flörke (1959) disagreed with von Gliszczynski and Stoicovici's (1938) conclusions, and stated that it was unlikely that melanophlogite was a quartz paramorph after cristobalite. He did not object to the statement
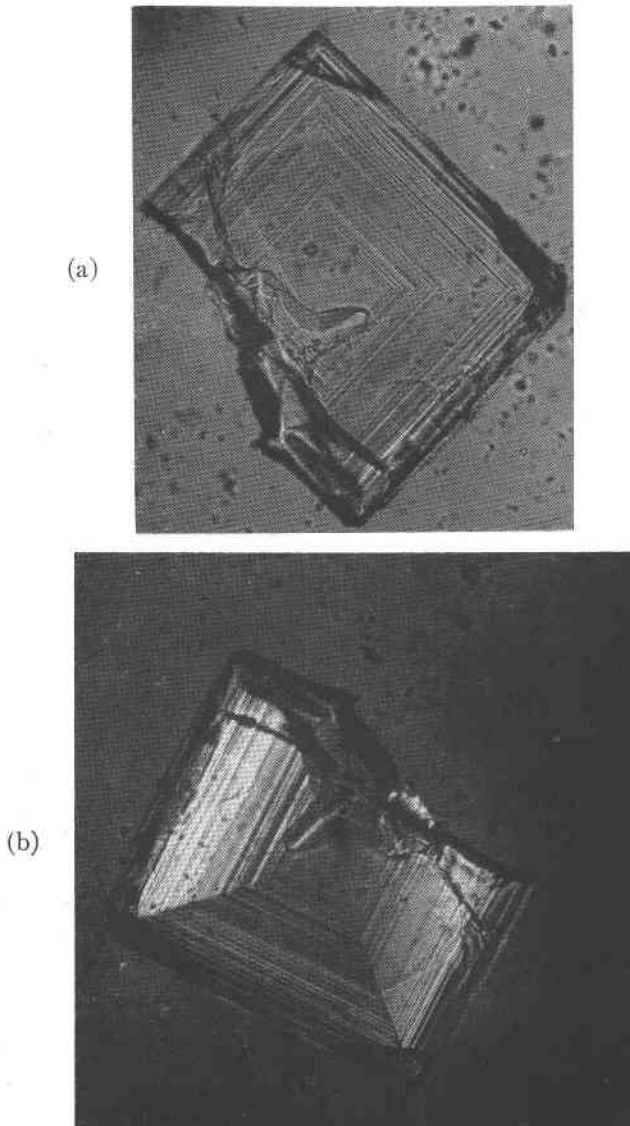
Fig. 1. Single crystal of melanophlogite 0.5 mm on an edge, U. S. National Museum No. C-1279. (a) Taken in plane-polarized light. Note the fine, regular zoning due to sub-microscopic films and inclusions of organic matter. (b) Taken with crossed nicols and with the gypsum plate inserted to emphasize the weak birefringence, which is due to the optical anisotropism of the included organic matter.

that SiO_2 was present in the form of quartz, but he preferred to consider fluorspar as the parent material.

Present Investigation. While in Europe in 1912, Dr. Waldemar T. Schaller purchased several fine specimens of melanophlogite from the mineral dealers Grebel and Wenden in Geneva. It was his curiosity about the nature of this strange mineral which first led us to investigate it further, and he graciously placed his specimens at our disposal. We were also fortunate to be able to examine U. S. National Museum specimens Nos. 93011 and C-1279. Both Dr. Schaller's specimens and those of the U. S. National Museum came from the Racalmuto sulfur mines in Sicily.

DESCRIPTION OF THE SAMPLES

Authentic melanophlogite has been described only from the Sicilian sulfur deposits;[1] from Racalmuto in Agrigento province and from Lercara in Palermo province. All the specimens available for the present study came from Agrigento province, but it is apparent from published descriptions that the Palermo samples are very similar.

Melanophlogite occurs as regular cubes with a maximum size of 2 mm on an edge, encrusting sulfur, calcite and, according to von Lasaulx (1876b), celestite crystals. The melanophlogite is sometimes, but not invariably, separated from the sulfur and calcite crystals by a thin film of opaline silica. In many instances it has grown on a nucleus of quartz or opal.

Crystals of melanophlogite can be found, on rare occasions, as single, undistorted individual cubes. More commonly, however, they occur as complex intergrown, rounded aggregates which may even coalesce to form a continuous crust over the sulfur crystals. The unaltered melanophlogite cubes range from colorless through pale yellow to a deep red-brown. They are all finely zoned (Fig. 1), and it is possible that many individual zones are smaller in width than the limit of resolution of the microscope.

From the specimens examined it is apparent that the sulfur and calcite crystals were the earliest minerals, and all evidence indicates that the opaline silica had ceased depositing before any melanophlogite formed. The sulfur crystals had not ceased growing when melanophlogite started forming, because some minor overgrowths of melanophlogite by sulfur are found. There is no evidence on any specimens that melanophlogite grows as oriented overgrowths on either sulfur or calcite.

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[1] Through the kindness of Dr. Wayne Ault we examined "melanophlogites" from the Hawaiian locality described by Payne and Mau (1946) and found them to be an opaline silica.

According to Friedel (1890) and others, quartz pseudomorphs after melanophlogite are very common, and fresh, unaltered crystals of melanophlogite are rare. Samples of altered melanophlogite examined by us were easily distinguished from unaltered materials by their opacity; altered material has a turbid-white color and lacks the sparkle and luster of the unaltered single crystals. The conditions under which this alteration occurs are not known.

Composition

Numerous analyses of melanophlogite, made on samples of unquestioned homogeneity, have been reported in the literature. They all show at least 88% SiO_2, with the remainder consisting of hydrogen, sulfur and carbon.

We carefully handpicked one gram of clear, colorless melanophlogite crystals from U. S. National Museum sample no. C-1279, making sure that no microscopically visible solid inclusions were present. This material was analysed by Blanche L. Ingram, U. S. Geological Survey, with the results shown in Table 1. The high content of silica confirms results of previous workers. Sulfur was reported as SO_3 but the form of its incorporation was not determined; a test for sulfur present as sulfide was negative.

Infrared absorption studies were carried out in collaboration with Dr. Henry Fales, of the National Institutes of Health, Bethesda, Md., using thin polished slivers cut from single crystals of melanophlogite. All possible care was taken to reduce absorption and surface scattering by the specimens. The presence of abundant hydrocarbon compounds was easily demonstrated, but specific compound identification proved impossible, although the presence of H_2O and CO_2 was confirmed and a doubtful identification of H_2S was obtained. It is unlikely that H_2S is actually present in the samples however, because of the negative sulfide test.

TABLE 1. CHEMICAL ANALYSIS OF MELANOPHLOGITE, U. S. NATIONAL MUSEUM
No. C-1279, FROM RACALMUTO, SICILY. ANALYST, BLANCHE L. INGRAM

Constituent	Weight per cent
SiO_2	92.4
SO_3	5.7
H	0.81
C	1.2
	Total 100.11

TABLE 2. SPECTROGRAPHIC ANALYSIS OF MELANOPHLOGITE, U. S. NATIONAL MUSEUM No. C-1279, FROM RACALMUTO, SICILY. ANALYST, HELEN W. WORTHING

Element	Weight per cent	Element	Weight per cent
Al	<0.026	B	0.01
Fe	0.005	Ba	0.0005
Mg	0.0015	Cr	0.00015
Ca	<0.001	Cu	0.005
Na	0.015	Ni	0.001
Ti	0.0003	V	0.0003
Mn	0.0002	Zr	0.0007
Ag	<0.000082		

Looked for, but not detected: K,P,Au,Be,Bi,Cd,Ce,Co,Ga,Ge,Hf,Hg,In,La,Li,Mo,Nb, Pd,Pt,Re,Sb,Sc,Sn,Sr,Ta,Te,Th,Tl,U,W,Y,Yb,Zn,F.

The incorporation of organic material into melanophlogite crystals does not seem surprising, in view of the abundant bituminous liquids in the sulfur mines. Friedel (1890) stated that all the galleries he entered in the sulfur mines were dripping with bitumen, and it is possible that the melanophlogite may actually have been deposited from the bitumen.

Spectrographic analysis by Helen W. Worthing, U. S. Geological Survey (Table 2) did not reveal the presence of any elements in quantities greater than 0.02%, other than the major elements reported in the chemical analysis (Table 1).

PHYSICAL PROPERTIES

Optical properties. All melanophlogite crystals examined were zoned. The zoning is parallel to the cube faces and very regular (Fig. 1a), and individual zones do not measurably vary in width around the crystal. The color zoning makes it difficult to measure indices of refraction for two reasons. First, the density of pigmentation affects the refractive index so that the measured value varies slightly from zone to zone. Second, the pigmenting materials form almost continuous films, and because the zones are so closely spaced, it is not easy to get a good measurement of melanophlogite alone. The index of refraction measured is always the composite value for melanophlogite plus pigment. The average index for all melanophlogite crystals plus pigment, measured regardless of zones, is 1.467 ± 0.005. The true index of refraction for melanophlogite is best measured on a heated crystal, in which the organic pigments are broken down and can be more easily seen due to the production of opaque carbon. Once the pigment is clearly visible it can be avoided, although a very high magnification is necessary to do so. The index of refraction in sodium light, determined on crystals in which

the organic matter had been broken down by heating, is 1.425 ± 0.002. The great difference between the true index of melanophlogite and the apparent index, obtained on a composite crystal, indicates a high index of refraction for the organic pigment. This is probably caused by the sulfur, present perhaps as an organic sulfur compound or even as finely divided free sulfur in the pigment.

Bertrand (1880) first observed that crystals of melanophlogite always appear to be composed of six individuals with the form of tetragonal pyramids. These individuals are related by an apparent twin law so that the bases of the pyramids are the faces of a cube, and the apices of the pyramids meet at the center of the cube. The "composition" surfaces between the apparent twinned individuals coincide with the planes parallel to {110} joining opposite edges of the cube. This phenomenon can be observed only under crossed nicols, and because the birefringence is low, the effect is enhanced by insertion of the gypsum plate (Fig. 1b).

We have confirmed the observations of earlier workers, previously mentioned, that the birefringence observed in melanophlogite is due entirely to the included organic pigment and is not a property of melanophlogite itself. The apparent twinning is also due to the optical anisotropy and orientation of this organic material. The organic pigment was trapped as the crystals grew, forming a series of concentric, uniform films parallel to successively larger {100} forms (Fig. 2). Since the organic material is not crystalline, it is probable that the birefingence is caused by the orientation imposed on the organic molecules while the pigment was being deposited as a film on the growing cube faces.

The pyramidal shape of an individual of the apparent twin is due, therefore, to a stack of thin, parallel, very closely spaced organic films, representing successive positions of a cube face of the growing crystal. The effect is analogous to the stacking of individual rock layers one upon the other to form the Great Pyramid of Cheops. The similarity of orientation in the organic molecules parallel to a particular (100) face causes pyramidal segments of the crystal to behave optically like individual members of a twin. The regularity of the zoning and the perfectly repeated optical effects do not bear witness to the perfection of twinning, as stated by Friedel (1890), but rather demonstrate the regularity of growth of the melanophlogite crystals.

Crystallographic properties. X-ray diffraction photographs of melanophlogite single crystals, taken by the Buerger precession method, show that the crystals are cubic, space group $P4_232$, with a cell edge $a = 13.41 \pm 0.02$ Å. The cell contains 48 formula units of SiO_2.

To dispel completely any notion that the optical anisotropy results from a symmetry lower than cubic, and to eliminate the possibility

that the peculiar pyramidal structures are in fact individual crystals twinned in such a manner as to give the precession photographs a false symmetry, we carefully ground a single cube so that only one such pyramidal individual remained. Buerger precession photographs of this individual, taken with MoKα radiation, were identical in all respects with those from complete single cubes and confirmed the cubic space group and cell edge given above.

X-ray powder diffraction data were obtained on a finely ground split from the sample submitted for chemical analysis. The data are presented in Table 3. The 49 lines measured can be unequivocally indexed on a cubic cell with $a = 13.402$ Å. The cell edge of melanophlogite was refined by measuring the positions of the (630) and (631) reflections relative to reflections from pure powdered metallic silicon, used as an internal standard. The cell edge of silicon used for the calculations was 5.43054 ± 0.00017 Å at 25° C. (Parrish, 1960). Repeated oscillations were made with a high-angle goniometer at a traversing speed of $\frac{1}{8}$° per minute, repacking the powder in the aluminum specimen holder

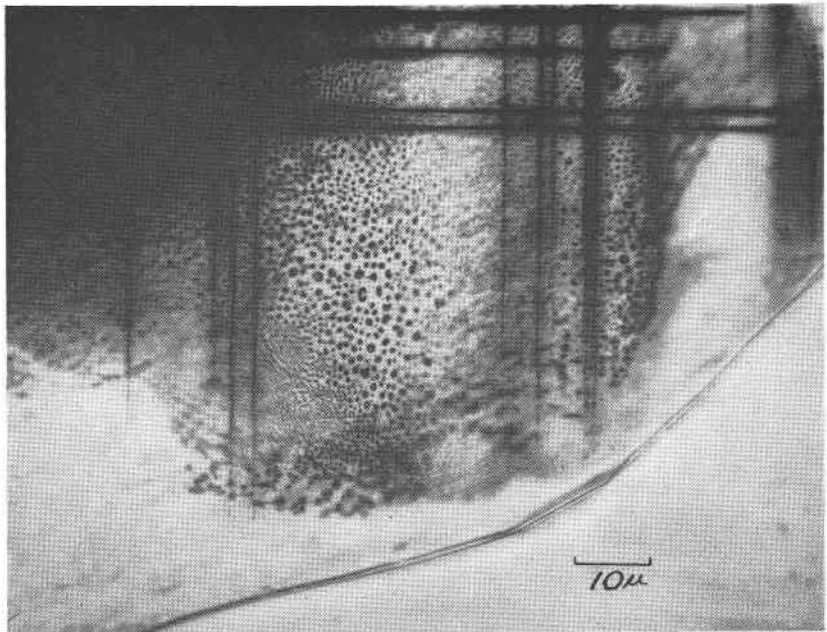

FIG. 2. Portion of a single crystal of melanophlogite heated to 800° C. for 2 hours. The included organic matter has broken down in part to opaque carbon. The photograph is taken perpendicular to a plane of tiny inclusions which is parallel to a cube face in the host melanophlogite crystal. The black lines are planes of inclusions, viewed edge on, parallel to the other two cube-face directions.

TABLE 3. X-RAY POWDER DIFFRACTION LINES, RECORDED IN CuKα RADIATION WITH A 114.59 MM DIAMETER CAMERA, WILSON TECHNIQUE

Intensities (I) are visual estimates based on a scale of 10 for the most dense line. Lines are indexed on a cubic cell with $a = 13.402$ Å. Cut-off on d = 15 Å.

I	hkl	$d_{obs.}$	$d_{calc.}$	I	hkl	$d_{obs.}$	$d_{calc.}$
3	110	9.470	9.477	2	631	1.976	1.976
3	200	6.700	6.701	4	444	1.938	1.934
8	210	6.000	5.994	$\frac{1}{2}$	700, 632	1.915	1.915
6	211	5.470	5.471	1	710, 550, 543	1.894	1.895
1	310	4.238	4.238	$\frac{1}{2}$	720, 641	1.842	1.841
7	222	3.870	3.869	1	721, 633, 552	1.824	1.824
5	320	3.717	3.717	$\frac{1}{2}$	642	1.791	1.794
10	321	3.579	3.582	$\frac{1}{2}$	730	1.760	1.760
1	400	3.350	3.351	2	650, 643	1.717	1.716
5	410, 322	3.251	3.250	1	732, 651	1.703	1.702
4	411, 330	3.159	3.159	1	810, 740, 652	1.663	1.662
$\frac{1}{2}$	420	2.994	2.997	2	811, 741, 554	1.650	1.650
2	421	2.925	2.925	$\frac{1}{2}$	820, 644	1.627	1.625
1	332	2.855	2.857	1	653	1.602	1.602
1	422	2.736	2.736	1	822, 660	1.580	1.579
$\frac{1}{2}$	500, 430	2.678	2.680	1	831, 750, 743	1.559	1.558
$\frac{1}{2}$	510, 431	2.625	2.628	$\frac{1}{2}$	662	1.538	1.537
3	520, 432	2.489	2.489	$\frac{1}{2}$	840	1.500	1.498
$\frac{1}{2}$	440	2.370	2.369	$\frac{1}{2}$	911, 753	1.471	1.471
3	530, 433	2.299	2.298	1	921, 761, 655	1.446	1.445
$\frac{1}{2}$	531	2.267	2.265	2	930, 851, 754	1.413	1.413
2	600	2.235	2.234	$\frac{1}{2}$	844	1.369	1.368
2	611, 532	2.175	2.174	1	941, 853, 770	1.355	1.354
2	541	2.068	2.068	$\frac{1}{2}$	1000, 860	1.340	1.340
1	630, 542	2.000	1.998				

after every third oscillation. The specimen was repacked five times. Line profiles were measured by projecting the center lines of the Kα₁ profiles down to an average radiation background level and measuring the peak positions relative to the position of the standard silicon peak with an accurately graduated scale. This procedure gave a cell edge of 13.402 Å at 25° C. with a standard deviation for an oscillation of ±0.004 Å, derived from fifteen oscillations.

Measurements were repeated on the samples of melanophlogite after heating them for various lengths of time and at different temperatures. No change from the unheated samples was observed in the cell edge. A sample heated in air at 800° C. for 16 days had a weight loss of 2.18% and had turned jet black in color. Under a high-power oil immersion lens the black color was observed to be due to myriad tiny carbon flakes

strung out on planes parallel to the cube faces. These flakes, representing the degraded organic pigment of the original crystal, can be seen in Fig. 2. X-ray powder diffraction patterns of the heated samples were just as clear and sharp as those of the unheated samples. The cell edge was determined in exactly the same manner as for the unheated sample and was found to be 13.402 Å at 25° C., with a standard deviation of ±0.005 Å.

We conclude that the organic pigment is mechanically included in the crystals, and does not affect the crystal structure of melanophlogite.

The calculated density of melanophlogite, using a value of 6.023×10^{23} for Avagadro's number, is 1.99 g/cc. The specific gravity was determined by repetitive measurements on 8 nearly colorless crystals of melanophlogite, ranging from 6 to 20 mg in weight, using toluene as an immersion liquid on the Berman torsion balance. Two observers made 64 separate measurements of the specific gravity, getting an average of 2.052 with a standard deviation of ±0.013. The discrepancy between the calculated and observed specific gravities is certainly due to the included pigmenting material. The fact that the pigment raises the apparent specific gravity is interpreted as being due to the high sulfur content, which might reasonably be expected to give the pigmenting material a specific gravity greater than 2.

Breakdown of melanophlogite. The obvious changes which occur when melanophlogite is heated, namely, the loss of apparent birefringence and the jet black color imparted to the specimen, are properties derived from the included organic matter. Melanophlogite itself is stable at high temperatures for long periods. Dry runs at 800° C. for periods as long as 20 days did not reveal any changes in physical properties. At 900° C. and 1000° C. however, changes can be observed after a few days heating, and the breakdown product is invariably cristobalite.

Hydrothermal runs at 300°, 400° and 500° C. and at 2000 bars H_2O pressure, with melanophlogite and water as starting materials, all yielded quartz, H_2S, and organic matter.

Melanophlogite is not stable in a stress field. A single crystal of melanophlogite ground in a Bond sphere grinder for five days inverted almost completely to fine-grained quartz. The quartz grains had random orientations with respect to the original melanophlogite crystal, the orientation of which was apparent from the still observable, and unchanged, zoning of the organic inclusions. The ground sphere gave an x-ray powder diffraction pattern characteristic of fine-grained quartz, with no evidence of preferred orientation.

After this experience with a single crystal which inverted to quartz,

we ground a 100 mg sample of melanophlogite in an ordinary mechanically driven laboratory mortar and pestle. Within half an hour, more than 90% of the melanophlogite had inverted to quartz, and within an hour total inversion had occurred.

CONCLUSIONS

Melanophlogite is a cubic polymorph of silica, less dense than silica glass. The organic matter and sulfur reported in all analyses are due to films of sulfur-bearing organic pigment, trapped on the faces of the crystals as they grew. This incorporation of organic matter suggests that melanophlogite may actually have precipitated directly from an organic medium; although the method of precipitation, whether by breakdown of organo-silica compounds, by direct precipitation of SiO_2 from solution or even by aggregation of colloidal silica, is not known.

The apparently anisotropic optical properties of melanophlogite are not those of the host mineral, but are properties of the included organic film, which is not crystalline but is birefringent by virtue of an orientation imposed on the organic molecules incorporated in the film. That melanophlogite itself is isotropic can be verified by destroying the birefringence of the organic film by heating it at temperatures as low as 150° C.; this treatment does not affect in any way the properties of the host mineral.

The occurrence of melanophlogite as crusts and overgrowths on sulfur crystals indicates that it must have formed at temperatures below 112° C., the melting point of sulfur. Dessau *et al.* (1962) have recently summarized the geology of the Sicilian sulfur deposits, pointing out that the sulfur is almost certainly of biogenic origin, and that suggestions for a volcanic origin cannot be substantiated. Thus, it seems possible that melanophlogite was formed as an end-product of the syngenetic-diagenetic processes which gave rise to the sulfur deposits and to their enclosed bituminous fluids.

The final proof that melanophlogite is a valid polymorph of silica is that it obeys the linear relation between the specific gravity and mean index of refraction, repeatedly demonstrated for silica polymorphs having four-coordinated silicon (Fig. 3). It is noteworthy that melanophlogite is less dense than silica glass. This is also true of the fibrous form of silica described by Weiss and Weiss (1954), which has a specific gravity of 1.96–1.98. Weiss and Weiss have shown that their fibrous silica is isomorphous with SiS_2 and is orthorhombic with a $a = 4.72$ Å, $b = 5.16$ Å, $c = 8.36$ Å. The new Weiss form of silica (silica W) has not been plotted on Fig. 3 because the indices of refraction are not known. There does not appear to be any structural similarity between melanophlogite and silica W.
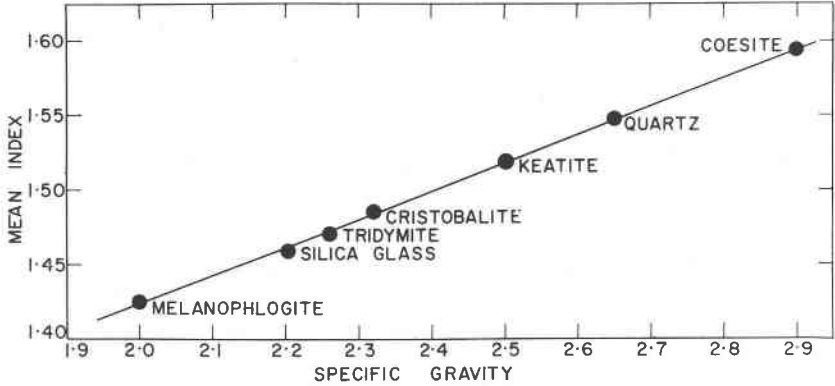
FIG. 3. A plot of mean index of refraction versus specific gravity, showing that melanophlogite follows the linear relation observed for the polymorphs of silica containing silicon in tetrahedral coordination. The data used to construct the plot are from Sosman (1927), Keat (1954), Dachille and Roy (1959) and Boyd and England (1960).

A complete crystal-structure analysis of melanophlogite is now in progress, the results of which will be published shortly in another paper.

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