

## THE NATURE OF CHRYSOCOLLA FROM INSPIRATION MINE, ARIZONA

MING-SHAN SUN,

*New Mexico Institute of Mining and Technology, Socorro, New Mexico.*

### ABSTRACT

Abundant chrysocolla occurs in the oxidation zones of the metallized Precambrian Pinal schist and Tertiary Schultze granite in the vicinity of Inspiration mine, Arizona. This chrysocolla is not a definite chemical compound but a hydrogel containing mainly  $\text{SiO}_2$ ,  $\text{CuO}$  and  $\text{H}_2\text{O}$ , and minor amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ . A cryptocrystalline phase is present in the chrysocolla, but its composition has not been determined. It does not have a montmorillonite structure according to DTA, dehydration, infrared and *x*-ray diffraction studies of the samples.

### INTRODUCTION

Inspiration mine is about one mile northwest of Miami, Arizona. Supergene enriched copper orebodies occur along the contact of Precambrian Pinal schist and Tertiary Schultze granite. Pinal schist is mainly a quartz sericite schist, containing locally minor amount of biotite, magnetite, andalusite, sillimanite, plagioclase and chlorite. Schultze granite grades into porphyry near margins. Intrusion of the Schultze granite into the Pinal schist was the cause for hypogene disseminated copper metallization both in the granite and in the schist.

Chrysocolla occurs in the oxidation zone of the metallized granite, granitic porphyry and the schist. It is especially rich on the surface of the granitic rocks in the vicinity of the Inspiration mine. It occurs in fissures, vugs, cracks and small openings. Commonly associated minerals are opal, quartz and malachite. Details of the geology and the copper deposits of the Miami mining district were reported by Ransome (1919).

### PHYSICAL PROPERTIES

Typical samples include moderate blue (5B 5/6) and light blue (5B 7/6) massive chrysocolla with colloidal structure; pale blue-green (5BG 7/2), very pale blue (5B 8/2), very pale green (10G 8/2), and light blue (5B 7/6) earthy and porous chrysocolla. The color is determined according to the National Research Council Rock Color Chart.

The colloform structure of many samples clearly indicates that the chrysocolla is formed from colloidal process. It usually associates with thin layers and vugs of opal and quartz. Some greenish samples contain malachite.

The index of refraction of chrysocolla grains varies from 1.45 to 1.55. It is higher for the massive variety, and lower for the earthy and porous

variety. All grains show aggregate polarization. The density of the grains varies from 1.93 to 2.30.

Chrysocolla grains between 100 and 120 mesh are leached in dilute hydrochloric acid. The form of the grains remains unchanged after their copper content was completely leached. Some of the leached grains are isotropic; most are anisotropic with very low birefringence. The anisotropic grains show aggregate, undulating and flamboyant extinction. Many grains show banded, fibrous, microspherulitic and microglobular structure. Capillary tubes filled with water in some leached grains are clearly seen through the microscope. Indices of refraction of air-dried leached grains range from 1.42 to 1.43.

#### CHEMICAL ANALYSIS

A complete silicate analysis of a bluish massive chrysocolla sample from Inspiration mine, Miami mining district, Arizona, is listed in Table 1. The percentage of water is derived by dehydration. The molecular ratio between  $\text{CuO}$ ,  $\text{SiO}_2$  and  $\text{H}_2\text{O}^{+100^\circ\text{C}}$  is 1.19:1.63:1.00. If the total water content is included, the ratio is 0.74:1.01:1.00.

The trace element content of the sample is shown in Table 2. The presence of Ni, Cr, Ag and B is characteristic of this chrysocolla.

Based on the chemical analyses, it is rather difficult to assign a chemical formula for the chrysocolla from Inspiration mine. A review of a number of selected publications indicates that this is rather a perennial

TABLE 1. CHEMICAL ANALYSES OF CHRYSOCOLLA

	I. Chrysocolla Inspiration mine, Arizona		II. Range of 18 analyses (Dana, 1911)
		(Mol. No.)	
$\text{SiO}_2$	41.28	.687	16.62-67.07
$\text{CuO}$	39.93	.502	19.0 -65.30
$\text{H}_2\text{O}$	7.60 <sup>+110° C.</sup>	.422	5.82-31.65
	4.60 <sup>-110° C.</sup>	.256	
$\text{Fe}_2\text{O}_3$	0.00		none- 1.97
$\text{Al}_2\text{O}_3$	3.53	.035	none-16.90 <sup>1</sup>
$\text{CaO}$	1.06	.019	none- 3.99
$\text{MgO}$	.42	.010	none- 3.15
$\text{P}_2\text{O}_5$	n.d.		none- 8.60 <sup>2</sup>
$\text{ZnO}$			none- 2.10
$\text{PbO}$			
etc.			

<sup>1</sup> Pilarite.

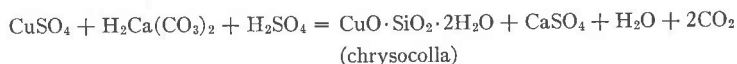
<sup>2</sup> Demidovite.

TABLE 2. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF CHRYSOCOLLA, INSPIRATION MINE, ARIZONA

Per Cent		Per Cent	
Fe	0.03	B	Trace
Mn	0.02	Ti	0.003
Ni	0.004	Ba	Trace
Cr	0.0008	Sr	Trace
Ag	Trace		

problem as far as the exact nature of chrysocolla is concerned. This problem is briefly discussed below.

Kemp (1906) suggested that the chemical formula of chrysocolla was  $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and its formation may be as follows:



Based on 18 analyses (Table 1), Dana stated that "true chrysocolla appears to correspond to  $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ " (Dana, 1911, p. 699).

Foote and Bradley (1913), based on the chemical analyses published in Dana's *System of Mineralogy* and Hintze's *Handbuch der Mineralogie*, calculated the molecular ratio of chrysocolla and found that only 12 out of 62 were reasonably close to the formula of  $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . The ratio of their three new analyses is also unsatisfactory for the assigned formula. They reached the conclusion that

"... chrysocolla is hydrogel or gelatinous precipitate . . . and the mineral is not a chemical compound and no formula should be assigned . . . but a solid solution of copper oxide, silica, and water as essential components, whose composition depends on the conditions of formation." (p. 184)

Schaller (1931) suggested that the name chrysocolla be restricted to a group name to include bisbeeite, cornuite, dioptase, plancheite and shattuckite. It may be appropriate to have a group name for all the hydrated copper silicates. However, the exact nature of bisbeeite, cornuite and plancheite is still unknown. De Leenheer (1937) reported black-gray chrysocolla from Congo mines, which contains a substantial amount of  $\text{Co}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . It is possible that the black-gray chrysocolla is a mixture of hydrogel of  $\text{Fe}_2\text{O}_3$ , hydrogel of  $\text{Co}_2\text{O}_3$  and chrysocolla. On the other hand, it is not clear whether  $\text{Co}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are essential constituents of the crystalline phase in chrysocolla. The crystalline phase of chrysocolla will be discussed in the section on x-ray analysis. De Leenheer also reported a black chrysocolla containing 4.24% of  $\text{Fe}_2\text{O}_3$  but without  $\text{Co}_2\text{O}_3$ . He concluded that both types evidently were formed

from colloidal solution along with katangite, a glassy blue or pale blue chrysocolla. Billiet (1942) in his investigation on the connection between chrysocolla, katangite, plancheite, bisbeeite, shattuckite and diopside did not question the validity of the assigned chemical formula of chrysocolla,  $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Chukhrov and Anosov (1950) came up with two chemical formulae for chrysocolla based on 14 chemical analyses:  $\text{Cu}_3(\text{OH})_2\text{Si}_4\text{O}_{10} \cdot n\text{H}_2\text{O}$ , and  $\text{Cu}_{3.5}(\text{OH})_2(\text{AlSi}_3)\text{O}_{10} \cdot n\text{H}_2\text{O}$ . They suggested that chrysocolla might be classified among the montmorillonite minerals for the following reasons:

- (1) The x-ray power diagrams are similar; (2) Medmontite and pilarite are intermediate members between montmorillonite and chrysocolla; (3) the presence of weakly bound water in both montmorillonite and chrysocolla; (4) the crystal habit of chrysocolla is tabular, the structure of a typical layer lattice such as that of montmorillonite; and (5) chrysocolla is biaxial negative.

Medmontite was defined as a copper-bearing mineral of the montmorillonite group by Chukhrov and Anosov (1950). It contains 13.25%  $\text{Al}_2\text{O}_3$  and was considered to be a Cu-end member of montmorillonite (see *Am. Min.*, Vol. 36, p. 793, 1951). Pilarite is defined as a  $\text{Al}_2\text{O}_3$ -rich chrysocolla (Dana, 1892, p. 699), which contains 16.9%  $\text{Al}_2\text{O}_3$ . Sumin and Lasheva (1951) reported three new modifications of chrysocolla from Mednorudyansk in the Ural, and they mentioned that chrysocolla was a Cu metasilicate with a variable content of  $\text{H}_2\text{O}$  and had a colloidal-amorphous structure. Yakhontova (1952) reported copper-rich varieties of chrysocolla and assigned two chemical formulae to these varieties:  $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and  $2\text{CuO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ . Furthermore, she rearranged these chemical formulae into a structural formula of montmorillonite according to Ross and Hendricks (1945) to show that chrysocolla has the same structure as montmorillonite. There are (OH) in octahedral positions of montmorillonite. It is very doubtful whether or not (OH) is present in chrysocolla. Shcherbina and Ignatova (1955) came up with another chemical formula for chrysocolla:  $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$ . Chukhrov *et al.* (1960) reported an aluminous chrysocolla whose formula is:  $1.05 (\text{Cu}, \text{Al}, \text{Fe})\text{O} \cdot 1.00 \text{SiO}_2 \cdot 0.72 \text{H}_2\text{O}^+ \cdot 0.78 \text{H}_2\text{O}^- \cdot \text{Al}_2\text{O}_3$  varies from 2.46 to 3.71%.

Because the amount of water in chrysocolla varies a great deal, many people prefer the following chemical formula:  $\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$ . Although numerous chemical analyses of chrysocolla are available, and many studies were carried out, the chemical formula and structure of chrysocolla have not been definitely determined. In other words, the so-called chrysocolla samples from many parts of the world do not have the same chemical composition.

TABLE 3. X-RAY POWER DIFFRACTION DATA OF THE CRYPTOCRYSTALLINE PHASE IN CHRYSOCOLLA, INSPIRATION MINE, ARIZONA  
RADIATION:  $\text{CuK}\alpha = 1.54178 \text{ \AA}$

d (Å)		I	d (Å)		I
15.0	(dark halo)		2.42	(diffuse)	1
4.39	(diffuse)	10	2.32	(diffuse)	1
2.77	(wide band)	5	1.585	(wide band)	3
2.88			1.642		
2.51	(wide band)	4	1.482	(diffuse)	8
2.62					
			1.321	(diffuse)	2

#### X-RAY ANALYSIS

Chrysocolla samples from the Inspiration mine were hand-picked with a pair of tweezers according to their texture and color, and x-ray patterns were taken. There are quartz, opal in the milky white and slightly greenish grains. Some green particles contain cryptocrystalline malachite. The pattern shown in Table 3 is quite persistent in most greenish and bluish samples, regardless of texture. Some samples are mostly amorphous, showing only the pattern of silica gel.

The 15.0 Å halo and the 4.39 Å diffuse line constitute a pattern of silica gel. This pattern is present in chrysocolla heated continuously to about 730° C. and also in chrysocolla after its copper content is completely leached in dilute hydrochloric acid. It is also present in silicic acid and in some opal. The other lines constitute another pattern which begins to disappear when the sample is heated to about 300° C., and which disappears completely at about 500° C. This pattern is characterized by several wide bands which have rather discernible edges. The d values of these wide bands were measured at the edges. This pattern may represent a cryptocrystalline phase in chrysocolla, the composition of which is unknown. It is called cryptocrystalline on the ground that its grain size is less than the optimum size for x-ray power diffraction, as indicated by the diffuse character of the powder lines. The amount of this cryptocrystalline phase in different samples is also unknown.

It is well known that the structure of many montmorillonite minerals persists to temperatures of the order of 800° C. or higher. None of the chrysocolla samples shows any crystalline structure after being heated to above 500° C. The 15.0 Å halo remains the same in chrysocolla heated

to about 730° C., whereas the basal reflection of montmorillonite, about 15.0 Å in many samples, changes according to the loss of interlayer water upon heating. This change is characteristic of the montmorillonite structure. One may suggest that the 15.0 Å halo of a copper-montmorillonite may remain unchanged upon heating. If so, we can only conclude that the structure of such copper-montmorillonite is different from the structure of a noncopper montmorillonite. Each pattern of the cryptocrystalline phase in chrysocolla and that of montmorillonite consists of a few powder lines, but their *d* values do not match each other. Medmontite has been suggested to be a copper montmorillonite. But its chemical composition, structure, and physical properties are still uncertain. Therefore, there are no substantial evidences to classify the chrysocolla from Inspiration mine among the montmorillonite minerals.

#### DEHYDRATION

A bluish massive chrysocolla was heated in a cylindrical electric furnace for five minutes at 100° C., and then cooled in a desiccator, and weighed. Heating of this sample is continued at 200° C., 300° C., up to 1000° C. The results indicate two steps of the loss of water. The first step ranges from room temperature to about 200° C., and the second step ranges from about 300° C. to 650° C. The first step represents 5.7 per cent absorbed water which occurs in capillary tubes and other openings. Half per cent of water is lost between 200° C. and 300° C. Removal of the absorbed water does not affect the *x*-ray powder pattern of the cryptocrystalline phase of chrysocolla. The amount of absorbed water varies in different samples. It also fluctuates depending upon the relative humidity. For instance, a sample, after being kept in a desiccator for several hours, weighed 7.5 mg. Its weight increased to a maximum of 9.3 mg in fifteen minutes when exposed to the humid atmosphere in the laboratory. The density of different chrysocolla grains at Inspiration mine varies from 1.93 to 2.30.

The second step of the dehydration curve represents 5.8 per cent water. Part of this water may be held in individual bubbles and requires higher energy for its removal. Because the cryptocrystalline phase of chrysocolla begins to disappear at about 300° C., and disappears completely at about 500° C., one may conjecture that some of the water of the second step belongs to this cryptocrystalline phase.

Leached chrysocolla which is dried at room temperature contains as much as 25 per cent water. Seventeen per cent of the water can be removed readily by heating the sample at 100° C. for five minutes, and the remaining eight per cent can be removed slowly by heating the sample to 800° C. The cryptocrystalline phase is absent in leached chrysocolla.

## DIFFERENTIAL THERMAL ANALYSIS

A DTA curve of chrysocolla was first published by Kauffman and Dilling (1950). Among many others, Toussaint (1957) studied natural hydrated copper silicates, including chrysocolla, by differential thermal analysis. Sun (1961), in comparing the DTA of shattuckite, published a short description of DTA of a chrysocolla sample of Tyrone, New Mexico. The DTA of the chrysocolla of Inspiration mine is substantially the same as those in previous publications. It is characterized by an endothermal peak of dehydration at 150° C. This peak corresponds to the first step of the dehydration curve. The down-drifting of the DTA curve between 400° C. and 625° C. may indicate another phase of dehydration which corresponds to the second step of the dehydration curve. A sharp exothermal peak at 700° C. indicates the crystallization of tenorite, and an exothermal peak at 950° C. indicates the crystallization of alpha-quartz, and in some samples alpha-cristobalite. An unknown phase represented by a few diffuse x-ray powder lines appears in samples heated to about 750° C. The thermal curve begins to show a strong endothermal reaction about 950° C., indicating the reduction of tenorite to cuprite. Trace amount of cuprite may appear in samples heated to about 850° C., when the partial pressure of oxygen in the furnace is low. None of DTA of the Inspiration chrysocolla and those published previously shows any endothermal peak around 500–700° C. indicating the removing of hydroxyl water, such as the case for montmorillonite of heptaphyllite type (Bradley and Grim, 1951). The chrysocolla DTA also does not include an endothermal peak at about 840° C. such as that of hectorite; it does not include endothermal peaks at 580° C. and 800° C. such as those in saponite. Therefore, it is rather clear that the DTA of the Inspiration mine chrysocolla is not the same as the DTA of montmorillonite.

## INFRARED ABSORPTION DATA

The infrared spectrum is obtained from a Perkin-Elmer 421 grating spectrophotometer with a NaCl prism. One mg of chrysocolla and 300 mg of KBr are used to form a KBr pellet at 18,000 psi pressure. The infrared spectrum of chrysocolla (Fig. 1) is characterized by a broad absorption band at 3410  $\text{CM}^{-1}$  ( $2.93\mu$ ), possibly indicating water molecules hydrogen bonded to each other and to SiOH (McDonald, 1958, p. 1170); a small band at 1614  $\text{CM}^{-1}$  ( $6.20\mu$ ) is assigned to absorbed water in pores and capillary tubes; a small band at 1450  $\text{CM}^{-1}$  ( $6.90\mu$ ) is of extraneous origin; a major band at 1010  $\text{CM}^{-1}$  ( $9.90\mu$ ) is assigned to the stretching vibration of Si-O. Two minor bands at 770  $\text{CM}^{-1}$  ( $12.99\mu$ ) and 660  $\text{CM}^{-1}$  ( $15.15\mu$ ) have no assignments. Chukhrov and Anosov (1950) suggested

that chrysocolla has the same structure as that of montmorillonite. Nevertheless, infrared absorption data indicate that the structure of the cryptocrystalline phase of chrysocolla and the structure of montmorillonite are not the same, as explained below.

There are two groups of OH in montmorillonite. One group occupies the octahedral positions and the other group constitutes the interlayer water. The amount of OH in the octahedral positions is usually definite, whereas the amount of the interlayer water varies according to the exchange cations in the interlayers and to the dehydration of the sample. The octahedral OH infrared absorption band is at about  $3590\text{ CM}^{-1}$  ( $2.79\mu$ ), and the OH absorption band of the interlayer water is at about  $3388\text{ CM}^{-1}$  ( $2.95\mu$ ). The frequency of these two bands varies slightly in different montmorillonite minerals. The intensity of the absorption band is proportional to the amount of OH in the sample. Buswell and Dudenbostel (1941) pointed out that Ca- and Mg-montmorillonite usually have one big absorption band at about  $3450\text{ CM}^{-1}$  ( $2.90\mu$ ). This big band is rather a coalesced band of the octahedral OH absorption band and the interlayer water absorption band. Ca- and Mg-montmorillonite have large amounts of interlayer water; therefore, the intensity of their inter-

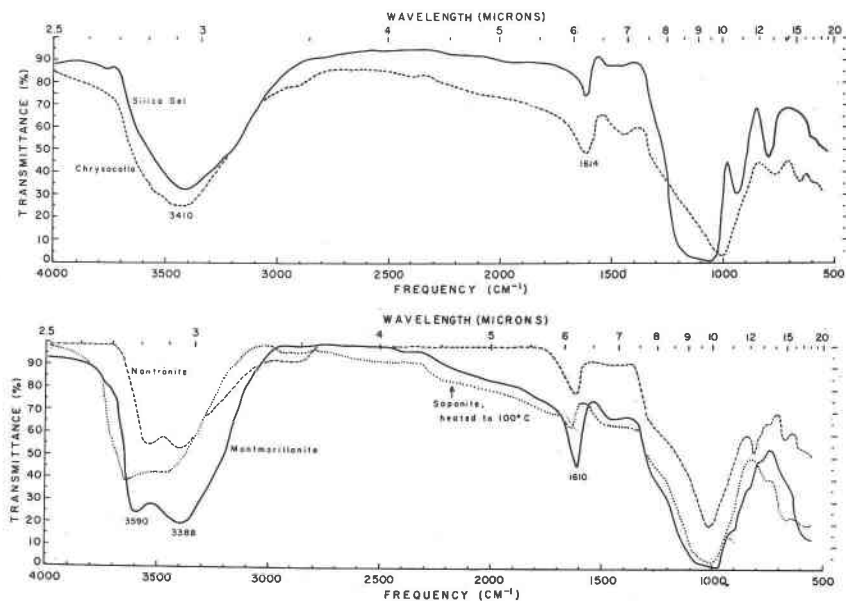


FIG. 1. Infrared absorption spectra of chrysocolla, silica gel, nontronite, montmorillonite and saponite.



layer water absorption band is usually greatly enlarged on the infrared spectrum. Thus, the absorption band of the octahedral OH is usually obliterated by the interlayer water absorption band. When the interlayer water is removed partly by dehydration, its absorption band becomes smaller and the octahedral OH band begins to appear on the spectrum. Because of poor resolution of older models of the infrared spectrophotometer, many previously published infrared spectra of montmorillonite minerals do not show clearly the two absorption bands of the octahedral OH and the interlayer water (Adler, Kerr, *et al.*, 1950). Roy and Roy (1957) showed that absorption band at  $2.9\mu$  of montmorillonite reduces in height upon heating of the sample, but remains strong even dried at  $300^{\circ}\text{C}$ . They thought that this band could not be assigned entirely to interlayer water. Nevertheless, the twin absorption bands at about  $2.90\mu$  is characteristic of montmorillonite minerals.

Infrared spectrum of a nontronite sample from Manito, Washington (API H-33-b) shows twin absorption bands at  $3540\text{ CM}^{-1}$  ( $2.82\mu$ ) and  $3388\text{ CM}^{-1}$  ( $2.95\mu$ ) (Fig. 2); a saponite sample from Reserve, New Mexico shows one broad band at  $3510\text{ CM}^{-1}$  ( $2.85\mu$ ) (Fig. 2). This saponite sample after being heated at  $100^{\circ}\text{C}$ . for five minutes shows a twin band, one at  $3640\text{ CM}^{-1}$  ( $2.75\mu$ ) and a broad one at  $3430\text{ CM}^{-1}$  ( $2.92\mu$ ). A hectorite sample from Hector, California (API H-34-c) barely shows a twin band, a sharp one at  $3650\text{ CM}^{-1}$  ( $2.74\mu$ ) and a broad one at  $3450\text{ CM}^{-1}$  ( $2.98\mu$ ). Some hectorite samples fail to show the band at  $3650\text{ CM}^{-1}$ . The transmittance per cent of these two bands is about the same. Hectorite samples heated to  $100^{\circ}\text{C}$ .,  $200^{\circ}\text{C}$ ., or  $300^{\circ}\text{C}$ . for five minutes show a clear band at  $3650\text{ CM}^{-1}$ , whereas the band at  $3450\text{ CM}^{-1}$  remains broad. In general, the infrared absorption spectra of hectorite are similar to that of saponite. Both hectorite and saponite are trioctahedral montmorillonites whose octahedral positions are completely filled. On the other hand, nontronite, common montmorillonite and beidellite are dioctahedral montmorillonite whose octahedral positions are only two-thirds filled (Ross and Hendricks, 1945). The vacant octahedral positions may help to produce better separation of the twin absorption bands of the two OH groups.

Infrared spectra of chrysocolla samples, including those heated to elevated temperatures, do not show twin absorption bands at about  $3500\text{ CM}^{-1}$ . It is similar to that of silica gel (Fig. 1). It is rather obvious that chrysocolla does not contain two groups of OH similar to that of the montmorillonite minerals. Therefore, it may be concluded that the structure of the cryptocrystalline phase of the chrysocolla samples from Inspiration mine is not the same as that of montmorillonite.

## REFERENCES

- ADLER, HANS H., PAUL F. KERR, *et al.* (1950) Infrared spectra of reference clay minerals. *API Project 49 Prel. Report No. 8*.
- BILLIET, V. (1942) Investigation on the connection between chrysocolla, katangite, plancheite, bisbeite, shattuckite, and diopside. *Verh. K. Vlaamsche Acad. Wetensch. Lett. Belgie*, vol. 4, 1-59 (see *Mineral. Abs.* 9, 231, 1946; or *Chem. Abs.* 38, 4219-5, 1944.)
- BRADLEY, W. F. AND R. E. GRIM (1951) High temperature thermal effects of clay and related materials. *Am. Mineral.* 36, 182-201.
- BUSWELL, A. M. AND B. F. DUDENBOSTEL (1941) Spectroscopic studies of base exchange materials. *Jour. Am. Chem. Soc.* 63, 2554-2558.
- CHUKHROV, F. V. AND F. JA. ANOSOV (1950) Nature of chrysocolla. *Zapiski Vsesoyuz Mineral. Obshch.* 79, 127-136 (see *Chem. Abs.* 44, 7724, 1950).
- S. I. BERKHIN AND V. A. MOLEVA (1960) Cuprous clay minerals. (see *Chem. Abs.* 55, 13188C).
- DANA, EDWARD SALISBURY (1911) *The System of Mineralogy*, 6th ed., John Wiley & Sons, New York.
- DE LEENHEER, L. (1937) Black-gray chrysocolla. *Naturv. Tijdschr.* 19, 86-90 (see *Chem. Abs.* 31, 5723-2).
- FOOTE, H. W. AND W. M. BRADLEY (1913) On solid solution in minerals. IV. The composition of amorphous minerals as illustrated by chrysocolla. *Am. Jour. Sci.* 4th ser. 36, 180-184.
- KAUFFMAN, A. J. JR. AND E. D. DILLING (1950) Differential thermal curves of certain hydrous and anhydrous minerals, with a description of the apparatus used. *Econ. Geol.* 45, 222-224.
- KEMP, JAMES FURMAN (1906) Secondary enrichment in ore-deposits of copper. *Econ. Geol.* 1, 11-25.
- MCDONALD, ROBERT S. (1958) Surface functionality of amorphous silica by infrared spectroscopy. *Jour. Phys. Chem.* 62, 1168-1178.
- RANSOME, F. L. (1919) The copper deposits of Ray and Miami, Arizona, *U. S. Geol. Survey Prof. Paper* 115.
- ROSS, CLARENCE S. AND STERLING B. HENDRICKS (1945) Minerals of the montmorillonite group, *U. S. Geol. Survey Prof. Paper* 205-B, 23-79.
- ROY, DELLA M. AND R. ROY (1957) Hydrogen deuterium exchange in clays and problems in the assignment of infrared frequencies in the hydroxyl region. *Geochim. Cosmochim. Acta*, 11, 72-85.
- SCHALLER, W. T. (1931) The chrysocolla group. *Am. Mineral.* 16, 112.
- SHCHERBINA, V. V. AND L. I. IGNATOVA (1955) New data on the geochemistry of copper in the supergene mineralization zone. *Zapiski Vsesoyuz. Mineral. Obshch.* 84, 353-4 (see *Chem. Abs.* 50, 6262, 1956).
- SUMIN, N. G. AND N. K. LASHEVA (1951) New modification of chrysocolla of the plancheite type from Mednorudnyansk in the Ural. *Trudy Mineral. Muzeya, Akad. Nauk S.S.S.R.*, 3, 106-121 (see *Chem. Abs.* 49, 12220, 1955).
- SUN, M.-S. (1961) Differential thermal analysis of shattuckite. *Am. Mineral.* 46, 67-77.
- TOUSSAINT, J. (1957) Thermal study of the natural hydrated copper silicates. *Ann. Soc. Geol. Belg.* 80, 287-95 (see *Chem. Abs.* 50, 8591a).
- YAKHONTOVA, L. K. (1952) Copper-rich variety of chrysocolla. *Vestnik Moskov. Univ.* 7 (6), Ser. Fiz. Mat. i Estestven Nauk 4, 123-30 (see *Chem. Abs.* 47, 12146i).

*Manuscript received, November 26, 1962; accepted for publication, January 8, 1963.*