THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

MINERALOGICAL NOTES

EVIDENCE FOR THE IDENTITY OF KAMAREZITE WITH BROCHANTITE, $Cu_4(SO_4)(OH)_6$[1]

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Introduction

In connection with a mineralogical investigation of several unidentified copper sulfate minerals, an attempt was made to obtain and authenticate specimens of the rare mineral kamarezite, a hydrated copper sulfate, presumed to have the formula $Cu_3(SO_4)(OH)_4 \cdot 6H_2O$.

Kamarezite was described and named by Busz (1893, 1895) from material found on a single specimen from the Kamareza mine, in Laurium, Greece. The mineral was said to occur as minute, transparent, bright, grass-green, flattened, needle-like crystals, probably orthorhombic, on a specimen that had been left by Prof. Dr. vom Rath as a gift to the Mineralogical Museum of the University of Bonn (Germany). Busz (1895) stated that at first he was inclined to consider the mineral to be brochantite, $Cu_4(SO_4)(OH)_6$, but that later he doubted its identity with bronchantite, especially because of the relatively large amount of water which a small sample of the mineral gave in the closed tube. Busz (1893, 1895) established kamarezite to be a new mineral, largely on the basis of his quantitative chemical studies, and assigned to it the formula $SO_4(CuOH)_2+Cu(OH)_2+6H_2O$ (or $3CuO \cdot SO_3 \cdot 8H_2O$), which he derived from the following average of four different, but closely agreeing, chemical analyses (in per cent): CuO 51.50, FeO 0.69, SO_3 17.52, H_2O [30.29] (by difference). From its composition Busz (1895) suggested that kamarezite, though similar to brochantite, $Cu_4(SO_4)(OH)_6$, and langite, $Cu_4(SO_4)(OH)_6 \cdot H_2O$, differed from them in water content. In his description of kamarezite, Busz (1895) included a detailed outline of the different analytical procedures that he followed for determining the water content of the new mineral, as well as the results of a microscope stage study of the morphology of the kamarezite crystals and a crystal drawing (Fig. 1); these data have proved very valuable in our study.

"Kamarezite" Specimens

Through the kindness of Prof. Neuhaus, curator of the Mineralogical Institute of the University of Bonn, a careful search was made for the type specimen of kamarezite in the mineral collections there; the specimen could not be located. Prof. Neuhaus (written comm., 1959) reported

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

that failure to find the species listed in the mineral catalogue that had been compiled after World War II strongly indicated that the type specimen had been among those lost when parts of the museum were destroyed by bombs. Specimens labeled kamarezite were located in the collections of only five museums (Table 1). Data obtained from the investigation of these specimens served as a basis for the present study.

PHYSICAL, OPTICAL AND CRYSTALLOGRAPHIC CONSIDERATIONS

X-ray powder diffraction patterns were taken of all specimens of kamarezite made available for study. A description of the specimens examined and the results of the *x*-ray investigation of each are tabulated for comparison in Table 1. Specimens labeled kamarezite gave either the *x*-ray powder pattern of bronchantite, $Cu_4(SO_4)(OH)_6$, or that of rosasite, $(Cu,Zn)_2(OH)_2(CO_3)$. The *x*-ray powder patterns of the latter were identical with that obtained from a specimen of rosasite from the type locality —Rosas mine, at Sulcis, Sardinia (USNM 194836; film no. 14608). Material from the specimens which gave the rosasite patterns were checked further by *x*-ray fluorescence analysis and found to contain appreciable zinc, thus confirming its identity. It was not necessary to consider further those specimens that were identified as rosasite.

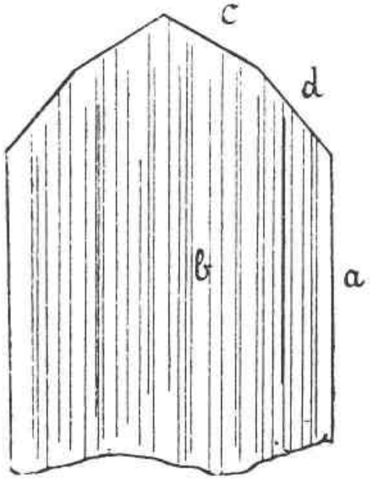

FIG. 1. A reproduction of Busz's crystal drawing of kamarezite (Busz, Fig. 2 on p. 118, 1895). The forms in Busz's orientation: *b*{010}, *a*{100}, *c*{101}, *d*(201}.

Tabulation of the physical, optical, and crystallographic properties that are cited in the literature for kamarezite and bronchantite (Table 2 revealed that many of the data for the two minerals are the same or similar: the physical properties, especially hardness and specific gravity, the optic sign and 2V, the interfacial angles and the axial ratios.

The crystal drawing of kamarezite made by Busz (Busz, Fig. 2, p. 118, 1895), the angles he obtained by measurement of the domical terminations on the microscope stage, $(101)\wedge(100)\sim 59°$ and $(201)\wedge(100)\sim 40°$, and the axial ratio derived from these angular elements, $a:c=1:0.601$ (erroneously reported by Busz as $b:c$; corrected without comment in footnote 1 under *Ref.* on p. 589 in Dana's *System of Mineralogy* (Palache *et al.*, 1951) can all be related to brochantite by interchanging the *a* and *b* axes of kamarezite. A photographic enlargement of a crystal of brochantite found in the cavity of a specimen from the Ural Mountains, U.S.S.R., (private collection of Owen Ramsburg), shown in Fig. 2, emphasizes its morphological similarity to Busz's crystal drawing of kamarezite, reproduced in our Fig. 1. Another crystallographic error that was noted in Busz's paper (1895) is his reference in the text to the face *b* as a brachypinacoid but his designation of that form, as {011}; it should read {010}. If Busz's *a*- and *b*-axes are interchanged (Fig. 1), then his *d* {201} becomes *d* {021}, and *c* {101} becomes *c* {011}. From elements derived from

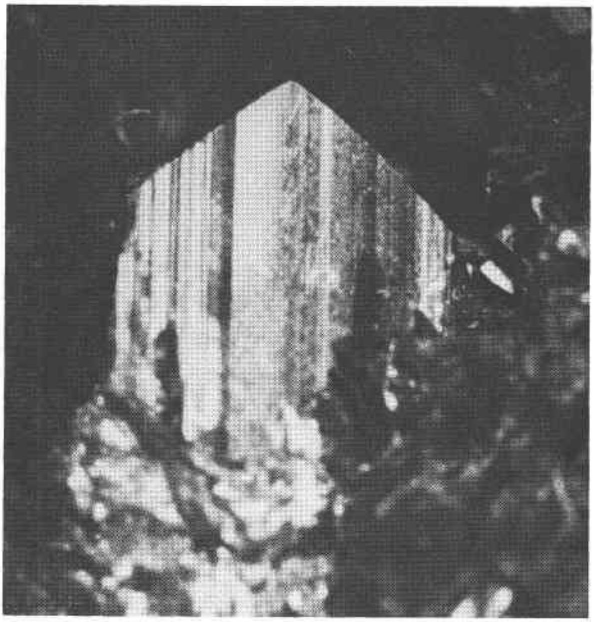

FIG. 2. A greenish-black crystal of brochantite in cavity, Ural Mts., U.S.S.R., (Ramsburg collection). Magnification 10×. Compare striations and habit to Fig. 1. Considerably smaller, vertically striated, emerald-green crystals of brochantite were noted on a specimen from the Tintic district, Utah (USNM C4630).

TABLE 1. SUMMARY OF DATA OBTAINED FOR MUSEUM SPECIMENS LABELED KAMAREZITE

Specimen Identification[1]	Locality	Description of Specimen Material	*X*-ray identification
MIUM numbered specimen)	Kamareza, Laurium, Attica, Greece	emerald green crystalline crust, consisting, in part, of aggregates of minute crystals	brochantite, $Cu_4(SO_4)(OH)_6$ (f. 15664)
BM 70393[2]	Laurium, Greece		brochantite, $Cu_4(SO_4)(OH)_6$[2]
USNM R6786	Laurium, Greece	blue green, warty crust with a fibrous radiating structure	rosasite, $(Cu,Zn)_2(OH)_2(CO_3)$ (f. 14369)
AMNH 17984	Kamareza, near Laurium, Greece	blue green botryoidal crust with spherulitic structure	rosasite, $(Cu,Zn)_2(OH)_2(CO)_3$ (f. 15651)
ANSP 208057	Laurium, Greece	blue green botryoidal aggregates with radiating fibrous structure, in cavities associated with smithsonite, $ZnCO_3$	rosasite, $(Cu,Zn)_2(OH)_2(CO_3)$ (f. 18211)

[1] MIUM: Mineralogisches Institut der Universität, Marburg, Germany; BM: British Museum (Natural History), London, England; USNM: U. S. National Museum, Washington, D. C.: AMNH: The American Museum of Natural History, New York City, New York; ANSP: Academy of Natural Sciences, Philadelphia, Pennsylvania.

[2] Data on note filed with specimen (courtesy of P. Embrey, written comm., 1960): "B.M. 70393. Bought in April, 1893, from Mr. W. Terrill Swansea as brochantite, Laurium, Greece. Examined by L. J. Spencer (1894)—Cu, SO_4, H_2O found to be present. Renamed (by?) kamarezite. Examined by H. A. Miers—biaxial negative, large axial angle, extinction ||, striations length of needles. Examined by K. Busz (Sept. 1897) who said it did not look like the kamarezite described by him; his crystals were 'much smaller.' *X*-rayed (Feb. 1957) and found to be brochantite."

goniometric measurements of brochantite crystals by Palache (1939), the $\rho^2 = B$ angles for {021} and {011} of brochantite were calculated and found to be 40°12′ and 59°10′, respectively. These are in excellent agreement with the corresponding angles given by Busz (1895) for these same forms in his orientation (Table 2). Hence Busz's ratio $a:c = 1:0.601$ is in good agreement with the brochantite ratio $b:c = 1:0.611$ (x-ray) and 1:0.6135 (goniometry), cited by Palache (1939). In the brochantite orientation, the perfect cleavage of kamarezite becomes {010}, the same as that of brochantite (Table 2). The discrepancy between the optical orien-

TABLE 2. COMPARISON OF THE PROPERTIES OF KAMAREZITE AND BROCHANTITE

	Kamarezite, Busz (1893, 1895)	Brochantite, Palache (1939)
Formula	$Cu_3(SO_4)(OH)_4\cdot 6H_2O$	$Cu_4(SO_4)(OH)_6$
Color	bright grass green	emerald to blackish green; also light green
Diaphaneity	transparent	translucent to transparent
Habit	minute crystals elongated [001] and flattened {010} with domical terminations	stout prismatic to acicular [001], but sometimes elongated [010] or more rarely, [100]; also tabular {001}.
Striations	vertical (‖ to elongation)	vertical
Hardness	3	3½–4
Specific Gravity	3.98	3.97
Cleavage	{100} perfect	{010} perfect
Crystallography	probably orthorhombic $(100)\wedge(101)\sim 59°$ $(100)\wedge(201)\sim 40°$	monoclinic $(010)\wedge(011)=59°10'$[1] $(010)\wedge(021)=40°12'$[1]
Optic Sign	biaxial	biaxial
2V	very large	77°
Opt. Orient.	$Y=b$; $Bx_\alpha=a$	$Y=b$; $X\sim a$
Axial Ratio	$a:c=1:0.601$[2]	$b:c=1:0.611$ (x-ray)[3]

[1] Calculated by present authors from elements of Palache (1939).

[2] Erroneously given in the original paper as $b:c$ (Busz, 1895).

[3] Richmond in Palache (1939).

tation of kamarezite and brochantite, in the brochantite setting, cannot be accounted for. However, the preceding crystallographic evidence is strong support for the contention that the mineral described by Busz (1895) as kamarezite actually is brochantite, $Cu_4(SO_4)(OH)_6$.

CHEMICAL CONSIDERATIONS

Chemical evidence for the support of the identity of kamarezite, supposedly $Cu_3(SO_4)(OH)_4\cdot 6H_2O$, with brochantite, $Cu_4(SO_4)(OH)_6$, is not as well defined as that afforded by a comparison of their physical, optical, and crystallographic properties. The procedures outlined and followed by Busz (1895) in determining the water content of kamarezite are open to question. The chemical data cannot, therefore, be weighted to the same extent as the physical, optical, and crystallographic evidence.

The chemical analyses of kamarezite are compared in Table 3 to the average of two analyses of brochantite from Collahurasi, Chile (Ford, 1910). Attention is called to the fact that the value reported by Busz (1895) for the SO_3 content (17.52%), representing the average of four analyses of kamarezite, is in excellent agreement with the average SO_3 content (17.54%) of these two analyses of brochantite.

Busz (1895) remarked that because of unexpected difficulties encountered in the determination of the water content of kamarezite he was unable to determine H_2O directly. Busz (1895) outlined in considerable detail the procedures he followed for obtaining the water content. One method, by loss on ignition, resulted in a total loss of 30.98%, after a series of three timed heating experiments carried out on one sample: first, for $1\frac{1}{2}$ hours, at beginning red heat over a Bunsen burner; then, successively, for 5 hours and $1\frac{1}{2}$ hours, strongly heated with a blast lamp. This loss (30.98%) is in good agreement with the SO_3+H_2O value (29.50%) given for brochantite (col. 6, Table 3). An initial weight loss of 13.46%, obtained after $1\frac{1}{2}$ hours of heating kamarezite "up to beginning red heat over a Bunsen burner," was assumed by Busz to represent only a loss of water; it undoubtedly included some loss of SO_3, a fact which has been demonstrated by detailed ignition loss studies carried out in the present study on brochantite, following as closely as possible the procedures outlined by Busz (1895). These ignition studies indicate that Busz's initial weight loss of 13.46% probably represents not only a loss of the total H_2O in kamarezite, but, in addition, some SO_3. The weight loss for brochantite heated in an uncovered porcelain crucible in the furnace at 350° C. for 22 hours was 11.00%; and at 400° C. for 16 hours, 12.80% (water content for brochantite of theoretical composition is 11.94%). In another of Busz's experiments, a forerunner of the Penfield method, the kamarezite sample "was heated to medium red heat in a porcelain boat in a glass tube with lead chromate placed before it and the escaping water was

TABLE 3. CHEMICAL ANALYSES OF KAMAREZITE COMPARED TO BROCHANTITE

	Kamarezite, $Cu_3(SO_4)(OH)_4\cdot 6H_2O$						Brochantite, $Cu_4(SO_4)(OH)_6$	
	Kamareza mine, Laurium, Greece					Theoretical Composition	Collahuasi, Chile (6)	Theoretical Composition
	(1)	(2)	(3)	(4)	(5)			
CuO	51.45	51.97	—	51.09	51.50	51.57	70.29	70.36
FeO	n.d.	n.d.	0.69	—	0.69	—	—	—
SO_3	17.34	17.60	17.70	17.45	17.52	17.29	17.54	17.70
H_2O	—	—	—	—	[30.29]	31.14	11.96	11.94
Total					[100.00]	100.00	99.79	100.00

1,2. Analyst, Klingemann (Busz, 1895); 3,4. Analyst, K. Busz (Busz, 1895); 5. Average of analyses 1–4. 6. Average of two closely agreeing analyses; analyst, W. E. Ford (Ford, 1910).

collected in an H_2SO_4 tube"; the loss of water obtained by this technique was reported to be 13.49%. Busz failed to mention whether this water was checked for the presence of any escaped SO_3.

No mention is made by Busz concerning the method by which the CuO figures reported for kamarezite both by Klingemann and himself were obtained (Table 3). If we assume the identity of kamarezite with brochantite, the discrepancy between the three closely agreeing results for CuO (51.45, 51.97, and 51.09; av. 51.50%) reported for kamarezite and that of the much higher CuO figures (70.41 and 70.16; av. 70.29%) given by Ford for brochantite is difficult to explain. The possibility that Busz and Klingemann (Busz, 1895) had overlooked another cation of equivalent weight near that of copper was considered. Because zinc-bearing minerals are fairly abundant at the Kamareza mine, the kamarezite (=brochantite) specimen from the University of Marburg (unnumbered specimen, MIUM; Table 1) was examined for zinc; an *x*-ray fluorescence analysis of material from this specimen, by Harry J. Rose, Jr. of the U. S. Geological Survey, showed zinc present only in small amount; the limited amount of available material precluded quantitative determination of ZnO. Dr. Max Hey of the British Museum (Natural History) also recognized that kamarezite might be a zincian brochantite (Hey, written comm., 1964); a colorimetric determination for zinc in the kamarezite (=brochantite) specimen (B.M. 70393) made by Dr. Alfred A. Moss, also of the British Museum, showed 1.9% ZnO.

Hey offered several suggestions that might explain the grossly low figures for copper oxide obtained in the original kamarezite analyses made by Klingemann and Busz as compared to those for brochantite (Table 3): 1) that their method was consistently wrong; 2) that their calculations were in error; or 3) that they used the wrong factor in converting from whatever weighing form was used (probably Cu_2S). Hey also added, "At that date (1895), Cu would be estimated either as CuO or as Cu_2S; it *is* possible in an estimation as Cu_2S in a Rose crucible to overheat and get reduction to *Cu*, but quantitative reduction to Cu would only bring the CuO up to 64.4% (theory for brochantite, 70.36%)." We are unable to offer a completely satisfactory explanation for the discrepancy between the CuO values of kamarezite and brochantite, assuming the identity of the two minerals.

CONCLUSIONS

The optical, physical, crystallographic, and chemical evidence that have been presented, based on the comparison of the kamarezite data with those of brochantite, is strong support for the contention that the mineral described as kamarezite by Busz (1893, 1895) is brochantite. Because the name brochantite (Levy, 1824) has priority over kamarezite

(Busz, 1893), we recommended that kamarezite be removed from the list of accepted mineral species; this recommendation has been accepted by a majority vote of the Commission on New Minerals and Mineral Names, I.M.A. (Chairman of the Commission, written comm., 1964).

ACKNOWLEDGMENTS

The authors are grateful to Prof. Clifford Frondel of Harvard University, Dr. Brian Mason[1] of The American Museum of Natural History, Dr. George Switzer of the U. S. National Museum, and Dr. Helmut Winkler[2] of the University of Marburg, who made available to us specimens labeled "kamarezite." Appreciation is also expressed to the following: Prof. Neuhaus, for his assistance in attempting to locate the type specimen of kamarezite; Dr. Max Hey, for his helpful comments and suggestions relating to possible interpretations of discrepancies between the analyses of kamarezite and brochantite; Dr. Alfred A. Moss, for the zinc analysis on the British Museum's specimen of kamarezite; Mr. Owen Ramsburg, private mineral collector of Washington, D. C., for the loan of his specimen of brochantite; and Harry J. Rose, Jr., our colleague at the U. S. Geological Survey, for *x*-ray fluorescence analyses.

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THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

MELANTERITE-ROZENITE EQUILIBRIUM

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INTRODUCTION

Samples of altered pyrite were collected from an abandoned mine dump in the upper reaches of Sandy Run in Brown Township, Vinton County, Ohio, as part of a study dealing with the oxidation of iron sulfides. The