BROCKITE, A NEW CALCIUM THORIUM PHOSPHATE FROM THE WET MOUNTAINS, COLORADO[1]

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ABSTRACT

Brockite, a new calcium thorium phosphate mineral from the Wet Mountains, Colorado, is found as massive reddish aggregates and as earthy yellow coatings in veins and altered granitic rocks. Although similar in composition to grayite, it corresponds in hexagonal symmetry to rhabdophane. Color is red-brown to pale yellow, translucent, with greasy luster. $G = 3.9 \pm 0.2$. In transmitted light it is moderately birefringent or opaque due to hematite stain, uniaxial (+), with parallel extinction and positive elongation. $W = 1.680 \pm .002$; $E = 1.695 \pm .002$. The formula is $Ca_{0.43}Sr_{0.03}Ba_{0.02}Th_{0.41}RE_{0.11}[(PO_4)_{0.83}(CO_3)_{0.17}] \cdot 0.9H_2O$; $Z = 3$. An analysis of the rare earth content shows an unusually high proportion of Nd_2O_3 with respect to CeO_2, La_2O_3, and Y_2O_3. The low ratio $Ce/(La+Nd)$ of 0.58 is believed to reflect the formation of brockite under oxidizing conditions. The x-ray diffraction pattern nearly identical to that of rhabdophane; thus distinct from grayite, which is pseudohexagonal. The cell dimensions are $a = 6.98$ Å, $c = 6.40$ Å, $V = 270$ Å³. Upon heating, brockite acquires a monzaite-type structure, with spacings close to those of cheralite.

Introduction

Recent mineralogical studies have unearthed a group of hydrous phosphates related to rhabdophane, the rare earth phosphate. Rhabdophane is known from its occurrences at Cornwall, England, and at Salisbury, Connecticut, from which the mineral has been redescribed by Hildebrand and others (1957). The related minerals contain calcium and uranium or thorium in place of rare earths, and are either isostructural with rhabdophane (hexagonal) or are orthorhombic (pseudohexagonal).

The two orthorhombic members of the group are ningyoite, calcium uranium phosphate, from Ningyo Pass, Japan (Muto *et al.*, 1959) and grayite, calcium thorium phosphate, from Southern Rhodesia (Bowie, 1957), currently under further investigation by Bowie. The pseudohexagonal symmetry of grayite has been established since the 1957 report (J.E.T. Horne, written communication, 1960).

Brockite, the new calcium thorium phosphate from the Wet Mountains, Colorado, is hexagonal, with an x-ray pattern indistinguishable from that of rhabdophane. An incompletely described mineral which shows strong similarities to brockite has been found in Sebungwe, Southern Rhodesia (Horne, written communication, 1960); a thorium mineral known only in an impure form but resembling brockite in x-ray diffraction pattern has been reported by Dooley and Hathaway (1961) from Fremont County, Wyoming, and from Gunnison, Colorado. Mem-

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bers of the Geological Survey of Great Britain are investigating a hexagonal mineral from Cornwall which is apparently the uranium analog of brockite (Horne, written communication, 1960).

Brockite is named for Maurice Brock, of the U. S. Geological Survey, who in the course of geologic mapping in the area, came into possession of the specimen and referred it to us for identification.

The study of the new mineral was undertaken as a part of the continuing investigation of the geochemistry of thorium in the Wet Mountains by the U. S. Geological Survey. A recent publication (Phair and Fisher, 1961) summarizes present data bearing upon the origin of the thorium veins.

Occurrence

A small specimen containing the new mineral was collected from a prospect pit one-half mile east of the Bassick mine, Querida, Custer County, Colorado. The pit is located in deeply weathered granitic rocks of the Precambrian plateau near the boundary with overlying volcanic rocks. In general, the thorium-bearing minerals in the area occur in veins localized along shear zones and are associated with abundant hematite, carbonates (mostly calcite), and barite. The geology of the Wet Mountains has been summarized by Christman *et al.* (1953).

In the specimen studied, 5B–52, reddish-brown brockite occurs as very fine grained massive aggregates in nodules up to 35 mm in diameter with abundant euhedral inclusions of pyrite. These nodules, along with blebs of brecciated quartz and albite and vein quartz, are enclosed in pale yellow earthy material which is largely brockite. Irregular cavities in the ore are lined with earthy hematite, then fine-grained apatite, and filled with apatite and (or) quartz; this sequence of mineralization is not clear-cut, since some cracks in apatite and quartz are filled with brockite and hematite.

Brockite was later identified as the material composing yellow earthy coatings in samples WM87, 89A from the Hardwick mine and WM121A from the Nightingale shaft, Custer County, Colorado, collected by George Phair in 1957. These are aggregates of red K-feldspar typical of the potassic alteration zones cutting granitic rocks throughout the thorium-bearing area. Thorite, barite and hematite fill the spongy matrix. Finely crystalline brockite has formed at the expense of thorite adjacent to small cavities.

Physical and Optical Properties

Fragments of brockite, seen under the binocular microscope, are deep red-brown, grading to pale yellow on thin edges. The mineral is translu-

cent, with greasy to vitreous luster and conchoidal fracture. The specific gravity, determined by pycnometer, is 3.9 ± 0.2.

In thin section, brockite appears predominantly as radial aggregates of fibroid grains, with undulatory extinction. It also forms stubby, imperfect hexagonal prisms, usually with granulated margins. Color variation from pale yellow to deep red, is apparently due to variation in grain size and the amount of hematite stain; most of the material is red in reflected light. Grains in the nodules average 20 microns in length, with a few as much as 50 microns long; all of the earthy material is virtually cryptocrystalline.

Brockite is uniaxial positive; the grains have parallel extinction and positive elongation. Considerable difficulty was encountered in determining the indices of refraction. The cryptocrystallinity of the material and the presence of hematite inclusions and coatings prevented the conoscopic orientation of fragments in immersion oils. Repeated efforts to isolate optically uniform grains were fruitless. The problem was overcome by mounting the finely powdered mineral on a gelatin-coated slide, according to the method described by Olcott (1960); grains were then oriented on the universal-stage by the extinction method, and the indices measured in sodium light. The immersion oils were checked with an Abbé refractometer immediately after the determinations. The indices are $\omega = 1.680 \pm 0.002$; $E = 1.695 \pm 0.002$; the stated limits of accuracy include possible error in orientation of the extremely small grains. Birefringence is generally masked by hematite stain.

Separation

The preparation of a pure sample of the new mineral was a lengthy process, complicated by the abundance of minute pyrite inclusions.

The specimen was first crushed and sized between 200- and 350-mesh sieves. Repeated washings in an ultrasonic separator removed earthy hematite coatings from the grains. Bromoform was used to float quartz and plagioclase; apatite and some pyrite were removed by the Frantz isodynamic separator. Finally, by careful selective handpicking over a period of several months, an 0.1 gram sample was prepared virtually free of pyrite inclusions and other mineral impurities.

In the resulting sample, impurities could not be detected by x-ray examination.

Analytical Procedures

The selection of methods for the chemical analysis of brockite was guided by the semiquantitative spectrographic analysis of the mineral, (Table 1). Micro- and semimicrochemical procedures were used for the various determinations upon separate splits of the 100 mg sample. The

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF BROCKITE FROM THE
WET MOUNTAINS, CUSTER CO., COLORADO

Analyst: K. V. Hazel, U. S. Geological Survey

Per Cent[1]	Elements
10	Th
7.0	P
3.0	Fe, Ca
0.3	Y
0.15	Si, Ba, Gd, Sr
0.07	Mg, Ce, Dy, Eu, Pb
0.03	Na, Er, La, Nd, Sm
0.015	Mn, As, Yb, Zr
0.003	Ti, Be, Cu, Lu, V
0.0007	Sc
0.00003	Ag
0.01	Al
0.001	B
0.0003	Cr
Not looked for	F

[1] Figures are reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc. These numbers represent midpoints of group data on a geometic scale. Comparisons of this type of semiquantitative results with data obtained by quantitative methods either chemical or spectrographic, show that the assigned group includes the quantitative value about 60% of the time (Waring and Annell, 1953). Other elements were looked for but not found.

entire sample was used for the determination of the specific gravity with a 0.5-ml pycnometer and toluene. The sample was air-dried to remove the toluene before starting the chemical analysis.

One portion of the sample was used for total water and carbon dioxide determinations; a second portion for the $H_2O(-)$, (1+1) HCl insoluble, total uranium, ThO_2, CaO, Fe_2O_3, SrO, and P_2O_5 determinations; a third portion for combined ThO_2 and rare earth oxides; and a fourth portion for the quantitative spectrographic determination of BaO and the individual rare earth oxides.

The first portion of the sample was decomposed by ignition at 900° C. in a stream of oxygen. V_2O_5 was added to the sample to insure the complete decomposition of all carbonates present. Total water and carbon dioxide were determined by use of a modified microcombustion train of the type used for the determination of carbon and hydrogen in organic compounds.

The second portion of the sample was dried to constant weight at 110±5° C. and then boiled with (1+1) HCl to determine the insoluble residue. An Emich microbeaker and sintered glass filter stick were used for the separation of the insoluble residue which was dried to constant weight at 110±5° C. The residue was washed with dilute HCl and then with water before drying to constant weight.

Aliquots of the filtrate from the acid insoluble determinations were used for the total uranium, ThO_2, CaO, Fe_2O_3, SrO and P_2O_5 determinations.

ThO_2 was determined spectrophotometrically using "Thoron," the disodium salt of 2-(2-hydroxy-3, 6-disulfo-1-naphthylazo)-benzenearsonic acid. CaO was determined by flame photometry (wavelength $=554m\mu$). The solution was compared to standard calcium solutions containing approximately the same concentrations of thorium, phosphorus, and iron present in the solution analyzed. Fe_2O_3 was determined spectrophotometrically by the o-phenanthroline procedure using a sodium citrate medium. The valence state of the iron was determined by dissolving an impure sample of the mineral in boiling $(1+3)$ H_2SO_4 and titrating the resulting solution with standard approximately $0.03N$ $KMnO_4$. SrO was determined by flame photometry (wavelength $=461m\mu$). The solution was compared to standard strontium solutions containing approximately the same concentration of calcium, thorium, phosphorus, and iron as the solution analyzed. P_2O_5 was determined spectrophotometrically by the molybdovanadophosphoric acid procedure. Uranium was determined fluorimetrically by J. W. Budinsky, of the U. S. Geological Survey.

The third portion was decomposed using a mixture of HNO_3 and HF. The combined ThO_2 and rare earth oxides were determined gravimetrically as the combined oxides. They were separated first as the fluorides, converted to the nitrates and then reprecipitated with NH_4OH from a solution alkaline to phenolphthalein and containing an excess of NH_4OH to insure complete precipitation of the rare earths. The rare earth oxide content was calculated by difference using the values for combined ThO_2 and rare earth oxides and for ThO_2 determined spectrophotometrically.

The individual rare earth oxide content and the BaO content were determined by quantitative spectrographic analysis (Table 3) by Harry Bastron, U. S. Geological Survey, using the fourth portion. The mineral was spectrographically analyzed without first separating the rare earths from the ThO_2.

ANALYTICAL RESULTS

The chemical analysis of the purified sample is given in Table 2. CaO, ThO_2 and P_2O_5 are present in a molecular ratio of approximately $1:1:1$; thus, Ca and Th must substitute in nearly equal proportions for the rare earths in the rhabdophane structure. The general formula for brockite is $(Ca, Th)PO_4 \cdot H_2O$, with $Ca:Th=1:1$.

The ferric oxide in the analysis is regarded as an impurity and omitted from calculation of the formula. The 2 per cent insoluble material could not be recovered for identification.

Calcite or apatite may possibly be present, though in such slight amount as to be undetected by optics and x-ray; in either case, the available CaO would be insufficient to account for all of the CO_2 in the analysis. With the sole exclusion of Fe_2O_3 from the analysis, the summed ratios of cations and anions balance satisfactorily, as shown in the last column of Table 2. We conclude that the [minor] constituents are held in the brockite structure, with (CO_3) substituting for (PO_4). The presence of structural (CO_3) in rhabdophane from Salisbury, Conn., has been demonstrated by Hildebrand et al. (1957).

TABLE 2. MICROCHEMICAL ANALYSIS OF BROCKITE FROM THE WET MOUNTAINS, CUSTER COUNTY, COLORADO

Analyst: Robert Meyrowitz

Constituent	Per Cent	Recalculated to 100%[1]	Molecular Ratio	Atomic Ratio		
ThO_2	42.7	44.7	.169	.169 ⎫ .215		
Rare earth oxides	6.6	6.9	.023	.046 ⎭		.416
Fe_2O_3	4.6					
CaO	9.7	10.2	.181	.181 ⎫		
SrO	1.3	1.4	.013	.013 ⎬ .201		
BaO	1.1	1.1	.007	.007 ⎭		
CO_2	3.1	3.2	.073	.073 ⎫ .419		
P_2O_5	23.6	24.7	.173	.346 ⎭		
Total H_2O	7.5	7.8	.436	.872		
Insolubles	2.0					
Total	102.2	100.0				
H_2O (⁻)	0.9					
$ThO_2 + RE$ oxides	49.3					
U	0.06					

Specific gravity $= 3.9 \pm 0.2$.

[1] Less iron oxide and insoluble.

In the formula obtained for brockite, the valence difference between Th^{4+} and RE^{3+} is balanced by the substitution of $(CO_3)^{2-}$ for $(PO_4)^{3-}$. The analyzed brockite has the formula

$$Ca_{0.43}Sr_{0.03}Ba_{0.02}Th_{0.41}RE_{0.11}[(PO_4)_{0.83}(CO_3)_{0.17}] \cdot 0.9H_2O.$$

The Gladstone and Dale rule was applied to the experimental data to check the consistency of physical properties with the analyzed chemical composition. Values for the specific refractive energies of the major rare earth oxides were obtained from Jaffe (1956); for the remaining constituents, the values given by Larsen and Berman (1934) were used. The formula yields a density of 4.0, compared with the pycnometer measurement of 3.9.

TABLE 3. QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF RARE EARTH OXIDES AND
BARIUM OXIDE IN BROCKITE

Analyst: Harry Bastron, U. S. Geological Survey

Oxide	Per Cent[1]
Y_2O_3	1.27
La_2O_3	0.49
CeO_2	1.23
Pr_6O_{11}	0.06
Nd_2O_3	1.52
Sm_2O_3	0.72
Eu_2O_3	0.30
Gd_2O_3	0.99
Tb_4O_7	0.35
Dy_2O_3	0.64
Ho_2O_3	0.16
Er_2O_3	0.19
Tm_2O_3	0.01
Yb_2O_3	0.02
Lu_2O_3	0.01
Total rare earth oxides	7.96
BaO	1.1

[1] The figures reported have an overall accuracy of ± 15 per cent, Bastron *et al.* (1960).

Table 3 gives the results of a quantitative spectrographic analysis for
the individual rare earth elements. The analysis shows an unusual excess
of Nd_2O_3 over CeO_2, La_2O_3 and Y_2O_3. The deficiency in Ce relative to Nd
probably reflects the prevalence of oxidizing conditions at the time
brockite was formed. Robinson *et al.* (1958) have shown that low Ce
proportions are the result of valence change in an oxidizing environment:
Ce tends to become fixed in its quadrivalent state and is not extractable
by ion-exchanging solutions during weathering. A normal average ratio
Ce/(La+Nd), based on values from igneous rocks, shales, and cerium
minerals, was given as 1.0; Salisbury rhabdophane, presumably formed
in a zone of weathering, was found to have an extremely subnormal ratio
of 0.01. The brockite has an atomic ratio Ce/(La+Nd) of 0.58.

X-RAY DIFFRACTION DATA

X-ray diffraction patterns of brockite were made with nickel-filtered
copper radiation. On the best film obtained of the analyzed brockite the
lines were rather broad, which may indicate poor crystallinity of the
mineral. The pattern was indexed on a hexagonal lattice by analogy with
rhabdophane, which yields a nearly identical pattern.

The interplanar spacings d(Å) for brockite and two rhabdophanes are
given in Table 4. Spacings of the unanalyzed brockite from a second

TABLE 4. X-RAY POWDER DIFFRACTION DATA IN Å FOR BROCKITE AND FOR RHABDO-
PHANE FROM SALISBURY, CONNECTICUT

Symbols: vs—very strong, s—strong, m—moderate, w—weak, vw—very weak,
f—faint, b=broad.

Rhabdophane (Salisbury)[1]				Brockite			
d (obs.)	I	d (calc.)	hk.1	5B52	WM89A	I	d (calc.)
				d (obs.)[2]			
6.07	m	6.05	10.0	6.06	6.04	mw	6.05
4.40	s	4.39	10.1	4.37	4.39	s	4.39
3.49	m	3.49	11.0	3.47	3.47	m	3.49
		3.06	11.1				3.06
3.02	vsb	3.02	20.0	3.03	3.02	vsb	3.02
2.83	s	2.82	10.2	2.83	2.83	s	2.83
		2.73	20.1				2.73
2.36	w	2.36	11.2	2.37	2.36	w	2.36
2.28	vw	2.29	21.0		2.28	vw	2.29
2.15	s	2.15	21.1	2.15	2.15	s	2.16
		2.13	00.3				2.13
2.02	f	2.02	30.0				2.02
1.920	w	1.923	30.1	1.92	1.92	w	1.92
1.859	m	1.859	21.2	1.86	1.86	m	1.86
		1.741	20.3				1.74
1.743	vwb			1.75	1.74	wb	
		1.746	22.0				1.74
1.704	vw	1.705	30.2	1.69	1.70	mw	1.70
1.675	vw	1.678	31.0	1.67	1.67	w	1.68
					1.62	f	
				1.55	1.55	w	
					1.53	f	
					1.48	f	
				1.46	1.45	vw	
				1.35	1.35	vw	
				1.31	1.31	w	

[1] From Muto et al. (1959).

[2] Measured on x-ray powder diffraction film, camera diameter 114.59 mm. Ni-filtered Cu radiation, $\lambda = 1.5418$ Å; d (obs.) cut-off at 11 Å. Film measurements corrected for shrinkage.

locality (sample WM89A) are included because slightly sharper and more numerous lines could be more reliably measured. The cell constants for brockite and rhabdophane are closely similar, as shown in Table 5.

After heating at 800°–900° C., brockite gives an x-ray diffraction pattern of the monazite type with spacings close to those given by Bowie and Horne (1953) for synthetic cheralite, Ca, Th $(PO_4)_2$.

The difference in symmetry between brockite and grayite was con-

TABLE 5. CELL CONSTANTS IN Å FOR BROCKITE AND TWO RHABDOPHANES

Brockite	Rhabdophane	
Wet Mts., Colo.	Cornwall, England[1]	Salisbury, Conn.[2]
$a = 6.98 \pm .03$	$a = 6.96$	$a = 6.98 \pm .03$
$c = 6.40 \pm .03$	$c = 6.38$	$c = 6.39 \pm .03$
$a:c$ 1:0.917	$a:c$ 1:0.917	$a:c$ 1:0.915
V 270 Å^3	V 267.6 Å^3	V 269.4 Å^3

[1] X-ray film supplied by J. E. T. Horne.
[2] From Muto et al., 1959.

TABLE 6. CALCULATION OF THE NUMBER OF FORMULA WEIGHTS IN THE UNIT CELL

Constituent	Metal Equivalent	Oxygen Equivalent	Number of Atoms in Unit Cell
ThO_2	0.169	0.338	1.10
RE_2O_3	0.046	0.069	0.30
CaO	0.181	0.181	1.18 } 2.71
SrO	0.013	0.013	0.08
BaO	0.007	0.007	0.05
CO_2	0.073	0.146	0.48
P_2O_5	0.346	0.865	2.25 } 2.73
H_2O	0.872	0.436	5.68
		2.055	13.38

firmed when the x-ray data were compared with a grayite film kindly supplied by J. E. T. Horne. Grayite lines at 4.54 Å and 1.81 Å (not present on brockite films) cannot be indexed on a hexagonal lattice, and the angle a∧b departs from 60° C.; it is thus pseudohexagonal orthorhombic, while brockite is truly hexagonal.

The available x-ray data suggest that brockite belongs to the same space group as that of rhabdophane, $P_622(D_6^4)$, which requires a minimum of three molecules in the unit cell (Mooney, 1950). Table 6 shows the calculation of the number of formula weights in the unit cell of brockite on the basis of cell volume = 270 Å^3 and cell weight = 651. The metal equivalents (atomic ratios from Table 2) and the sum of oxygen equivalents are multiplied by 0.01 × unit cell weight to obtain the number of atoms of each constituent. The results approximate three formula weights. The low values obtained for the analyzed sample may reflect structural vacancies resulting from substitution of (CO_3) for (PO_4) and of Ca and Th for the rare earths of rhabdophane.

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