

BRAITSCHITE, A NEW HYDROUS CALCIUM RARE-EARTH
BORATE MINERAL FROM THE PARADOX BASIN,
GRAND COUNTY, UTAH¹

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ABSTRACT

Braitschite, a new hydrous calcium rare-earth borate mineral occurs in the Cane Creek potash mine of the Texas Gulf Sulphur Company and in a core hole one mile south of the mine, near Moab, Grand County, Utah. The braitschite is in white to reddish-pink nodules which constitute a zone in anhydrite rock immediately overlying a potash bed, throughout the workings of the mine. The nodules contain approximately 65 percent braitschite and about 35 percent quartz, anhydrite, dolomite, halite, small amounts of hematite, and a few crystals of chalcopyrite. Crystals of braitschite are colorless to white, very small hexagonal plates with only pinacoid and prism forms. Specific gravity is 2.903 ± 0.002 (meas.), 2.837 (calc.). Optically uniaxial positive, $\epsilon = 1.647$, $\omega = 1.646$. The analyzed sample contained minor amounts of quartz, dolomite, hematite, and a chlorite-like mineral. The analysis of braitschite, recalculated for these impurities, is CaO 21.8, Na₂O 1.68, Y₂O₃ 1.50, La₂O₃ 4.57, Ce₂O₃ 7.64, Pr₂O₃ 1.00, Nd₂O₃ 3.67, Sm₂O₃ 0.941, Eu₂O₃ 0.390, Gd₂O₃ 0.320, Tb₂O₃ 0.103, Dy₂O₃ 0.250, Ho₂O₃ 0.054, Er₂O₃ 0.081, Tm₂O₃ 0.023, Yb₂O₃ 0.018, Lu₂O₃ 0.010, B₂O₃ 48.2, H₂O 7.75, sum 100.00%. The unit cell is hexagonal, $a = 12.156 \pm 0.001$ Å, $c = 7.377 \pm 0.005$ Å, $V = 944.02 \pm 0.13$ Å³, $Z = 1$. Strongest lines of the X-ray diffraction pattern (in Å) are: 10.52 (54) (100); 4.283 (100) (201); 3.168 (45) (301); 3.155 (38) (112); 3.021 (92) (202); 2.8090 (53) (221); 2.1430 (30) (402); 1.9117 (34) (233); 1.8805 (35) (313).

Braitschite is named in memory of the late Professor Dr. Otto Braitsch, University of Freiburg, Germany.

INTRODUCTION

White to reddish-pink nodules were observed in sample material collected May 1966, from anhydrite rock overlying the potash zone in the Cane Creek mine of the Texas Gulf Sulphur Company near Moab, Grand County, Utah. Optical, spectrographic, and X-ray diffraction powder studies made in July 1966, indicated that the nodules contained a new rare-earth mineral species. Reference to recent comprehensive works on marine evaporites (Lotze, 1957; Kühn, 1959; Braitsch, 1962; Stewart, 1963; Borchert and Muir, 1964), as well as discussions with Michael Fleischer of the U. S. Geological Survey (oral commun., 1966) and with Robert Kühn of the Potash Institute, Hannover, Germany (written commun., 1967), indicate that this is the first known occurrence of a rare-earth mineral in marine evaporites. This is also the first known

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

rare-earth borate (Tennyson, 1963; Vlasov, 1964). Braitschite is the "rare-earth mineral" reported by Raup, Gude, and Groves (1967).

This mineral is named in memory of the late Professor Dr. Otto Braitsch, University of Freiburg, Germany, who, in his regrettably short career, made great contributions to the field of evaporite mineralogy and geochemistry.¹ The name is pronounced brätsch'ite. Type material will be preserved at the U. S. National Museum, Catalog Number 120627.

OCCURRENCE

Braitschite occurs in nodules in anhydrite rock that is part of a thick sequence of marine evaporites of the Paradox Member, Hermosa Formation of Pennsylvanian age, in the Paradox Basin in southeastern Utah (Hite, 1960; 1968). The nodules containing braitschite occur in a 6-inch, locally as much as 3-foot, zone in the basal part of an anhydrite bed that immediately overlies a sylvite-rich salt bed in the Cane Creek potash mine of the Texas Gulf Sulphur Company about eight miles southwest of Moab in the SE $\frac{1}{4}$ sec. 24, T26S, R20E, Grand County, Utah (Fig. 1) and (Raup, Gude, and Groves, 1967). The zone of nodules, which occurs throughout the workings of the mine and in a drill core (CC-1 well) one mile south of the mine, ranges in depth from 3,000 to 3,500 feet.

The nodules occur in a host rock, predominantly anhydrite, that contains varying amounts of dolomite and halite and small amounts of pyrite, and detrital quartz and mica. The detrital quartz and mica are in the clay to silt size range. The nodules are composed of a finely crystalline aggregate of braitschite (approximately 65 percent) and anhydrite, dolomite, halite, small amounts of hematite, and a few crystals of chalcocopyrite. The nodules are roughly spherical—the smaller, the more regular the shape—and range in size from about 0.05 to 8 mm (Fig. 2). Some of them appear to be compound—two, three, and four nodules having grown together from separate centers.

The finely disseminated crystals of hematite give the nodules a color ranging from pink to red. Most of the nodules are lighter in color toward their outer edge than at the center. This variation can be explained by the fact that the hematite is not evenly distributed throughout the nodules (Fig. 3a); at the outer edges the hematite appears to be in very small crystals and evenly distributed, whereas at the center it is more coarsely crystalline and the crystals are aggregated into small clots. Very small nodules appear to contain little or no hematite and are white.

Preliminary studies of the red mineral grains yielded a weak X-ray pattern similar to that of hematite. Electronprobe analysis, however,

¹ The name braitschite has been approved in advance of publication by the Commission of New Minerals and Mineral Names, IMA.

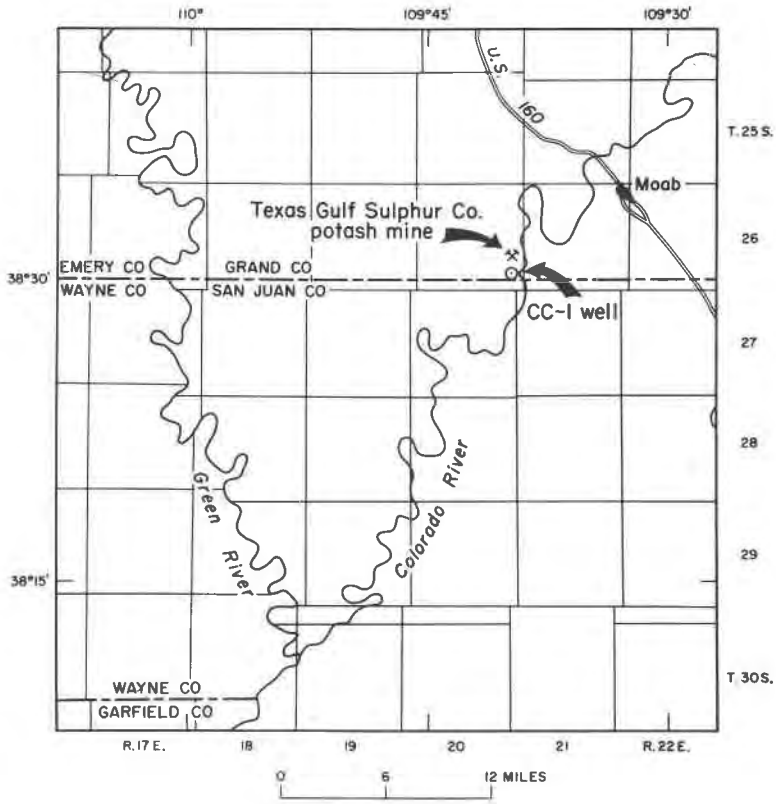


FIG. 1. Map showing the location in Grand County, Utah, of the two known occurrences of braitschite. Depth of occurrence in drill hole is 2,678 feet.

showed significant content of Ce, La, and Nd, in addition to major Fe. We obtained X-ray diffraction patterns on 4 of the 20 micron grains by use of microdiffraction camera developed by G. Desborough, U. S. Geological Survey, in an effort to describe the mineral grains more completely. The pattern obtained yielded 13 measurable lines which are coincident with the hematite standard. The true mineral composition of the reddish hematite grains is revealed in the scanning electron micrographs (Fig. 3b). With an enlargement of approximately 3000 \times and the favorable depth of focus of the instrument, it is seen that the red mineral grains are aggregates of intimately intergrown crystals of hematite and braitschite. This association accounts for the detection of the rare-earth elements in the preliminary analyses.

Many of the larger nodules contain small sulfide crystals which have

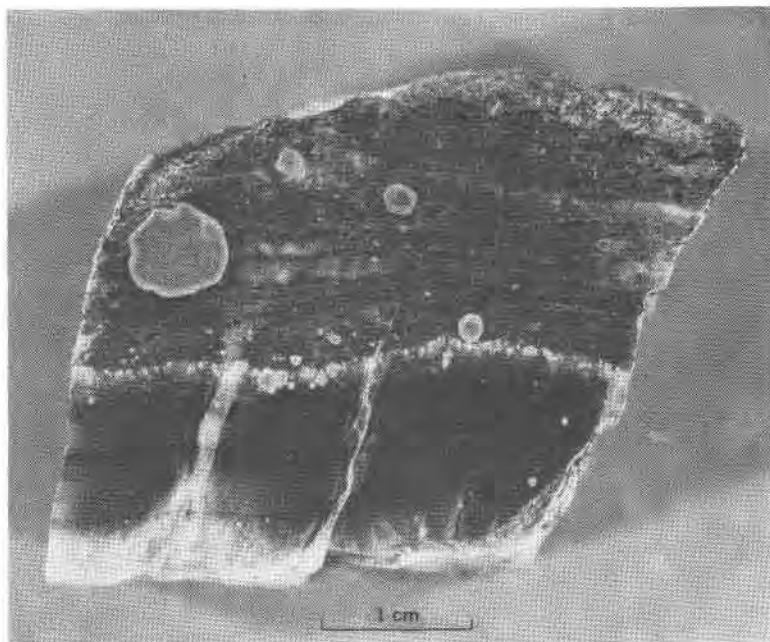


FIG. 2. Polished specimen of anhydrite rock with modules containing braitschite.

been identified as chalcopyrite by electron microprobe and X-ray diffraction analysis.

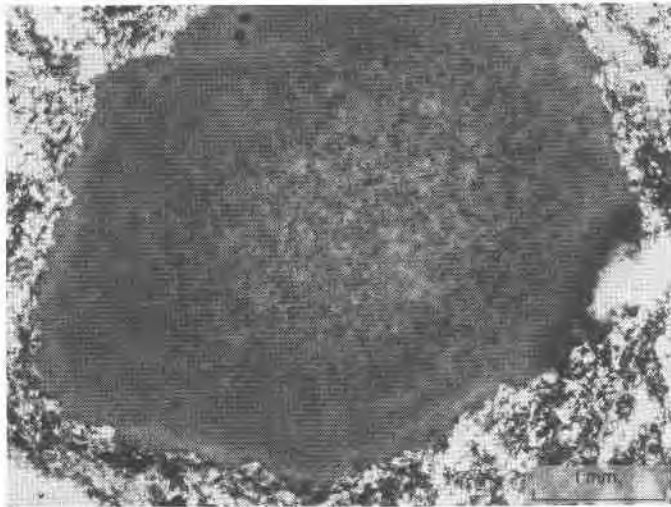
MORPHOLOGY

The crystals of braitschite are simple hexagonal plates, having only prism and pinacoid faces, and range from 0.1 to 70 microns in diameter. The thickness of the plates varies inversely proportional to the diameter. The smaller crystals (0.1–10 μ) have an average thickness: diameter ratio of 1:3; the larger (50–70 μ) have an average ratio of 1:8.

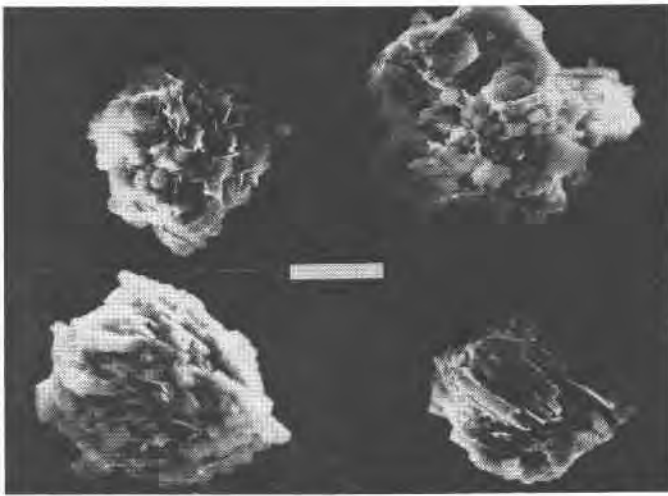
All crystals that were observed are euhedral. Variations in shape are due to different degrees of development of the prism faces (Figs. 4, 5). The outline, as observed on the pinacoid, ranges from regular hexagonal to almost triangular with a progressive decrease in alternate prisms. In some crystals one pair of prisms is much better developed than the others, resulting in a "lozenge" shape.

PHYSICAL AND OPTICAL PROPERTIES

The minute crystals of braitschite are colorless to white and have a vitreous luster.



(a)



(b)

FIG. 3. Braitschite (a). Thin section of nodule containing braitschite showing distribution of hematite. Two dark spots at top of nodule are crystals of chalcocopyrite. Plain light. b. Scanning electron micrographs of hematite grains. The bar represents 10 microns.

Specific gravity of braitschite, measured by centrifuge flotation in methylene iodide plus N,N-dimethylformamide, is 2.903 ± 0.002 . Calculated specific gravity is 2.837.

Optical properties were determined by Ray E. Wilcox, U. S. Geological

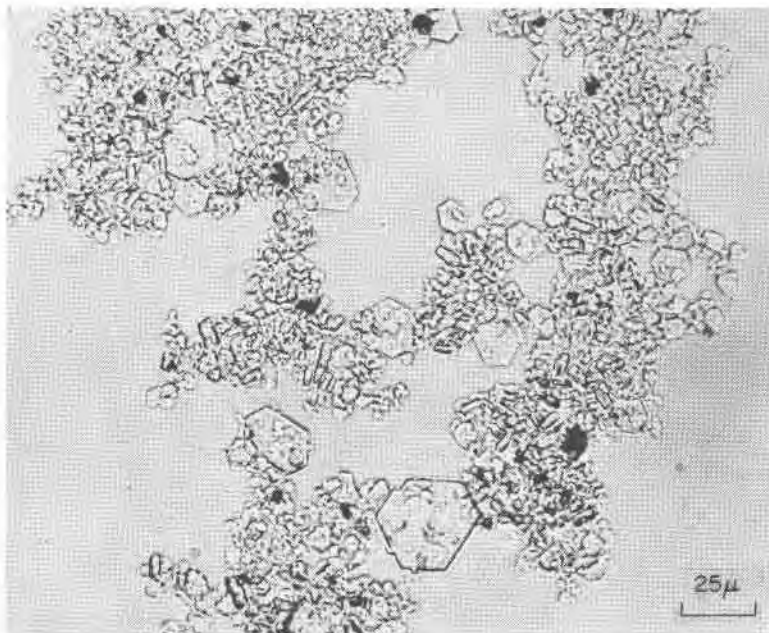


FIG. 4. Photomicrograph of braitschite crystals showing variation in shape.

Survey, on some of the largest crystals available (60–70 microns). These large crystals were obtained by means of an elutriating tube developed by Irving C. Frost, U. S. Geological Survey (1959). A concentrate of braitschite was placed in the elutriating tube in a very weak counter-current of water. Because all the material in the sample had the same specific gravity, the small crystals were held in suspension and the large crystals slowly settled to the bottom of the tube. Indices of refraction and optic sign were determined for single crystals in checked immersion oils by the use of a spindle stage developed by Wilcox (1959). The crystals were optically uniaxial positive, $\epsilon = 1.647 \pm 0.002$, $\omega = 1.646 \pm 0.002$. Birefringence was measured by means of a rotatable compensator and was determined to be 0.0015 ± 0.0002 .

Braitschite fails to show absorption spectra in the visible region for praseodymium and neodymium through a microspectroscope in the technique described by Adams (1965). Weak absorption spectral bands, similar to those of solution spectra, are observed, however, when braitschite is dissolved in a borax bead. The lack of absorption spectra in crystalline braitschite is probably related to properties of the crystal structure (Adams, 1965, p. 362; oral commun., 1967).

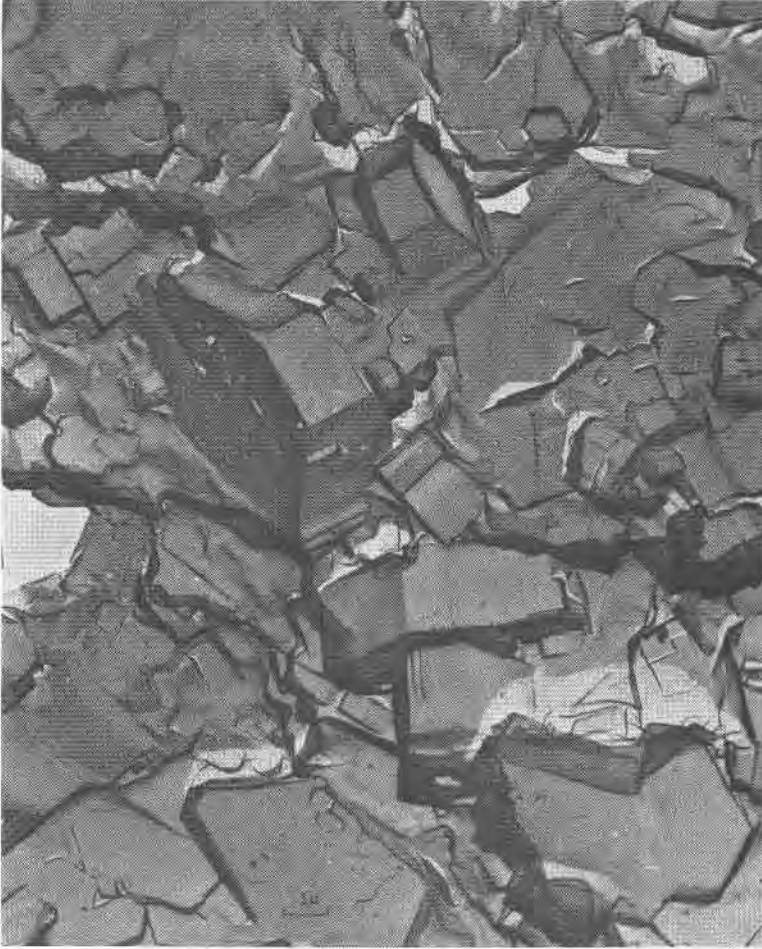


FIG. 5. Electron micrograph of a water-etched surface of nodule containing braitschite. Hexagonal crystals of braitschite are seen standing in relief on etched surface. Electron micrograph by Paul D. Blackmon.

X-RAY DATA

A precession pattern was made by Joan R. Clark, U. S. Geological Survey (oral commun., 1967), of a crystal 65 microns in diameter and approximately 10 microns thick. Just enough usable reflections were obtained after a 100-hour exposure to index the pattern as hexagonal. The data were too scant to determine the space group. From these preliminary cell constants ($a = 12.150 \text{ \AA}$, $c = 7.378 \text{ \AA}$) the powder pattern was success-

TABLE 1. X-RAY DIFFRACTION POWDER DATA FOR BRAITSCHITE
 (Diffractometer, Copper Radiation, Nickel Filter, Si internal standard)
 Hexagonal: Primitive(?) $a = 12.256 \pm 0.001 \text{ \AA}$
 $c = 7.377 \pm 0.005 \text{ \AA}$
 $V = 944.02 \pm 0.13 \text{ \AA}^3$

<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i>
100	10.53	10.52	54	332	1.7757		
001	7.377	7.381	3	114	1.7649	1.7653	6
110	6.078	6.074	15	600	1.7545		
101	6.042	6.050	17	422	1.7510	1.7514	24
200	5.264	5.260	19	204	1.7406	1.7406	8
111	4.691	4.686	2	430	1.7306		
201	4.285	4.283	100	323	1.7231		
210	3.979			601	1.7069		
002	3.689	3.688	8	520	1.6857	1.6857	4
300	3.509			431	1.6849		
211	3.502	3.501	5	512	1.6826		
102	3.481			413	1.6787		
301	3.169	3.168	45	214	1.6733		
112	3.153	3.155	38	521	1.6433		
220	3.039			304	1.6326		
202	3.021	3.021	92	610	1.6054		
310	2.9197	2.9199	7	503	1.5993		
221	2.8098	2.8090	53	602	1.5844	1.5843	4
311	2.7148	2.7136	18	224	1.5767	1.5771	4
212	2.7051	2.7072	16	611	1.5686		
400	2.6318	2.6300	5	432	1.5668	1.5666	3
302	2.5424	2.5418	22	333	1.5636		
401	2.4788	2.4786	12	314	1.5593		
003	2.4591	2.4589	5	423	1.5467	1.5470	5
320	2.4151	2.4161	3	522	1.5332		
103	2.3947	2.3926	3	440	1.5194		
222	2.3454	2.3451	6	404	1.5104	1.5109	3
410	2.2972			530	1.5039		
321	2.2952			513	1.4989		
312	2.2893	2.2894	4	441	1.4882		
113	2.2796			005	1.4755		
203	2.2280	2.2280	18	701	1.4736		
411	2.1933			612	1.4720		
402	2.1424	2.1430	30	324	1.4658		
500	2.1054			105	1.4612	1.4609	4
213	2.0918	2.0914	21	620	1.4598		
330	2.0259			414	1.4382		
501	2.0246			115	1.4338		
322	2.0205	2.0196	14	621	1.4321	1.4320	5
303	2.0138	2.0136	10	603	1.4282		
420	1.9894	1.9885	7	205	1.4207	1.4207	6
331	1.9536			433	1.4153	1.4158	6
412	1.9500	1.9505	15	442	1.4049		
421	1.9208	1.9190	15	710	1.3943		
223	1.9116	1.9117	34	702	1.3926		
510	1.8907			523	1.3904		
313	1.8809	1.8805	35	504	1.3873		
004	1.8444			215	1.3834		
511	1.8315			711	1.3701		
502	1.8285			344	1.3638		
104	1.8167			305	1.3601		
403	1.7968			622	1.3574		

Note: Pattern indexed and cell dimensions computer calculated by least-squares refinement.

TABLE 1--(Continued)

<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (o' s)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>I</i>
424	1.3525			720	1.2861		
540	1.3478			533	1.2830		
613	1.3443			604	1.2712	1.2712	5
225	1.3273	1.3275	3	721	1.2670		
630	1.3263			542	1.2660		
541	1.3259			434	1.2620		
514	1.3202			325	1.2591		
315	1.3169	1.3168	4	623	1.2553		
800	1.3159			632	1.2481		
631	1.3054			524	1.2443		
712	1.3043			415	1.2414		
801	1.2955			802	1.2394		
443	1.2926	1.2926	5	810	1.2321		
405	1.2870			006	1.2296	1.2294	7

fully computer processed by the least-squares refinement procedure (Evans *et al.*, 1963).

X-ray diffraction powder data for braitschite are given in Table 1. Five separately prepared braitschite samples yielded patterns that vary less than 0.1 percent in the refined unit cell dimensions. Each pattern was made for approximately 5 mg of braitschite crystals ground and mixed with 0.5 mg of Si as the internal standard. The unoriented powder was mounted on a collodion membrane (Gude and Hathaway, 1961) and scanned to at least 60 degrees two theta at $1/4^\circ$ 2θ /min. using nickel filtered copper radiation. The specimen for which the tabulated data are given was scanned from 5 to 80° 2θ . All diffraction maxima were considered as $\text{CuK}_{\alpha 1}$ reflections for determining the 52 observed and 132 calculated spacings. Relative intensity values, measured as peak height above background, are consistent among the five patterns. Lines contributed by small amounts of quartz and dolomite were observed but not included in Table 1.

CHEMICAL COMPOSITION AND ANALYTICAL METHODS

Braitschite is insoluble in water from 25° to 100°C . It is readily soluble in dilute HCl, HNO_3 , and H_2SO_4 .

Material for analysis was prepared from about 5 grams of handpicked clean nodule fragments from crushed anhydrite rock. This material was leached in boiling distilled water, disaggregated ultrasonically, and filtered, repeated 20 times to remove halite and anhydrite. The few grains of chalcopyrite and most of the hematite was removed by centrifuge flotation in methylene iodide. Most of the quartz and dolomite was removed by flotation in bromoform. It was impossible to remove all of the very fine-grained quartz, dolomite, hematite and a chlorite-like mineral from the sample, and therefore they are included in the analysis.

The cleanest material obtained (760 mg.) was analyzed by means of an integrated system of chemical and instrumental micro-techniques. Twenty-seven individual constituents were determined from less than 225 milligrams of this cleanest mineral separate.

Mg, Na, and K were determined by atomic absorption whereas total rare earths, carbonate C, organic C, H₂O+ and H₂O- were determined gravimetrically. SiO₂, Al₂O₃, total iron as Fe₂O₃, CaO, Sc, Y, and the individual rare earths were determined by X-ray fluorescence spectroscopy. The Sc, Y, and individual rare earth contents were measured by a solution-dilution technique (Rose, Cuttitta, and Larson, 1965) on a 3-milligram portion of preconcentrated and separated oxides. This suite of elements produces a complex X-ray spectrum in which many of the analytical emission L_α lines coincide with the L_β lines of a rare earth element several atomic numbers away. A micro-analytical method had to be developed by Cuttitta and Rose to correct for these interferences. The measurement of the boron content was accomplished by a modification (Martin and Hayes, 1952) of the NaOH titrimetric procedure in the presence of invert sugar. Boric acid was separated from interfering cations prior to the titration by ion exchange (Dowex 50×4, hydrogen form, 50-100 mesh, resin). The analytical results are presented in Table 2.

The molecular ratios (Table 2) indicate a formula for braitschite as follows:



This formula provides only 50 oxygens and 22 borons in each unit cell for a structure that is clearly hexagonal from the optical and X-ray evidence. These numbers of atoms, however, do not fit an ideal hexagonal space group. This problem is further complicated by the disparity between the density calculated from the X-ray cell values and the measured specific gravity.

An alternative formula has been suggested (Robert Kühn, 1968, written communication) as follows:



which fits the hexagonal symmetry requirements. This formula can only be derived from the chemical analysis by assuming more contamination from clay minerals and dolomite, and reevaluating the boron value. Until further work on the crystal structure can be done and more material for chemical analyses can be acquired, the 7:1:11:7 formula must be considered as an approximation.

Figure 6 shows that the rare-earth oxides from Table 2 conform to Oddo and Harkins' rule, the alternation of high and low abundances of the even- and odd-numbered elements (Rankama and Sahama, 1950).

ORIGIN

The origin of the nodules containing braitschite is difficult to explain. Because there are no other known rare-earth minerals in marine evaporites, and also no other known rare-earth borate minerals, there are no similar deposits to use for comparison. There are, however, a number of factors concerning the occurrence of this mineral which tell us something

TABLE 2. CHEMICAL ANALYSIS AND CALCULATIONS FOR THE CHEMICAL FORMULA OF BRAITSCHITE

Oxide	Analysis ¹ weight percent	Recalculated analysis ² weight percent	Molecular proportions	Molecular ratio RE ₂ O ₃ = 1	Molecular Ratio H ₂ O = 7
SiO ₃	6.0				
Al ₂ O ₃	1.8				
Fe ₂ O ₃	1.6				
CaO	19.6	21.8	.389		
Na ₂ O	1.5	1.68	.027		
Σ CaO + Na ₂ O			.416	6.50	6.77
MgO	0.31				
B ₂ O ₃	42.9	48.2	.692	10.81	11.26
H ₂ O ⁺	6.9	7.75	.430	6.72	7.0
H ₂ O ⁻	0.42				
CO ₂	0.33				
C (Organic)	0.20				
Y ₂ O ₃	1.34	1.50	.007		
La ₂ O ₃	4.07	4.57	.014		
Ce ₂ O ₃	6.81	7.64	.023		
Pr ₂ O ₃	0.89	1.00	.003		
Nd ₂ O ₃	3.27	3.67	.011		
Sm ₂ O ₃	0.84	0.941	.003		
Eu ₂ O ₃	0.35	0.390	.001		
Gd ₂ O ₃	0.29	0.320	.001		
Tb ₂ O ₃	0.092	0.103	.000		
Dy ₂ O ₃	0.23	0.250	.001		
Ho ₂ O ₃	0.048	0.054	.000		
Er ₂ O ₃	0.072	0.081	.000		
Tm ₂ O ₃	0.021	0.023	.000		
Yb ₂ O ₃	0.016	0.018	.000		
Lu ₂ O ₃	0.009	0.010	.000		
Σ RE ₂ O ₃	18.348	20.570	.064	1.0	1.04
Total Σ	99.91	100.000			

¹ Analysis of braitschite sample which contained minor amounts of quartz, dolomite, hematite and a chlorite-like mineral as determined by X-ray diffraction and optical methods. B₂O₃, Na₂O, CO₂, H₂O⁺, H₂O⁻, and organic C were determined by Blanche Ingram. K₂O was reported as <0.1 (limit of detection) and was omitted from the Table. The remaining elements were determined by Harry J. Rose, Jr. and Frank Cuttitta.

² Recalculated analysis to 100% braitschite after elimination of constituents attributed to the above contaminants.

about its origin. The braitschite nodules are restricted to a thin stratigraphic zone, yet have a fairly wide areal extent. This zone is at the base of an anhydrite bed that immediately overlies an 11-foot thick sylvite bed that is near the top of a thick section of evaporite beds. The thick sequence of salt below this mineral-bearing zone (approx. 4,500 ft.) makes it unlikely that ascending hydrothermal solutions were the source of rare-earth elements. The braitschite nodules crosscut primary layering (Fig. 2) and also occur in halite veins that extend a few feet into the overlying anhydrite. Thus, a younger age is indicated for the nodules than for the enclosing rock, eliminating a detrital origin. Another factor arguing

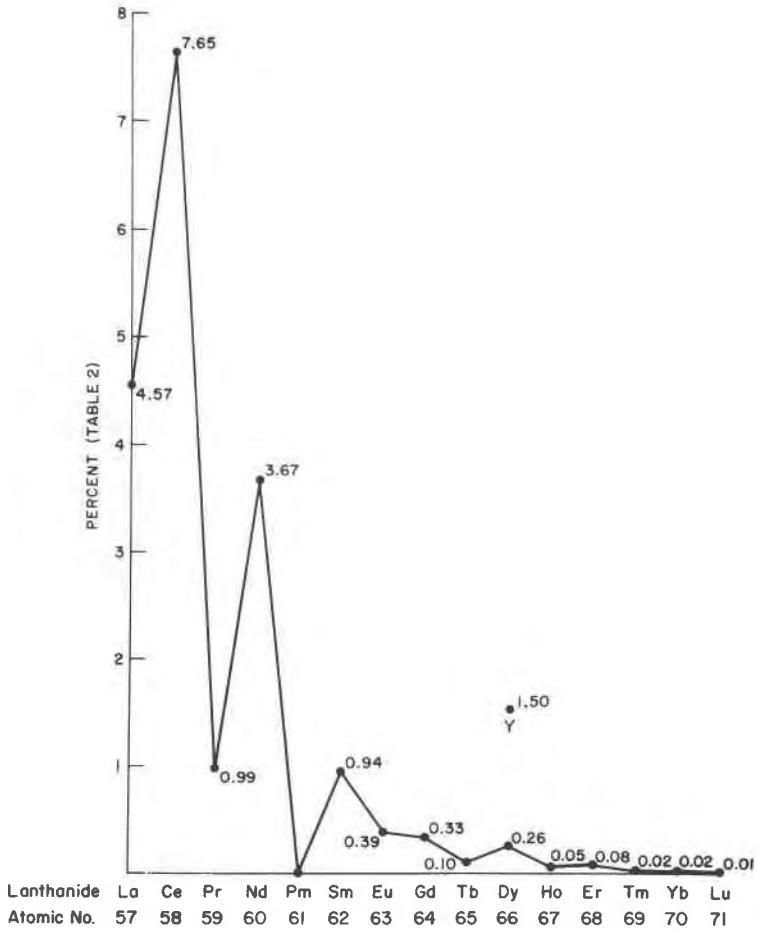


FIG. 6. Oddo and Harkins' Rule exemplified in braitschite. Yttrium is plotted above dysprosium (66).

against a detrital origin is that there are no rock or mineral fragments in these sediments that are hydraulic equivalents of the nodules. Therefore, the nodules probably formed as the result of a diagenetic process, and the elements involved were derived from the evaporite brines.

It might be assumed that the rare-earths in sea water could have been concentrated simply by evaporation and then precipitated as a rare-earth borate in the final stages of evaporation. The total rare-earth plus yttrium content of sea water is 0.00034 ppm (Goldberg, 1965). The total content of Na, K, and Cl is 2.9 percent. Thus, the ratio of rare-earths plus yttrium

to $\text{Na} + \text{K} + \text{Cl}$ is 1:88,000,000. If we assume a 1 millimeter layer of rare-earth oxides in the braitschite zone, this would require that 88,000 meters of halite and sylvite be deposited. To be conservative we will assume that half of the salt in the Paradox basin was lost to refluxing brines. This would still require the deposition of 44,000 meters of halite and sylvite which is about 20 times greater than the amount of salt that is in the basin. On the basis of this ratio it is reasonable that some process other than simple evaporation and precipitation from sea water was required.

It is possible that some, if not most of the rare-earth elements could have been carried into the Paradox basin by streams from the adjacent highlands. The Uncompahgre uplift, which flanks the northeast side of the basin was a positive area during Pennsylvanian time. The rare-earth content of the igneous and metamorphic rocks of the uplift ranges between 300 and 500 ppm based on 53 semiquantitative spectrographic analyses. The streams draining this area could have contributed substantial quantities of rare-earths to the brines in the closed basin. Further concentration by evaporation in the basin could have yielded brines with a rare-earth content much higher than could have been achieved by concentration of sea water. A relevant fact in this discussion is the rare-earth distribution in braitschite (Fig. 6), which shows a "normal" Oddo and Harkins distribution—cerium is in greater abundance than lanthanum. The rare-earth distribution in the rocks of the Uncompahgre uplift is very similar to that for braitschite—these also have a high cerium content. The rare-earth distribution in sea water, however, is different from braitschite in that the cerium content of sea water is lower than either lanthanum or neodymium. Had the rare-earths in braitschite been concentrated from sea water, and the nodules formed by inorganic chemical precipitation, the distribution in braitschite should be similar to that in sea water. The fact that the distribution is similar to that in the uplift rocks indicates those as a possible source.

The mineral assemblage in the braitschite nodules indicates a complex chemical environment during their formation. The nodules are an intimate intergrowth of braitschite, anhydrite, halite, authigenic quartz, hematite and chalcopyrite. The anhydrite, halite and quartz are normal in marine evaporites. Hematite frequently occurs in sylvite and carnallite and is probably the result of an exsolution phenomenon (Braitsch, 1962, p. 171). Hematite can also be formed by the action of iron reducing bacteria-Leptothrix (Müller and Schwartz, 1955). Chalcopyrite is unusual in this environment in that this is the first known occurrence in marine evaporites. Because of the low copper content in sea water it is likely that the source of the copper is the same as that for the rare-earths. The association of hematite and chalcopyrite seems anomalous. Garrels and

Christ (1965, p. 169) however, show that hematite and chalcopyrite can coexist in equilibrium under very limited conditions.

In summary, the postulated mode of origin of the braitschite nodules is as follows: rare-earth elements, boron, calcium, iron and copper were concentrated in the basin brines. This brine could have occupied the interstitial space in the crystal "mush" of sylvite and halite at the top of the salt bed. During lithification the brine might have been expelled against the overlying anhydrite to react with it, to form the braitschite nodules.

ACKNOWLEDGMENTS

The writers wish to acknowledge the assistance and cooperation of H. V. W. Donohoo, K. O. Linn, and G. R. Grandbouche of the Texas Gulf Sulphur Co., who made the mine workings available for sample collecting, made core material available, and granted permission to publish the data. Many of our colleagues in the U.S. Geological Survey assisted in this study. Experimental results were made available by the following: A. L. Sutton and H. W. Worthing, spectrographic analyses; B. Ingram, partial chemical analyses; J. R. Clark, single-crystal X-ray precession patterns; D. E. Appleman, refinement of X-ray diffraction powder data; R. E. Wilcox, optical determinations; H. L. Groves, Jr., and I. C. Frost, mineral separations; M. E. Johnson, thin sections; P. D. Blackmon, electron micrograph. J. W. Adams tested the mineral for absorption in the visible region. Discussions with Michael Fleischer and C. L. Christ and critical comments on the manuscript by R. C. Erd, J. W. Adams, R. Kühn and R. J. Hite were most helpful. The assistance of R. Anstead of NASA in preparation of the scanning electron micrographs is also acknowledged.

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Manuscript received, January 5, 1968; accepted for publication, March 23, 1968.