

# CRYSTALLINE CARNOTITE FROM UTAH

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## OCCURRENCE

*Contributed by Frank L. Hess.*

The carnotite deposits of Colorado, Utah, and Arizona have been watched carefully since they first became known, in the hope of finding the mineral in visible crystals. Many specimens of a crystalline yellow uranium mineral have been collected, but when tested they invariably proved to be the calcium mineral, tyuyamunite, so that crystal form or waxy body was and may yet be taken as almost surely indicating the mineral with the name of Siberian ancestry. The carnotite fields have yielded a number of new minerals, vanoxite, pintadoite, uvanite, rauvite, and rossite, and when in examining a carnotite deposit on a little flat known as Bridger Jack, on the west side of Cane Springs Pass which leads over a low shoulder of the La Sal Mountains 16 miles southeast of Moab, I discovered veinlets of a golden yellow mineral beautifully crystallized in plates, the broadest of which were between one and two millimeters across, I did not know whether the mineral was a new one or an old one in a new guise.

The mineral formed compact crusts one or two millimeters thick and 15 or 20 centimeters broad on the walls of narrow cracks. Where the crusts did not entirely fill the cracks the exposed surface had a dull greenish color and showed indistinct crystal terminations.

The veinlets were in a buff porous sandstone of the McElmo formation, presumably of either Lower Cretaceous or Upper Jurassic age. The rocks are here in the drainage basin of Grand River (now by congressional enactment the upper part of the Colorado) and erosion has entirely removed the rocks above the McElmo.

Dutton<sup>1</sup> concluded that the erosion of the Grand Canyon began in Eocene time. Situated as it is on a small tributary near the upper end of the Grand Canyon, erosion probably exposed the Bridger Jack area to oxidation and the action of meteoric water at a considerably later period in the Tertiary.

The veins are later than the usual carnotite deposits of the plateau region, for the ordinary deposits are impregnations of sandstone in connection with leaves or fillings of cavities in old tree trunks (*auracarioxylon*) some of which were hollow and all were partly decayed before petrification. What the form of the minerals may have been when deposited is uncertain, but carnotite and other minerals now present were not formed until the rocks were eroded and exposed to the percolation of meteoric waters. Generally carnotite and related minerals have moved out far enough to make an aureole around the vegetal masses, but after the soft sandstones were brought near enough to the surface to allow the formation of open cracks, the carnotite at this place was moved from the aureole and deposited in the cracks.

#### PHYSICAL AND OPTICAL PROPERTIES

*Contributed by William F. Foshag*

The carnotite (U.S.N.M. 95332) forms crusts from 1–2 millimeters in thickness and with rough botryoidal surface on calcareous sandstone. The outer surface is colored greenish to brownish yellow and shows only faint suggestions of crystal faces. The inner portion is made up of coarse plates in parallel position or roughly radiated. These plates are of a deep lemon yellow color with a decided tinge of green and have a pearly silky luster. The powdered mineral is of a strontian yellow color.

Under the microscope the mineral is seen to be made up of clear yellow plates showing a perfect platy cleavage. There appears however, to be no other cleavage. These plates show no pleochroism but grains oriented normal to the cleavage are strongly pleochroic. The scheme is: X grayish yellow with strong absorption, Y lemon yellow, Z lemon yellow. As far as could be determined the plates show parallel extinction. The cleavage flakes show a biaxial interference figure and a medium dispersion of the optic axes. The axial angle ( $2V$ ) on material containing 1.32 per cent of water was measured with the aid of a micrometer ocular and found to be  $50^\circ \pm 2^\circ$ . The indices of refraction of the mineral were found to be somewhat higher than amorphous sulphur. Material dried over concentrated sulphuric

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<sup>1</sup>Dutton, Clarence E. The physical geology of the Canon district. U. S. Geol. Survey, Second Ann. Rep., p. 119, 1882.

acid ( $H_2O=1.32$  per cent) showed, with sulphur-selenium melts, the following indices of refraction:  $\beta=2.06$  and  $\gamma=2.08$  for Na light. The mineral left over sulphuric acid of a water vapor pressure of 19 mm. ( $H_2O=1.72$  per cent) was somewhat lower,  $\beta=2.04$ ,  $\gamma=2.06$ .

#### CHEMICAL PROPERTIES

*Contributed by William F. Foshag*

For analysis there were selected the thicker crusts that were easily detached from the rock. These had a maximum thickness of 2 mm. and were entirely made up of coarse, clean plates. The lower surface of the crusts was pared with a knife to remove any adhering sand grains or calcite from the sandstone cement. The mineral was then crushed to pass 100 mesh and the material thus prepared was examined under the petrographic microscope for impurities. The sample consisted almost wholly of clear, coarse, transparent plates of carnotite of a bright yellow color. Some of the larger grains had a clouded appearance but reflected light showed this effect to be due to included air spaces. A careful search revealed no visible grains of calcite.

The analysis of the carnotite was accomplished as follows: Water was determined both directly and as loss on ignition. As these two determinations gave essentially the same amounts of water later determinations were made wholly as ignition loss. The vanadium was separated from the other constituents by volatilization as vanadium chloride in a stream of dry hydrochloric acid gas. The distillate was examined for molybdenum, phosphorus, iron, arsenic, and lead and found to be essentially free of these elements. The vanadium was then reduced with sulphur dioxide and titrated with potassium permanganate solution after removal of the  $SO_2$  by boiling in a stream of carbon dioxide. The residue in the boat, left from the distillation of the vanadium was entirely soluble in water except for a small amount of gangue. Hydrogen sulphide passed into this acidified solution gave only traces of lead and copper. The uranium, iron, and alumina after oxidation of the iron were separated from the lime and magnesia by three precipitations with carbonate free ammonia. The separations of these constituents were made by the usual methods. Alkalis were determined in a separate portion after the vanadium was separated by distillation, uranium, iron, and alumina by freshly prepared ammonium sulphide and lime and magnesia by ammonium carbonate and ammonium oxalate. The results of the analysis together with the calculated ratios and the theoretical composition for the compound  $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 2/3H_2O$ . is given in the table below.

*Analysis, ratios, and theoretical composition of carnotite from Moab, Utah*

Analysis		Ratios		Theoretical composition
H <sub>2</sub> O	1.35	0.075	2/3	1.4
CuO, PbO	Tr.			
MgO	.22			
BaO	None.			
CaO	.64	.011		
K <sub>2</sub> O	9.58	.101	1 × 1.008	10.9
Na <sub>2</sub> O	.35	.005		
Fe <sub>2</sub> O <sub>3</sub>	.04			
Al <sub>2</sub> O <sub>3</sub>	.16			
UO <sub>3</sub>	65.62	.229	2 × 0.996	66.6
V <sub>2</sub> O <sub>4</sub>	None.			
V <sub>2</sub> O <sub>5</sub>	21.12	.116	1 × 1.000	21.1
P <sub>2</sub> O <sub>5</sub>	Tr.			
As <sub>2</sub> O <sub>5</sub>	None.			
MoO <sub>3</sub>	None.			
Inso <sup>l</sup>	.32			
	99.40			

From these results it is readily seen that the mineral from Cane Springs Pass is an unusually pure carnotite. It is interesting to note the absence of barium and copper, elements reported by Hillebrand in the finer grained carnotites, as well as of phosphorus, arsenic, and molybdenum. The lime content is appreciable, and since no calcite could be detected in the analyzed sample it probably belongs to the mineral where it replaces potash. If the lime is calculated with the alkalis, the ratios come out very close to the theoretical values. The soda content is so small as to be of doubtful significance.

It will be noted that the water content is much lower than that ordinarily given for carnotite. The air-dried material carried a water content of 1.36 per cent, while material kept over sulphuric acid having a water vapor pressure of 19 mm. had a water content of 1.72 per cent. The water content is therefore quite variable, a characteristic common to the members of the uranite groups. The water content is not only determined by the vapor pressure of the water but probably by the size of the grains as well.

## RADIUM—URANIUM RATIO

*Contributed by Frank L. Hess*

It is not surprising, considering the geology of the veins, that lead could not be determined chemically. Sufficient time had not elapsed since the solution and redeposition of the carnotite for the disintegra-

tion of the uranium to form lead in chemically measurable quantity unless much more carnotite than was available could be used. However, that some lead is present was shown spectroscopically by E. G. Zies, who was kind enough to test the mineral for us. He found also copper and tin, together with gold and silver, the amount of the last two being very small.

The problem of the age of the mineral had therefore to be attacked through the proportional equilibrium of the radium present. Rutherford<sup>2</sup> estimated that equilibrium of radioactivity—that is, the maximum possible quantity of radium present with its ancestral uranium—was reached after a period of 10,000,000 years. Mr. C. W. Davis, of the Reno station of the Bureau of Mines, was therefore asked to make a determination of the proportional radioactivity, which he kindly did, using a part of the analyzed material. Concerning the determination Mr. Davis wrote:

The carnotite from Foshag's analysis contains 65.6 per cent  $UO_2$ , which, using the atomic weight of uranium as given in the international table of atomic weights for 1925,<sup>3</sup> gives the uranium content of 54.60 per cent.

Standard pitchblende, part of the sample used by Lind and Roberts in their determination of the absolute value of the radium: uranium ratio,<sup>4</sup> containing 66.12 per cent U, was used to standardize the instruments and the Ra/U ratio found by them ( $3.40 \text{ by } 10^{-7}$ ) was used in my calculations.

Four samples of the carnotite of about 60 milligrams each and four samples of the standard pitchblende of about 50 milligrams each were accurately weighed into thin glass bulbs on an assay balance, and the bulbs, which were provided with a neck, were sealed off by drawing out the neck. After from 35 to 38 days (it took 4 days to make the final determinations) these samples were analyzed for radium.

The method described by Lind and Whittemore<sup>5</sup> as the "solution emanation method in a single operation" was chosen as the most satisfactory for the purpose. This prevents any loss of radium that might occur from the long standing of solutions and eliminates errors that might occur in determining the "emanating power" of the minerals used. It also makes the use of equilibrium tables unnecessary. The details of boiling off, collection, and measuring of the radon are given by Lind.<sup>6</sup>

The electroscopie chambers were treated so that the natural leak was satisfactory (0.033 divisions per second), and a blank test on the reagents and apparatus gave precisely the same rate of leaf fall. This natural leak remained constant during the four days on which the tests were made.

Fifteen electroscopie readings were made for each determination, the pressure in the chambers being kept at less than atmospheric until about 30 minutes before readings.

At the times during which readings were taken the barometric pressure was within the limits 644 mm. and 642.9 mm., and the temperature was within the limits 20° C. and 18.5° C., so that no correction is necessary for these factors.

<sup>2</sup> Rutherford, E. Radioactive substances and their radiations. Cambridge, p. 431, 1913.

<sup>3</sup> Journ. Amer. Chem. Soc., vol. 47, p. 600, 1925.

<sup>4</sup> *Idem*, vol. 42, p. 1170, 1920.

<sup>5</sup> Bureau of Mines Technical Paper 88, pp. 12-13, 1915.

<sup>6</sup> Journ. Industrial & Engineering Chemistry, vol. 7, p. 1024, 1915.

The results are given in tabular form below :

Chamber No.	D. P. S. per g.		Ra per g. $\times 10^7$			
	Standard pitch-blende	Carnotite	Standard	Carnotite	Upper g carnotite	$\frac{R}{U} \times 10^7$
1	30. 579	17. 152	-----	-----	-----	-----
	30. 148	17. 132	-----	-----	-----	-----
Average	30. 364	17. 140	2. 248	1. 269	0. 5460	2. 32
2	32. 027	17. 522	-----	-----	-----	-----
	31. 720	17. 774	-----	-----	-----	-----
Average	31. 873	17. 648	2. 248	1. 244	0. 5460	$\left\{ \begin{array}{l} 2. 28 \\ 2. 30 \end{array} \right.$

You will notice that the Ra:U ratio ( $2.30 \times 10^{-7}$ ) is only about 68 per cent of the normal ratio ( $3.40 \times 10^{-7}$ ) determined by Lind and Roberts.

From Mr. Davis's determination that the radioactivity is about 68 per cent of that present when radium is in equilibrium, it follows that the mineral is about 6,800,000 years old—say 7,000,000 years, and such a figure accords well with the geology of the deposit.

The ordinary carnotites of the region show as much as 0.80 per cent PbO, indicating an age of about 42,000,000 years.<sup>7</sup> Owing to the movement of the mineral the lead here too is probably lower than it would be if the mineral occupied exactly its original position.

The Grand Canyon of the Colorado, although much deeper and more imposing farther down the river, nevertheless has a very considerable development at Moab, where the drainage from Bridger Jack joins the main stream. Concerning the age of the Grand Canyon in years, Dutton<sup>8</sup> said:

No doubt the question will often be asked, how long has been the time occupied in the excavation of the Grand Canyon? Unfortunately there is no mystery more inscrutable than the duration of geological time. On this point geologists have obtained no satisfactory results in any part of the world. Whatever periods may have been assigned to the antiquity of past events have been assigned provisionally only, and the inferences are almost purely hypothetical. In the Plateau country, Nature, has, in some respects, been far more communicative than in other regions, and has answered many questions far more fully and graciously. But here, as elsewhere, whenever we interrogate her about time other than relative, her lips are sternly closed, and her face becomes as the face of the Sphinx.

Through the crystallized carnotite just described Nature partly answers the question of age. Possibly other discoveries of radioactive minerals will allow a still further determination of the age of the Colorado Canyon as they do of many other earth features.

<sup>7</sup> Hess, Frank L. New and known minerals from the Utah-Colorado carnotite region. U. S. Geol. Survey Bull. 750, p. 78, 1924.

<sup>8</sup> Dutton, C. E., U. S. Geol. Survey, Second Ann. Rep., p. 166.