

ART. XIV. — *On Carnotite and Associated Vanadiferous Minerals in Western Colorado*; by W. F. HILLEBRAND and F. LESLIE RANSOME.

INTRODUCTION.

W. F. HILLEBRAND.

THE rather wide-spread occurrence in western Colorado of considerable quantities of a canary-yellow ore of uranium has been known for a few years past. It has been marketed to the extent of a few tons, but its mineralogical nature was unknown or incorrectly surmised until about a year ago.

In the spring of 1899 a specimen of this ore first reached my hands through Dr. Geo. P. Merrill of the U. S. National Museum, and was speedily recognized to contain a mineral or minerals new to science. Within a week appeared the announcement by MM. C. Friedel and E. Cumenge\* of a new mineral, carnotite, a hydrous vanadate of uranium and potassium, obtained through Mr. Poulot of Denver, from Roc Creek, Montrose Co., Colo. Mr. Poulot had already identified vanadium in it. It was at once seen, despite certain differences in composition, that the two were identical.

According to the French authors the mineral is of simple composition, as above expressed, with only a little iron and mere traces of Al, Ba, Cu, Pb, and also according to M. and Mme. Curie, of the radio-active substances radium and polonium. The empirical formula  $2\text{U}_2\text{O}_3, \text{V}_2\text{O}_5, \text{K}_2\text{O}, 3\text{H}_2\text{O}$ , was assigned to it, some doubt attaching to the water.

Since then I have been able to examine carnotite from several localities in western Colorado, finding in each case the same lack of agreement with the analyses of Friedel and Cumenge.

While engaged in this work there were brought to my attention certain more or less greenish sandstones from the vicinity of Placerville on the San Miguel River, San Miguel Co., Colo., which were said to be highly vanadiferous and of considerable extent, and in which a zone a few inches thick was rather strongly impregnated with a yellow mineral resembling and probably identical with carnotite. This latter appeared also scattered through the sandstone at other points in sporadic small patches, sometimes only visible by aid of a lens.

This occurrence led to the thought that the carnotite bodies farther west might also be associated with existing or depend-

\* Bull. Soc. Chim. de Paris (3), xxi, 328, 1899; Bull. Soc. Franc. Min., xxii, 26, 1899; Comptes Rend., cxxviii, 532, 1899; Chemical News, lxxx, 16, 1899. The papers as published in French differ slightly.

ent on preëxistent vanadiferous sandstones. For the carnotite of Montrose and Mesa Counties, as mentioned by the French authors, occurs mixed in all proportions with quartz-sand grains, the remnants beyond doubt of former sandstone bodies, and it was soon recognized that in the carnotite bodies the vanadium existed in two conditions, the larger part by far as pentavalent vanadium in the easily soluble carnotite, and a smaller and sometimes hardly distinguishable portion as trivalent vanadium in a much less soluble silicate which was free from uranium.

It was hoped that by a field reconnaissance, observations bearing on these points would be obtained and material assembled which would on analysis help to solve the nature and explain the association of these two entirely different classes of mineral substances.

The field and microscopical observations of Messrs. Ransome and Spencer are embodied in the pages immediately following these introductory remarks. Unfortunately their collections, except from Placerville, came to hand so late that the chemical work on the more western occurrences has been confined to the carnotite bodies alone, of which material was already in my hands. Greenish sandstones have been observed by Messrs. Ransome and Spencer in those regions, but whether any of them are highly vanadiferous, or what their connection with the carnotite may be, remains yet unknown. The only two examined did not owe their color to vanadium. Meanwhile the chemical results thus far obtained, which it is advisable to put on record at once, will be found in the concluding section of this paper.

In this place it is my pleasure to record my appreciation of the readiness with which the following gentlemen have supplied me with material for study: Messrs. Poulot and Voillequé of Denver, Mr. A. B. Frenzel of Placerville, and Mr. J. R. Duling of Paradox. These gentlemen have, also, not hesitated to furnish me with all information at their disposal as to occurrence, etc., of these interesting ore bodies.

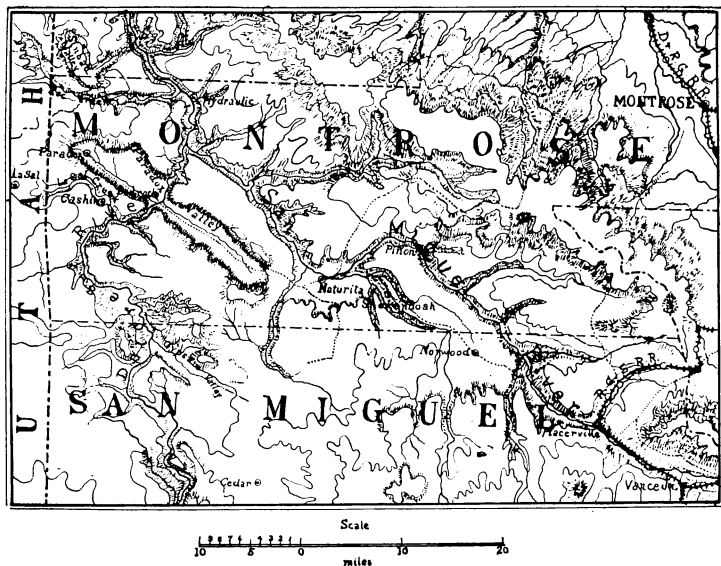
#### OCURRENCE OF THE URANIUM AND VANADIUM ORES.

F. L. RANSOME.

*General.*—In the autumn of 1899, a brief reconnaissance trip was undertaken into the western portions of San Miguel, Montrose and Mesa Counties, near the Utah-Colorado line. I was accompanied by Dr. A. C. Spencer, whose knowledge of the stratigraphy of the region was of great assistance. The primary object of the expedition in accordance with a suggestion from Mr. S. F. Emmons, was to investigate the

copper deposits of La Sal Creek, Paradox and Sinbad Valleys, and the vicinity, which had been responsible for some mining excitement a few months previously. A memorandum from Dr. W. F. Hillebrand, received just before starting, indicated that it would be well also to examine certain prospects on which some preliminary work had been done, looking toward the extraction of ores of uranium and vanadium. It is to the latter that these present notes are confined.

## 1



The most convenient way of reaching Paradox Valley was found to be the stage road, which, starting from Placerville, a settlement and station on the Rio Grande Southern R.R., runs by way of Norwood, Shenandoah and Naturita to Paradox, a distance of 60 or 70 miles.

The region can also be reached from the west by way of Moab, in Utah. The Placerville route and the general geographical relations are roughly indicated in the accompanying sketch map, fig. 1.

The topography of the region west of Placerville is that characteristic of the "mesa country" of western Colorado and southeastern Utah. Broad stretches of plateau are intersected by steep-walled cañons and cliff-encircled valleys. The underlying rocks comprise the "red beds" of the Dolores forma-

tion\* (Triassic), the La Plata formation (Jurassic), the McElmo formation (Jurassic), the Dakota sandstone (Cretaceous), and the Mancos shales (Cretaceous). Carboniferous rocks occur in Sinbad Valley, and a series of gypsum-bearing shales of unknown age in the bottoms of Sinbad and Paradox Valleys, but as the ore-deposits to be described all occur in the beds of the La Plata and McElmo formations, these older rocks need not be again referred to. The sediments making up these various formations lie usually nearly horizontal, but they are sometimes flexed and frequently faulted.

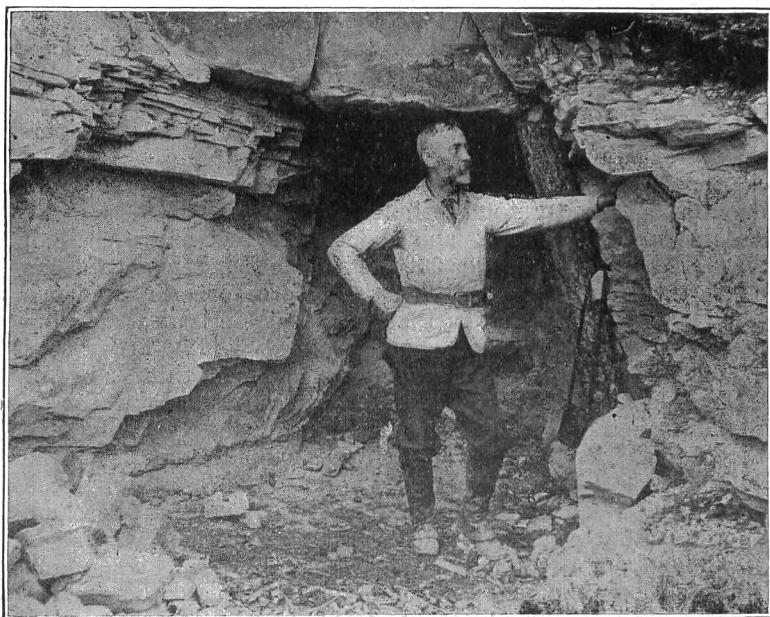
In all of the prospects examined, the ore of uranium occurs in the form of the recently described bright yellow carnotite. In one case this is intimately associated with a dull olive-green mineral which according to Dr. Hillebrand is either identical with, or very closely allied to, the vanadium-mica roscoelite. Deposits of one or both of these minerals occur widely scattered over San Miguel and Montrose Counties, Colorado, and in the Blue Mountain (Sierra Abajo) district of southeastern Utah; but a portion only of the known deposits were personally examined.

*The Placerville Deposits.*—These are essentially vanadium deposits, and occur 4500 feet nearly northeast of the railway station near Placerville, and about 1000 feet above the San Miguel River. The lower 900 feet of the San Miguel cañon is cut in the typical "red beds" of the Dolores formation. Above the Dolores comes the La Plata sandstone in typical development as described in the Telluride folios, viz., two heavy beds of light-colored sandstone, separated by a much thinner bed of dark limestone. The roscoelite occurs as an impregnation in the lower bed of the La Plata sandstone, about 100 feet above the base, and just beneath the bed of dark limestone. All the beds at this point are practically horizontal. The dark green vanadiferous sandstone occurs in a nearly continuous band, approximately parallel to the bedding planes, and varying in thickness from a few inches up to five or six feet. This band extends along the sandstone cliffs for an estimated distance of about 2000 feet. The roscoelite occurs more or less thoroughly impregnating portions of the fine-grained sandstone which constitutes the mass of the bed. It sometimes makes up more than 20 per cent of the vanadiferous facies. Normally the sandstone of this lower bed of the La Plata is light buff in color, with patches, mottlings, and stripes of pale pink, the latter color being apparently due to small amounts of ferric oxide. But when richly impregnated with roscoelite, this light-

\* The formation names used in these notes are those adopted by Cross in the text of the Telluride Folio, of the U. S. Geol. Survey. The reader is referred to this folio for fuller descriptions.

colored sandstone becomes dark olive-green, the contrast being most marked when the cliffs are wet. Although fairly continuous for the distance stated, this zone of vanadiferous sandstone is by no means regular. It varies much in thickness, and in one place splits into two or more branches. At some points two or more distinct streaks of roscoelite-bearing sand were found at different horizons in the main sandstone bed. The carnotite is not nearly so abundant as the roscoelite at this locality. It occurs as minute yellow specks in the sandstone, and particularly as thin horizontal seams or streaks near the bottom of the vanadiferous zone.

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The work thus far done on the several claims which have been located along these deposits is of the most superficial character. On the Canary claim a tunnel of about 18 feet has been run by Mr. A. B. Frenzel which exposes a typical section of the impregnated zone (fig. 2). The roof of the tunnel is formed by the underside of the bed of dark limestone previously referred to. This limestone is underlain by a few inches of sandy limestone which passes into the light-buff La Plata sandstone without break. The latter contains abundant calcite

as a cement or matrix for the sand grains. At a distance of a foot below the limestone, the sandstone shows, on close inspection, numerous specks of carnotite and gives a qualitative reaction for vanadium (Hillebrand). Examined in thin section under the microscope, this portion of the bed shows a fine-grained homogeneous sandstone, in which well rounded grains of quartz are held together by a rather abundant matrix of calcite. The latter is crystallized as a fine granular aggregate and includes small indeterminable particles of various kinds. Many of the quartz grains as seen in section are entirely surrounded by calcite, and so isolated from adjacent grains. A pale lemon-yellow substance occurs sporadically in the section as an interstitial material between the quartz grains. This is probably the carnotite which was seen as small yellow specks in the hand specimen. It is very minutely crystalline, recalling the habit of some obscure chloritic aggregates in decomposed igneous rocks, and is too indistinct for successful optical study. Small crystal grains of zircon are scattered through the sandstone, and are readily concentrated in the residue after treating with hydrofluoric acid.

In the next two feet below where it exhibits the foregoing facies, the sandstone becomes pinkish in color, due to the presence of ferric oxide, and the lens fails to reveal any roscoelite or carnotite. But just below the pink coloration, the sandstone begins to show yellow and green specks. The latter especially become more numerous and larger, until at from 3 to 4 feet below the limestone the sandstone has a decided green tint. This deepens, going downward, until near the floor of the tunnel the sandstone is a deep uniform olive-green, rich in roscoelite (over 20 per cent) and showing many small yellow specks of carnotite. This is regarded as the first-class ore, and the chief value of the deposit is supposed to be in its vanadium, the uranium being very subordinate. In this respect the Placerville deposit differs from those on La Sal and Roc Creeks, presently to be described, where the mineral sought for and occurring most abundantly is carnotite.

Thin sections of the green-spotted sandstone, when examined microscopically, resemble those of the light-buff sandstone just above it, as far as character of quartz grains and relative abundance of matrix are concerned. But the character of the matrix or cement is different. Calcite is much less abundant and its place is largely taken by roscoelite. This is grass-green in thin section, and might readily be mistaken for indistinct wisps and areas of chlorite. It sometimes forms a distinct envelope around the quartz grains, showing an indistinct foliated or fibrous structure normal to the surface of the latter.

The uniformly dark green sandstone richest in roscoelite does not effervesce with acids and shows no calcite cement in thin section. The usual quartz grains are held together by roscoelite. This is crystalline, but the highest available powers show only an indistinct and minute foliation, such as may be observed in some very finely crystallized chlorites.

Close to the floor of the tunnel is a fairly regular, nearly horizontal streak of carnotite, varying in width, but usually less than an inch, and showing noticeable diminution in thickness in the face of the tunnel. This small seam is not solid carnotite, but is merely a zone in the sandstone impregnated with the bright-yellow uranium mineral. It is not nearly so continuous as the main vanadiferous belt, and was seen only at three or four places along the 2000 feet or so of outcrop of the latter. When this seam is closely examined, it is seen that narrow bands rich in carnotite alternate with green bands carrying mostly roscoelite. There is also usually present a seam generally about an eighth of an inch in thickness (though often thicker) which is almost wholly quartz. The microscope shows it to be a true quartzite, in which the original rounded detrital grains of quartz have been cemented by fresh quartz in optical continuity with the older granules. A similar quartzite occurs in the green vanadiferous sandstone above the carnotite, where it forms concretionary knots and nodules. It was not noted in the buff sandstone however, where the cementing material is calcite.

Immediately below the carnotite seam there is a parting or "floor" in the sandstone, probably originally a very thin layer of shale, which forms the working floor of the tunnel. The sandstone below this floor is plainly impregnated for a short distance with roscoelite, but the thin shale seam is regarded as the practical bottom of the deposit.

The questions of the origin and actual extent of this deposit are closely related, and of much interest. Their discussion will be deferred until the other deposits visited have been described.

Some distance below the Placerville vanadium deposit, sandstone, presumably belonging to the Dolores formation, was observed to be colored green, of a somewhat brighter hue than the vanadiferous sandstone higher up the slope. As there are some copper prospects near by, from which ore has been taken, this was supposed to be a copper stain. Qualitative tests by Dr. Hillebrand show however that the color is due to a compound of chromium.

Similar green sandstones occur on the western side of Sinbad Valley in what is apparently the La Plata formation, and were originally supposed to be impregnated with roscoelite. Dr. Hillebrand's investigations, however, show that they too owe

their color to some chromium mineral. These occurrences are interesting as showing that a green color in sandstones may result from various causes, and that even a bright green tint cannot be taken as an infallible indication of copper.

*The La Sal Creek deposits.*—These occur in the extreme western portion of Montrose County, southwest of Paradox, and about six miles up La Sal Creek from Cashin P. O. They are reached by trails from Paradox Valley and from Cashin. The deposits are on the south side of La Sal Creek and about 700 feet above the stream. They occur for a distance estimated at more than a quarter of a mile, along the sandstone cliffs which descend from the mesa into the cañon of La Sal Creek, and only a few feet below the level of the mesa surface.

In the absence of continuous stratigraphic work, it is impossible to correlate certainly and finally the rocks on La Sal Creek with the divisions established by Cross and Spencer in the Telluride quadrangle to the eastward. It seems probable, however, that the La Plata sandstone attains a much greater thickness in this portion of western Colorado than it does between Telluride and Placerville. The limestone bed, so characteristic a feature of the formation near Placerville and further east, is not uniformly present in this western region, and the La Plata sandstone (Variegated Beds, in part, of the Hayden Survey) is not always readily differentiated from the underlying Dolores formation (Red Beds). For a vertical distance of about 400 feet above the bed of La Sal Creek the rock is a heavy-bedded, rather fine-grained, light-colored sandstone, which is considered by Dr. Spencer to be the La Plata. Above this come thinner-bedded sandstones, with some conglomerates and shales, which are included in the McElmo formation. It is in this upper series that the uraniferous deposits occur. All the beds are here approximately horizontal.

As revealed by numerous small openings near the crest of the bluff, the carnotite, which is the material here sought, is found chiefly in a massive bed of nearly white sandstone. Some of the ore, however, lies between the sandstone and a lower bed of light-gray shale. Although the prospecting openings all lie at about the same level along the cliffs, the deposit is not nearly so regular as the vanadiferous band near Placerville.

The carnotite of La Sal Creek occurs as irregular, bunchy "pockets" in the sandstone, or along the contact of the sandstone with the underlying shale. These have all the appearance of being impregnation deposits, the solutions carrying the uranium compounds having deposited the ore wherever they found ready passage through the rock—usually along bedding planes. No roscoelite was detected with the carnotite.



The most remarkable and interesting fact in regard to the La Sal Creek deposits is their very superficial character. The ore bodies are usually flat-lying streaks, a few inches thick, which grade above and below into the common light-buff sandstone, and which die out and disappear when followed into the hillside. In tunnels run but a few feet underground the yellow impregnation of carnotite can be seen to gradually die out, to be succeeded by light-colored sandstone, showing no apparent trace of the mineral. It is doubtful whether any appreciable quantity of carnotite occurs as much as 20 feet from the surface, on any of the locations, although this distance is given from memory and not from measurements on the ground. As before stated, the impregnation has usually taken place along bedding planes; it has also proceeded along surfaces of minor and superficial movement in the rocks. In one case it was observed that a portion of the overlying sandstone had moved upon the underlying shales, the disturbance being apparently a superficial one, of a kind commonly enough observed where massive beds rest on yielding shales on a steep hillside. In other words, the movement appeared to be directly related to the present topography. The deposition of carnotite was here plainly subsequent to the movement and had taken advantage of the small openings and dislocations in the shale afforded by this very recent disturbance. It was reported that some of the best nests of ore had been found in "slide rock," i. e., rock which had slipped to same extent down the slope; but I was unable to verify this statement further than is indicated in the preceding description. There can be little doubt but that the deposits of carnotite on La Sal Creek are not only very superficial in character but very recent in age.

*The Roc Creek Deposit.*—The principal claim is the Copper Prince, owned by J. R. Duling, on the north side of Roc Creek, 3 or 4 miles above its mouth, and near the foot of the Miller trail to Paradox. It is reached by this trail from Paradox Valley, or by trail from Hydraulic on the Dolores River. This deposit is in the La Plata sandstone according to Dr. Spencer's observations, and has been more extensively exploited than any other seen. The sandstone, which at this point is nearly horizontal, is cut by an east and west fault, the fault plane dipping north at about 70°. The amount and character of the throw could not be determined. It is probably less than 50 feet. The carnotite occurs in the hanging wall of the fissure as small irregular branches in a loose mass of crushed sandstone and also as an impregnation of some of the firmer portions of the bed. No roscoelite was seen. Several small tunnels have been run in on the hanging wall side of the fissure (which itself carries no vein or ore-body), but they had

been securely closed by planking, and no examination of their inner ends could be made. I am thus unable to tell what becomes of the deposit as it is followed in from the surface. A few hundred pounds of picked carnotite ore has been shipped from this claim and is reported to have sold for \$1.25 a pound in Denver. The character of this deposit is similar to others examined, except that in this case a well-defined fault has provided a zone of crushed and porous rock in the hanging wall, along which impregnation could take place. A few hundred feet farther west the crushed sandstone adjoining the fault has been impregnated with cupriferous solutions and is spotted with stains of the blue and green carbonates of copper.

*Other Deposits.*—It is known that several carnotite claims have been taken up in Gypsum Valley in what is known as the Disappointment District. The impregnated sandstone is said to cap a hill and to constitute an extensive deposit, but it was not visited. Carnotite is also reported from the Blue Mountain District, but I have no personal knowledge of these occurrences. It seems highly probable that the material will be found widely distributed in the Mesozoic sandstones of western Colorado and eastern Utah, although perhaps nowhere in very extensive bodies.

*Origin of Deposits.*—That the deposits of carnotite and roscoelite were formed subsequently to the deposition of the sandstones is evident from the facts presented in the preceding pages. It is equally plain that the minerals could not have resulted from the alteration, in place, of other compounds of vanadium and uranium originally deposited with the sands. The shape and position of the deposits indicate clearly that the ores have been deposited in their present position only after transportation from a greater or less distance. Moreover, the recency of the deposits and the fact that they are sometimes directly connected with faults and dislocations in the sandstones shows that the vanadium and uranium compounds could not have been the original cementing material of the quartz grains, but have in all probability locally replaced the calcite which acts as matrix to the ordinary light-colored sandstone in which the ore-bodies occur. The deposits of roscoelite appear to be comparable to the impregnations of the sandstones with cupriferous solutions observed in many places in this region, particularly on La Sal Creek near Cashin and in Sinbad Valley, whereby the sandstone becomes colored bright green with the carbonate of copper. In these cases, however, the copper appears to have been previously deposited in part as chalcocite. An analogy might also be drawn with the green chromiferous sandstone near Placerville already referred to. In all these cases the actual sources of the materials which have

been deposited by solutions in their present position are not known. Dr. Hillebrand has shown,\* however, that vanadium in small amounts is widely distributed in sandstones, limestones, and igneous rocks. It is perhaps present in very small amounts in the bulk of the sandstone, and the deposits described may simply represent a concentration of this material under certain favorable conditions of solution and re-deposition.

In the absence of exploitation it is manifestly impossible to predict the probable shape and size of ore-bodies formed in this manner. The roscoelite as seen near Placerville appears, however, to be much more persistent than the carnotite. There is no apparent reason why a mass of sandstone, impregnated with roscoelite, which is continuously exposed for several hundred feet along a cliff, should not extend for a considerable distance inward from the cliff face. The carnotite, on the other hand, appears to be a much more superficial occurrence and, in fact, to have a not yet fully understood connection with the present surface of the ground. This would indicate that the carnotite results from a local concentration of material already existent in the sandstone, and the deposition of this material in the form of carnotite under conditions determined by proximity to the surface, and probably partly dependent upon a semi-arid climate.

#### CHEMICAL ANALYSES AND DISCUSSION.

W. F. HILLEBRAND.

##### *1. The Green Coloring Constituent of the Placerville Sandstone.*

As noted by Mr. Ransome, the greener the sandstone, the greater has been the replacement of the calcareous cementing material by the crystalline vanadiferous mineral. Fortunately the greenest available specimen was entirely free from carbonate, and this was used for analysis, 10 grams being taken for the main portion.

The green substance was but slightly attacked by cold acids and not rapidly by hot ones; nevertheless after 12–24 hours digestion on the water-bath with diluted nitric acid, the greenish color had been transferred to the liquid, the residue of sand was nearly white, and a rather voluminous separation of non-gelatinous silica had taken place. The filtration and washing of the insoluble matter was accomplished without difficulty. The free silica in it was extracted by two or three digestions of 15 minutes each on the water-bath with sodium carbonate solution of 5 per cent strength. The flocculent matter had entirely disappeared and the sandy residue was collected in a

\* This Journal, IV, vol. vi, pp. 209–216, 1898.

Gooch crucible and washed with hot sodium carbonate solution, followed by very dilute nitric acid and finally by alcohol to prevent turbid filtration. Drying of the sand was effected by allowing the pump to draw air through the crucible until no further loss in weight resulted.

The water in the sand was then determined at 105°, at 300° and above 300°. Similar water determinations having been made on the unattacked substance, the differences gave the water expelled at those temperatures from the soluble part.

The sodium carbonate solution was acidified, evaporated, and filtered, and the filtrate again evaporated, to recover the last of the silica. To this was added a very small portion which the nitric acid extract of the sandstone held in solution. The sum represents the total silica of the decomposed portion of the sandstone.

The further analysis of the nitric solution presented difficulty because of the vanadium it contained. It was carried out in a variety of ways, of which the following seemed to be most satisfactory.

Barium was first precipitated by sulphuric acid and subsequently separated from traces of lead, calcium and vanadium. Hydrogen sulphide then threw out further traces of lead and copper with much sulphur from reduction of  $V_2O_5$  to  $V_2O_4$ . After evaporation of the filtrate to reoxidize vanadium and iron, the alumina, iron and trace of uranium with much vanadium were separated from calcium, magnesium and alkalis by three precipitations by ammonia solution. The combined filtrates were evaporated, ignited, the residue transferred to a porcelain boat with nitric acid, evaporated therein to complete dryness, and exposed in a glass tube to a current of dry hydrochloric acid gas, as recommended by Smith and Hibbs\* for the expulsion of vanadium from alkaline vanadates. The removal of vanadium being incomplete, the contents of the boat were again evaporated with nitric acid and again distilled, and these operations were repeated till no further evidence of a brown distillate appeared. The boat now contained only magnesium and alkalis with a little calcium. The distillates, containing all the vanadium that was in the boat, had been collected in U-tubes charged with water, and were eventually obtained in sulphuric solution for further treatment by evaporating with sulphuric acid in porcelain.

The precipitate of  $Al_2O_3$ , etc., was dissolved in nitric acid, evaporated almost to dryness in platinum and boiled with sodium hydroxide solution. These operations were repeated on the precipitate after filtration. The iron and titanium thus

\**Jour. Am. Chem. Soc.*, xvi, 578, 1894.

purified were redissolved, precipitated by ammonia, weighed, redissolved by acid potassium sulphate, the ferric iron was reduced by hydrogen sulphide and titrated with permanganate after boiling out the reducing agent. The titanium was then found colorimetrically by hydrogen peroxide.

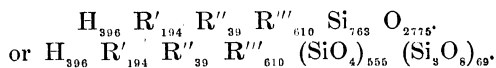
The combined alkaline filtrates were heated with excess of ammonium nitrate to separate alumina from most of the vanadium. The precipitate was redissolved in nitric acid, reprecipitated by ammonia, then ignited and weighed and redissolved by acid potassium sulphate. The sulphuric solution was reduced by hydrogen sulphide, boiled and filtered from platinum sulphide, again boiled in a current of carbon dioxide and titrated hot with permanganate. Sulphur dioxide gas was then introduced, boiled out in a current of carbon dioxide, and the titration repeated, this second result being taken as representing the  $V_2O_5$  equivalent to the  $V_2O_5$  that still contaminated the  $Al_2O_3$ . Deducting the  $V_2O_5$  thus found from the combined weight of  $Al_2O_3$  and  $V_2O_5$  gave the  $Al_2O_3$  of the soluble constituent of the sandstone.

The combined filtrates from the alumina were evaporated, ignited to remove ammoniacal salts, the residue converted to sulphates, and united with the earlier solution of vanadium sulphate. The vanadium in it was then determined precisely in the manner already described, and when added to that found with the alumina and calculated to  $V_2O_5$ , gave the total in the sandstone.

A check was made by dissolving the sandstone in hydrofluoric and sulphuric acids in a current of carbon dioxide and titrating the  $V_2O_5$  with permanganate. The figure thus obtained was a trifle below that found as above detailed, and this is to be attributed to the presence of a very little vanadium as  $V_2O_5$  in carnotite, and probably as a lead vanadate. All the uranium and most of the trifling amount of lead could be extracted by cold dilute nitric acid, thus showing them to be foreign to the green substance.

It is preferable to regard iron as in the ferric state rather than as ferrous, otherwise an equivalent amount of vanadium would have to be considered as  $V_2O_5$ , for which there is no occasion. It is quite possible that the iron is in part, if not wholly, foreign to the green matter, for it would be surprising to find an exposed sandstone free from ferric oxide.

If the iron is disregarded as probably extraneous, the ratios given below afford the following empirical formula:



Simplified this is  $H_{40} R'_{20} R''_4 R'''_{61} X_{62.4}$ .

Considering that the mineral is probably not perfectly pure and the uncertainties affecting the amount of water to be considered, etc., the above affords a close approach to the typical phengitic muscovite formula  $H_2KR''X_3$  in which X comprises the groups  $SiO_4$  and  $Si_3O_8$ .

*Analysis of the vanadiferous sandstone.*

|                                 |                                       | Sandstone. | Ratios. | Silicate. | Roscoelite.  |
|---------------------------------|---------------------------------------|------------|---------|-----------|--------------|
|                                 |                                       | Per cent.  |         | Per cent. |              |
| Soluble<br>in<br>Nitric acid.   | { $SiO_2$ -----                       | 12.56      | .763    | 46.06     | 45.17        |
|                                 | { $TiO_2$ -----                       | .02        |         |           | .78          |
|                                 | { $V_2O_5$ -----                      | 3.50*      | .0846   | } .305    | 12.84        |
|                                 | { $Al_2O_3$ -----                     | 6.15       | .2206   |           | 24.01        |
|                                 | { $Fe_2O_3$ -----                     | .20        | .0046   |           | 11.54        |
|                                 | { $CaO$ -----                         | .12        | .0078   |           | .73 FeO 1.60 |
|                                 | { $BaO$ -----                         | .37        | .0088   | } .039    | .44          |
|                                 | { $MgO$ -----                         | .25        | .0228   |           | 1.35         |
|                                 | { $K_2O$ -----                        | 2.41       | .0938   | } .097    | .92          |
|                                 | { $Na_2O$ -----                       | .06        | .0035   |           | 8.84         |
|                                 | { $H_2O$ at $105^\circ$ --            | .54        | .1100   |           | 10.37        |
|                                 | { $H_2O$ $105^\circ$ – $300^\circ$ -- | .14        | .0283   |           | .22          |
|                                 | { $H_2O$ above $300^\circ$ --         | .97        | .1978   | } .198    | .40          |
|                                 | { $UO_3$ -----                        | .05        |         |           | .17          |
|                                 | { $PbO$ -----                         | .06        |         |           | 4.12         |
|                                 | { $V_2O_5$ -----                      | .05        |         |           |              |
| Insoluble<br>in<br>Nitric acid. | { Quartz, etc. --                     | 72.24†     |         |           |              |
|                                 | { $H_2O$ at $105^\circ$ --            | .04        |         |           |              |
|                                 | { $H_2O$ above $105^\circ$ --         | .20        |         |           |              |
|                                 |                                       | 99.93      |         |           |              |
|                                 |                                       |            |         | 100.00    | 99.86        |

Traces of Li, Cu, Mo, Bi. No Cl,  $SO_3$ , or  $P_2O_5$ .

An attempt to satisfactorily distribute the constituents among different chemical molecules would be futile, since, for instance, we do not know whether to ascribe the barium to a biotite or muscovite molecule, but the close approach to the muscovite ratio leaves little room to doubt the character of the body. Notwithstanding the chloritic aspect of the mineral under the microscope, the analysis shows that it cannot be a chlorite, and we have undoubtedly to do with a body closely related to the mica roscelite, wherein, however, the percentage proportions of  $Al_2O_3$  and  $V_2O_5$  are reversed, thus affording a further striking example of the mutual replaceability of these two oxides.

\* Oxidation by permanganate of the HFl and  $H_2SO_4$  solution of the sandstone indicated 3.43 per cent  $V_2O_5$  (mean of 3.50, 3.32, 3.48, 3.43).

† Containing about 65 per cent  $SiO_2$ , 7 per cent  $Al_2O_3$  ( $Fe_2O_3$ ,  $TiO_2$ ) and about 0.3 per cent of zircon and other minerals not decomposed by repeated evaporations with HFl and  $H_2SO_4$ .

For comparison, the latest analysis of roscoelite from Placerville, Calif., is given a place in the above table. Peculiar, though unimportant, is the coincidence that the only two known localities for this mineral should bear the name Placerville.

## II. *Green Sandstone Colored by Chromium.*

Other sandstones much brighter green than the vanadiferous one were observed and collected by Dr. Ransome, both at Placerville and 60 miles distant in Sinbad Valley. The color suggested a salt of copper as its cause, but analysis showed it to be due to chromium. Time has failed for an examination as to the nature of this coloring body. It is very difficultly soluble, thus presenting greater hindrance to analysis than was the case with the vanadium compound. It would be interesting to find it to be a micaceous mineral analogous to the one just described. Under the microscope it presents a chloritic appearance (Ransome). If opportunity offers, the problem of its nature may yet be attacked.

In still another greenish sandstone from the west bank of the Dolores River, near the mouth of La Sal Creek, analysis failed to show either vanadium or chromium.

## III. *The Carnotite Ores.*

*Optical Examination.*—Dr. Geo. P. Merrill has kindly submitted the following notes.

"The carnotite powder appears under the microscope in the form of exceedingly minute dust-like particles, without crystal outlines and acting so faintly on polarized light as to at first seem almost amorphous. Much of the matter appears merely as a fine brownish clay, stained yellow by an amorphous pigment, but occasionally a well-defined fragment of a light yellow, translucent mineral is met with which doubtless represents the vanadium compound in its condition of ideal purity.

Working over a considerable amount of the powder, I have found occasional clusters of this yellow mineral in the form of flattened radiating crystals with pyramidal terminations which are without evident pleochroism, polarize only in dull colors, and give extinctions always parallel to the axis of elongation. These are so minute (not over 0.25<sup>mm</sup> in length) and so thin that I have never been able to find a crystal so oriented as to give an opportunity of determining its exact character, and I can only say that the general shape is such as to suggest a hexagonal mineral, though this is by no means certain."

*Chemical Examination of the Carnotite Ores.*—The chemical problems involved in the analysis of the carnotite ores were peculiarly intricate. Ideal material was quite unobtainable

and mechanical separation impossible. The first specimen received happened to be of a higher grade than any of the subsequent ones, containing about 5 per cent of sand grains and showing only very faint delicate reddish tracings indicative of some foreign iron mineral. In mass it was of a beautiful canary-yellow color and easily broken down by pressure. Other specimens were more coherent, the degree depending altogether on the extent to which the sandstone had been impregnated and altered, and they sometimes showed more of the peculiar reddish admixture.

A fact only suspected in making the first analysis was confirmed by subsequent work on lower grade ores, namely, that the vanadium existed in two conditions, in entirely distinct minerals; the greater part by far as pentavalent vanadium in the easily soluble carnotite, and a smaller, much less soluble portion, almost vanishing in the purest ores, in the trivalent state as a constituent of a silicate free from uranium. This observation explained the statement of Messrs. Poulot and Voillequé that they had found the low grade ores to be relatively richer in vanadium as compared with uranium than the high grade ores.

While the carnotite dissolves at once in cold dilute nitric acid, unfortunately the vanadiferous silicate is not quite insoluble, hence arose an important difficulty in the way of arriving at the true composition of the carnotite. It is true that in one case the silicate has been analyzed (p. 143), but it would be unsafe to correct the carnotite analysis on that basis. Moreover, the analyses were not all made on the same plan; some are less complete than others; they cannot in some respects be rigidly compared with each other.

As to the carrying out of the analysis, various procedures were tried and no one found which gave altogether satisfactory results as to each constituent, though many could be determined with the usual degree of accuracy. The difficulty was mainly due to vanadium and the small amount of phosphoric acid usually present. These two constituents were likely to be found in different precipitates and could not be separated from them at one stroke. Their complete removal from other bodies was at times impossible and the weight of the latter had then to be corrected for these residual amounts.

Two entirely different lines of attack were open. One, that of Friedel and Cumenge, described in their paper on carnotite, had already been used with apparent success. It depends on rendering the vanadium insoluble in water by evaporating the nitric acid solution to dryness. Water extracts the alkalies and uranium without dissolving the vanadium, iron, or aluminum. Repetition of this process yielded Friedel and Cumenge satis-



factory results. They recommended washing with water containing ammonium nitrate.

The other method contemplated the quantitative removal of vanadium by dry hydrochloric acid gas as already described (p. 131). This had been shown to be perfect for alkaline pyrovanadates by Smith and Hibbs and it was hoped might succeed even with such complex mixtures as the present. The distillations were made on the crude ore and also on the nitric acid solution after filtration from the insoluble matter and evaporation to thorough dryness. The action is immediate in the cold, copious red-brown vapors coming off and condensing in part as a dark red liquid in the tube. But repeated distillations and the application of heat were required to effect complete removal of the vanadium accompanied by the arsenic and molybdenum. After each distillation the contents of the boat had to be evaporated with nitric acid. The blue and green colorations apparent on adding this acid showed that the hydrochloric acid gas had reduced a good deal of the vanadium to a lower state of valence, and in this condition it was incapable of forming the volatile body.

A somewhat more satisfactory separation sometimes resulted when this distillation method was combined with that of Friedel and Cumenge by subjecting both the evaporated uranium nitrate solution and the residue insoluble in water to the action of hydrochloric acid gas.

The distillates obtained by either way were evaporated with sulphuric acid, the arsenic and molybdenum were separated by hydrogen sulphide, and the vanadium was then titrated by permanganate at a temperature near boiling and again after reduction by sulphur dioxide gas. In one or two cases when the temperature of distillation had been high and it was feared some iron had passed over, the distillates were evaporated in porcelain with nitric acid, transferred to a platinum crucible, evaporated therein with sulphuric acid and fused with sodium carbonate. The aqueous extract was then treated as above for arsenic, molybdenum and vanadium.

The separation of Friedel and Cumenge, while perhaps adequate for technical purposes in ores free from phosphorus,\* does not in my hands give perfect satisfaction even then. It is impossible to prevent a little of the vanadium, also of the iron and aluminum, from going with the uranium, and on the other hand a little uranium may stay with the vanadium.

\* With even only half a per cent of  $P_2O_5$  many times that amount of  $UO_3$  is rendered insoluble in water after evaporation to dryness with nitric acid. The compound formed is of a lemon-yellow color, which is masked by the separated vanadic acid until this has been removed by ammonia. This insoluble body was treated as follows in order to arrive at the  $P_2O_5$  and  $UO_3$  it contained. After solution in nitric acid the phosphorus was precipitated by ammonium molybdate, and from the filtrate the uranium by three precipitations by ammonia.

Again when the vanadic acid is extracted from the residue by ammonia, as prescribed by Friedel and Cumenge, a little of the other constituents of the residue accompany the vanadium into solution.

If the combination of the two methods is used, it is better after removal of the vanadium by distillation to further treat the two residues separately at first instead of to unite them at once. Full details of this treatment are unnecessary and would unduly extend this paper. Suffice it to say that from the uranium portion the little iron and aluminum present are separated by ammonium sulphide and carbonate, and after removal of the latter, and acidification, the uranium can be thrown down by ammonium sulphide, and then by at least two precipitations by ammonia, or far better, by precipitating the neutral hydrochloric solution by freshly precipitated and alkali-free mercuric oxide at boiling heat, as prescribed by Alibegoff.\* As pointed out by von Fouchon and also by Alibegoff, contrary to certain still widely disseminated statements, ammonium sulphide does not afford a good separation of uranium from calcium. This is perhaps especially true if the solution contains any phosphorus. Again, contrary to another statement, it seems perfectly possible to separate uranium completely from alkalis by a few ammonia precipitations.

The finally ignited and weighed  $U_3O_8$  was redissolved in nitric acid, filtered if necessary ( $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ), and divided into two parts of which the one was tested for the very little  $P_2O_5$  usually present, and the other for vanadium by conversion into sulphate, reduction by sulphur dioxide gas, and titration by very dilute permanganate solution.

*Table of Analyses of Carnotite Ores.*

I. Copper Prince Claim, Roc Creek, Montrose Co., Colo.

According to the donor of the specimen, Mr. J. R. Duling, I-a is from the same lot as that from which Mr. Poulot obtained the specimens afterwards analyzed by Friedel and Cumenge.

II. Yellow Boy Claim, La Sal Creek, Montrose Co., Colo.

III. Yellow Bird Claim, La Sal Creek, Montrose Co., Colo.

The last two claims belong to the same group and the ore is from the same "blanket" (Voillequé).

I-b and II-b, the first analyses made, are not strictly comparable with the other analyses since they represent the effect of warm dilute hydrochloric acid, whose greater action is shown by the nearly complete solution of the ferruginous admixture. Cold, dilute nitric acid was used for the other analyses.

\* Ann. Chem. u. Phar., vol. ccxxxiii, 133, 1886; Zeit. für anal. Chemie, xxvi, 632, 1887.

|                                      | I.    |       |        | II.    |       | III.                                     |
|--------------------------------------|-------|-------|--------|--------|-------|--|
|                                      | a     | b     | c      | a      | b     |  |
| Insol. ....                          | 7.10* | 8.34† | 19.00‡ | 10.33§ |       | ¶  |
| UO <sub>3</sub> .....                | 54.89 | 52.25 | 47.42  | 54.00  | 52.28 | 20.51                                    |
| V <sub>2</sub> O <sub>5</sub> .....  | 18.49 | 18.35 | 15.76  | 18.05  | 17.50 | 7.20                                     |
| P <sub>2</sub> O <sub>5</sub> .....  | .80   | .35   | .40    | .05    | tr.   | none                                     |
| As <sub>2</sub> O <sub>5</sub> ..... | tr.   | .25   | none   | none   | none  | none                                     |
| Al <sub>2</sub> O <sub>3</sub> ..... | .09   | ?     | .08    | .29    | ?     | .08?                                     |
| Fe <sub>2</sub> O <sub>3</sub> ..... | .21   | 1.77  | .72    | .42    | 3.36  | .25                                      |
| CaO .....                            | 3.34  | 2.85  | 2.57   | 1.86   | 1.85  | 1.64                                     |
| SrO .....                            | .02   | ?     | ?      | tr.    | tr.   | ?  |
| BaO .....                            | .90   | .72   | .65    | 2.83   | 3.21  | .29                                      |
| MgO .....                            | .22   | .20   | .24    | .14    | .17   | .07                                      |
| K <sub>2</sub> O .....               | 6.52  | 6.73  | 6.57   | 5.46   | 5.11  | 1.51                                     |
| Na <sub>2</sub> O .....              | .14   | .09   | .07    | .13    | .02?  | .01                                      |
| Li <sub>2</sub> O .....              | tr.   | ?     | ?      | tr.    | ?     | ?  |
| H <sub>2</sub> O 105°                | 2.43  | 2.59  | 1.85   | 3.16   | 4.52  | total<br>H <sub>2</sub> O in<br>ore 1.85 |
| H <sub>2</sub> O 350°                | 2.11  | 3.06  | 2.79   | 2.21   | 3.49  |  |
| H <sub>2</sub> O + 350°              | none  | none  | none   | none   |       | .19(+300°)                               |
| PbO .....                            | .13   | .25   | .18    | .07    |       | .09                                      |
| CuO .....                            | .15   | .20   | .22    | tr.    |       | tr.                                      |
| SO <sub>3</sub> .....                | none  | .12   | .18    | none   |       | none                                     |
| MoO <sub>3</sub> .....               | .18   | .23   | .18    | .05    |       | .04                                      |
| SiO <sub>2</sub> .....               | .15   | .06   | .13    | .20    |       | .07                                      |
| TiO <sub>2</sub> .....               | .03   | .10   | ?      | ?      |       | .06?                                     |
| CO <sub>2</sub> .....                | .56   | .33   | none   | none   |       |  |
|                                      | 98.46 | 98.84 | 99.01  | 99.25  |       |  |

\* Containing .54H<sub>2</sub>O, .09V<sub>2</sub>O<sub>5</sub>.

† The insoluble matter had the following composition: SiO<sub>2</sub> 5.18, V<sub>2</sub>O<sub>5</sub> .21, P<sub>2</sub>O<sub>5</sub> .09, K<sub>2</sub>O .26, Na<sub>2</sub>O .04, H<sub>2</sub>O (105°) .56, (350°) .32 (+350°) .48, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, etc., by diff. 1.20. The SO<sub>3</sub> of this analysis is not combined with BaO, for it is wholly extracted by dilute acids. Once in solution the acid used is sufficient to prevent its immediate precipitation as BaSO<sub>4</sub> by union with some of the barium present. The same holds true for the SO<sub>3</sub> of I-c.

‡ This material was obtained by floating off the finer matter, allowing it to settle, collecting on a Gooch filter, and drying it in a current of air drawn through the crucible. The insoluble matter held in addition to 16.41 quartz and silicates including .39 V<sub>2</sub>O<sub>5</sub> and a little UO<sub>3</sub>, H<sub>2</sub>O (105°) .83, (300°) .73, (+300°) 1.03; total H<sub>2</sub>O 2.59.

§ Containing .16 V<sub>2</sub>O<sub>5</sub> and 1.90 H<sub>2</sub>O.

|| The insoluble matter contained besides quartz and silicates .25 V<sub>2</sub>O<sub>5</sub>, .21K<sub>2</sub>O, .05 Na<sub>2</sub>O.

¶ This analysis was made purposely on a relatively poor ore, furnished by Messrs Poulot and Voillequé, with the object of determining, if possible, the composition of the vanadiferous silicate which it contained (see p. 143). The data for calculating the H<sub>2</sub>O values of both analyses are as follows:

| Ore.                          | After extraction of<br>carnotite by cold,<br>dilute nitric acid. | After extraction of<br>residue by hot nitric<br>acid, sod. carb., etc. |
|-------------------------------|--|--|
| (a)                           | (b)  | (c)  |
| H <sub>2</sub> O 105° .....   | 3.53   | 1.68   |
| H <sub>2</sub> O 300° .....   | 2.11   | .47  |
| H <sub>2</sub> O + 300° ..... | .83  | .64  |
|                               | 6.47   | 2.79   |
|                               |  | .07  |

a-b furnishes the values for the carnotite as shown in analysis III; b-c gives those for the less soluble silicate (p. 143).

*Discussion of the Carnotite Analyses.*—It will be noted that a somewhat marked deficiency appears in most of the analyses, the cause of which is quite unknown. Great care was exercised in most cases and especially in those which show the greatest loss. It seems hardly possible that any serious constant loss of a known constituent should have occurred, but the only alternative demands the presence of an element or elements unnoticed and which cannot have been weighed with the known constituents. The researches of M. and Mme. Curie have shown that these ores contain traces of radio-active elements, precipitated the one by hydrogen sulphide, the other by sulphuric acid. Their presence, however, in quantity sufficient to account for the observed losses in the above analyses, especially when 10 grams of ore were operated on, could not possibly have escaped observation. To whatever cause it may be due, this loss alone suffices to render somewhat uncertain any calculations based on the analytical figures, though if the loss is to be ascribed to uranium or vanadium the ratios would not be sufficiently affected to obscure any simple relations that might exist.\*

Another difficulty is the impossibility of knowing what constituents to exclude and what to include in deducing molecular ratios. It is certain that most if not all of the iron is foreign to the yellow body. It is probable that phosphorus is likewise so, since its extraction by dilute acids does not keep pace with that of the uranium and vanadium. It may possibly be in combination with the iron, in part at least. The alumina doubtless is derived from the vanadiferous silicate which seems to exist in all the ores and which is not quite insoluble in cold dilute acids. If so, a small portion of the vanadium, potassium, magnesium, and water are to be attributed to this mineral, but a general correction based on the analysis of this compound (see p. 143) would not be justifiable. Its application leads to nothing definite, even in the case of the particular ore No. III, from which the silicate analyzed was derived.

In the following tables are given first the recalculated analyses and then the molecular ratios. All those constituents have been excluded which pretty certainly do not belong to the carnotite, but small portions of some of those retained are unquestionably extraneous. In two cases (I-*a* and I-*b*) a certain proportion of lime has been arbitrarily excluded equivalent to

\* According to Dr. Harry C. Jones of Johns Hopkins University, who very kindly undertook to examine a specimen of the Copper Prince ore for rare gaseous elements, helium is not present. Faint hydrogen lines were observed, the source of which was ascribed to water vapor. Other lines, due probably to hydrocarbons, were fairly strong, but the specimen had been long enough exposed in our laboratory and elsewhere to have accumulated enough dust to account for them.

the acid anhydrides  $\text{CO}_2$ ,  $\text{MoO}_3$ , and  $\text{SO}_3$ , less what is needed to offset  $\text{PbO}$  and  $\text{CuO}$ .

*Carnotite Analyses Recalculated.*

|                                | I-a    | I-b    | I-c    | II-a   | II-b   | III    |
|--------------------------------|--------|--------|--------|--------|--------|--------|
| $\text{V}_2\text{O}_5$ ----    | 20.72  | 21.09  | 20.12  | 20.54  | 19.85  | 20.62  |
| $\text{P}_2\text{O}_5$ ----    | .90    | .40    | .51    | .06    |        |        |
| $\text{As}_2\text{O}_5$ ----   |        | .29    |        |        |        |        |
| $\text{UO}_3$ ----             | 61.53  | 60.06  | 60.55  | 61.44  | 59.31  | 58.75  |
| $\text{CaO}$ ----              | 3.03   | 2.77   | 3.28   | 2.11   | 2.10   | 4.70   |
| $\text{BaO}(\text{SrO})$ -     | 1.03   | .83    | .83    | 3.22   | 3.64   | .83    |
| $\text{MgO}$ ----              | .25    | .23    | .31    | .16    | .19    | .20    |
| $\text{K}_2\text{O}$ ----      | 7.31   | 7.73   | 8.39   | 6.21   | 5.80   | 4.33   |
| $\text{Na}_2\text{O}$ ----     | .15    | .10    | .09    | .15    | .02    | .03    |
| $\text{H}_2\text{O}-105^\circ$ | 2.72   | 2.98   | 2.36   | 3.59   | 5.13   | 5.30   |
| $\text{H}_2\text{O}+105^\circ$ | 2.36   | 3.52   | 3.56   | 2.52   | 3.96   | 5.24   |
|                                | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

|                                | I-a         | I-b      | Ratios.<br>I-c | II-a        | II-b      | III      |
|--------------------------------|-------------|----------|----------------|-------------|-----------|----------|
| $\text{V}_2\text{O}_5$ ----    | 1133 } 1196 | 1208 }   | 1101 } 1137    | 1124 } 1128 | 1081      | 1128     |
| $\text{P}_2\text{O}_5$ ----    | 63 }        | 28 }     | 36 }           | 4 }         |           |          |
| $\text{As}_2\text{O}_5$ ----   |             | 12 }     |                |             |           |          |
| $\text{UO}_3$ ----             | 2140        | 2088     | 2105           | 2136        | 2062      | 2043     |
| $\text{CaO}$ ----              | 541 }       | 495 }    | 586 }          | 377 }       | 375 }     | 839 }    |
| $\text{BaO}(\text{SrO})$ -     | 68 } 671    | 54 } 606 | 54 } 718       | 210 } 627   | 238 } 660 | 54 } 943 |
| $\text{MgO}$ ----              | 62 }        | 57 }     | 78 }           | 40 }        | 47 }      | 50 }     |
| $\text{K}_2\text{O}$ ----      | 776 }       | 826 }    | 891 }          | 659 }       | 616 }     | 460 }    |
| $\text{Na}_2\text{O}$ ----     | 33 } 809    | 22 } 848 | 20 } 911       | 33 } 692    | 4 } 620   | 6 } 466  |
| $\text{H}_2\text{O}-105^\circ$ | 1511        | 1656     | 1311           | 1994        | 2850      | 2944     |
| $\text{H}_2\text{O}+105^\circ$ | 1311        | 1956     | 1978           | 1400        | 2200      | 2911     |

These ratios lead to the following empirical formulas, in which only the water given off above  $105^\circ$  is considered. Since the water is wholly removable below  $350^\circ$  it is regarded as water of crystallization and not of constitution.

|         | R'   | R'' | R <sup>v</sup> | U    | O     | H <sub>2</sub> O |
|---------|------|-----|----------------|------|-------|------------------|
| I-a ..  | 1618 | 671 | 2392           | 2140 | 13880 | 1311             |
| I-b ..  | 1696 | 606 | 2496           | 2088 | 13958 | 1956             |
| I-c ..  | 1822 | 718 | 2274           | 2105 | 13629 | 1978             |
| II-a .. | 1384 | 627 | 2256           | 2136 | 13367 | 1400             |
| II-b .. | 1240 | 660 | 2162           | 2062 | 12871 | 2200             |
| III ..  | 932  | 943 | 2256           | 2043 | 13178 | 2911             |

If it be assumed that the bivalent elements offer the most accurate determinations, the above ratios may be reduced to the following simpler terms on that basis :

|            | R'   | R'' | R <sup>v</sup> | U    | O     | H <sub>2</sub> O |
|------------|------|-----|----------------|------|-------|------------------|
| I-a .....  | 2.41 | 1   | 3.56           | 3.19 | 20.68 | 1.95             |
| I-b .....  | 2.80 | 1   | 4.12           | 3.45 | 23.03 | 3.23             |
| I-c .....  | 2.54 | 1   | 3.17           | 2.93 | 18.98 | 2.75             |
| II-a ..... | 2.21 | 1   | 3.60           | 3.41 | 21.32 | 2.23             |
| II-b ..... | 1.88 | 1   | 3.27           | 3.12 | 19.50 | 3.33             |
| III .....  | .99  | 1   | 2.39           | 2.16 | 13.98 | 3.09             |

The results, however, show a great lack of agreement and wide variation. It is plain that no probable formula can be calculated for the yellow body. The variations are of such a nature as to indicate in the plainest manner that it is a mixture of several substances.

Such a detailed discussion as the foregoing would hardly have been justified in view of the negative conclusions arrived at, but for the fact that Messrs. Friedel and Cumenge in their paper announced a simple formula for the body examined by them and gave it the specific name carnotite. Their published analyses are as given below, from which they have excluded considerable sand and traces of barium, aluminum, lead, copper, and radio-active bodies as present in excessively small quantities. They make no mention of calcium, and admit that their values for water are open to doubt. The formula deduced by them is  $2\text{U}_2\text{O}_3,^* \text{V}_2\text{O}_5, \text{K}_2\text{O}, 3\text{H}_2\text{O}$ .

*Analyses of Carnotite by Friedel and Cumenge.*

|                                | Found. |       |      |      | Calculated. |
|--------------------------------|--------|-------|------|------|-------------|
| $\text{U}_2\text{O}_3^*$ ..... | 64.70  | 62.46 |      |      | 63.54       |
| $\text{V}_2\text{O}_5$ .....   | 20.31  | 19.95 |      |      | 20.12       |
| $\text{K}_2\text{O}$ .....     | 10.97  | 11.09 |      |      | 10.37       |
| $\text{H}_2\text{O}$ .....     |        |       | 5.29 | .481 | 5.95        |
| $\text{Fe}_2\text{O}_3$ .....  | .96    | .65   |      |      |             |
|                                |        |       |      |      | <hr/> 99.98 |

It appears from these analyses that Messrs. F. and C. by great good fortune obtained a variety of samples of the pure potassium compound, free from calcium and without appreciable admixture of barium. This is very remarkable in view of the fact that all the ores from different localities examined by me show large admixture of calcium or barium salts or both, even that which is certified to have come from the same lot as that from which their material was taken. The French authors give a brief outline of their methods of analysis. That one which afforded them the best results would involve the weighing of any calcium present as sulphate along with the potassium, on the assumption that the presence of that element had been overlooked. It is much to be desired that a re-analysis of their material should be made, if there is any of it still available, in order to clear up the doubt connected with the first analysis.

In the light of the evidence herein set forth, the existence of a distinct mineral species having the composition claimed for carnotite can by no means be considered as established.

\* Old notation equivalent to the modern  $\text{UO}_3$ .

*Average quality of marketed ore.*—As these carnotite ore bodies are being exploited for the market, it is of some interest to know the average quality of each commercial lot. A carefully prepared sample representing several tons of ore was received from one of the commercial houses of Denver and was found to carry 11.49 per cent of uranium counted as  $U_3O_8$ , and 6.40 per cent of vanadium counted as  $V_2O_5$ . Over one-sixth of the vanadium existed, however, in the trivalent state, not as a constituent of the yellow body, but doubtless of a silicate like the one whose composition is given on p. 143.

*Commercial assay.*—The commercial assay of these ores has presented difficulties to the technical chemist, the results being sometimes very discordant.

As to uranium this is not surprising. The methods that have probably been commonly employed will give varying results according to the contents of the ore in phosphorus and alkaline earths. Possibly the old Patera process, described in most text-books on analytical chemistry, might be made to serve, with modifications called for by the large amount of vanadium present.

The assay for vanadium presents little difficulty and does not require much time. The ore is fused with sodium carbonate, leached with water and the fusion repeated on the residue. The combined filtrates are acidified by sulphuric acid, arsenic and molybdenum are precipitated in the hot solution by hydrogen sulphide, whereby the  $V_2O_5$  is reduced to  $V_2O_4$ . After filtration and expulsion of hydrogen sulphide by boiling, the vanadium is titrated in hot solution by permanganate. It is then reduced by sulphur dioxide gas, and after boiling this out the titration is repeated. The results are exact, and they are not affected by the uranium that may be present.

#### IV. *Composition of the Vanadiferous Silicate in the Carnotite Ore.*

As already mentioned the ores contain a vanadiferous silicate free from uranium. To the end of ascertaining its composition if possible, ore No. III (p. 128), from the Yellow Bird claim, low in carnotite but relatively rich in vanadium, was treated as follows:

The carnotite from 10 grams was extracted by cold, dilute nitric acid, and the well washed residue, consisting of coarse sand and an utterly amorphous mud, by 4 per cent sodium carbonate solution to get rid of the small amount of silica presumably set free but not dissolved by the acid. This amounted to 0.35 per cent in duplicate determinations, and together with 0.06 per cent in the acid solution or 0.41 per cent in all, may

serve as a maximum figure by which to gauge the action of the cold acid on the silicate or silicates in the ore. The residue was then digested for several hours with warm nitric acid of about 1·2 sp. gr. until as shown by a companion test its action had ceased. It was then filtered, washed and digested with 5 per cent sodium carbonate solution to dissolve the copious deposit of silica. The final residue was collected in a Gooch crucible, washed with sodium carbonate, followed by dilute nitric acid to remove all alkali, then by alcohol to prevent turbidity in the filtrate, and dried by suction of the pump. In it the water was determined at different temperatures, also its general composition.\* From the sodium carbonate filtrate the silica was obtained by two evaporations and filtrations, also the trifling amount held by the acid solution. This latter was then fully analyzed and the complete results follow.

*Composition of vanadiferous silicate in carnotite ore.*

|                                      | Per cent<br>in ore.   | Per cent<br>calculated<br>to 100. | Ratios. |
|--------------------------------------|-----------------------|-----------------------------------|---------|
| SiO <sub>2</sub> .....               | 6·48                  | 43·94                             | ·7275   |
| Al <sub>2</sub> O <sub>3</sub> ..... | 2·445 (2·45 and 2·44) | 16·58                             | ·1622   |
| V <sub>2</sub> O <sub>5</sub> .....  | ·965 (·93 and 1·00)   | 6·54                              | ·0434   |
| Fe <sub>2</sub> O <sub>3</sub> ..... | ·875 (·87 and ·88)    | 5·93                              | ·0370   |
| CaO .....                            | ·035                  | ·24                               | ·0043   |
| MgO .....                            | ·654 (·652 and ·657)  | 4·43                              | ·1099   |
| K <sub>2</sub> O .....               | ·546                  | 3·70                              | ·0393   |
| Na <sub>2</sub> O .....              | ·03                   | ·20                               | ·0037   |
| H <sub>2</sub> O 105° C. ....        | 1·66†                 | 11·26                             | ·9222   |
| H <sub>2</sub> O 300° C. ....        | ·44†                  | 2·98                              | ·1655   |
| H <sub>2</sub> O above 300° C.       | ·62†                  | 4·20                              | ·2333   |
|                                      | 14·75                 | 100·00                            |         |

Also traces of titanium, manganese, and lithium.

On the improbable assumption that the iron is to be wholly included, and regarding only the water given off above 300°, the following ratios result:

$$H_{467} R'_{86} R''_{114} R'''_{455} Si_{727} O_{2575} ;$$

which become, if the iron is excluded,

$$H_{467} R'_{86} R''_{114} R'''_{411} Si_{727} O_{2462}.$$

These figures, while strongly suggesting definite ratios between certain of the constituents, do not under the circumstances warrant the deduction of a formula, nor do they lead

\* SiO<sub>2</sub> 48·89, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, zircon etc., ·44, TiO<sub>2</sub> ·08, MgO ·01, K<sub>2</sub>O ·11, Na<sub>2</sub>O ·03, H<sub>2</sub>O ·07; total 49·63.

† Determined on a separate portion of the same powdered sample. See p. 138 footnote for data.



to the same conclusion as in the case of the green cementing material of the Placerville sandstone. The phengite-muscovite ratio of that is not apparent here. Yet it is not at all unlikely that a mineral like the one from Placerville is present, but contaminated with some other. In fact it would be surprising to find in such thoroughly altered sandstones anything but a mixture. The fact of the existence of such vanadiferous transition products is itself highly interesting, and these tedious analyses cannot therefore be considered as made in vain. The mud-like amorphous character of this material precludes any hope of aid from the microscope in solving the question of its homogeneity.

#### *Summary.*

The body called carnotite is probably a mixture of minerals of which analysis fails to reveal the exact nature. Instead of being the pure uranyl-potassium vanadate, it is to a large extent made up of calcium and barium compounds. Intimately mixed with and entirely obscured by it is an amorphous substance—a silicate or mixture of silicates—containing vanadium in the trivalent state, probably replacing aluminum.

The deposits of carnotite, though distributed over a wide area of country, are, for the most part, if not altogether, very superficial in character and of recent origin.

The green coloring and cementing material of certain sandstones near Placerville, Col., is a crypto-crystalline aluminovanadio-potassium silicate resembling roscoelite, but with the percentage proportions of  $\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  reversed. It constitutes over 25 per cent of the sandstone at times, and contains nearly 13 per cent of  $\text{V}_2\text{O}_5$ , the latter amounting in the maximum case observed to 3.5 per cent of the sandstone.

As yet these highly vanadiferous sandstones have been found only at Placerville, where it is intended to work them for vanadium. Carnotite is associated with them in only trifling amount.

Other sandstones noticed owe their bright green color to chromium. In yet another case where the color was dull green, this was not due to either chromium or vanadium.

U. S. Geological Survey, April, 1900.