

ART. XIII.—*The Vanadium Sulphide, Patronite, and its Mineral Associates from Minasragra, Peru*; by W. F. HILLEBRAND.

IN the Engineering and Mining Journal, Sept. 1, 1906, p. 385, and in Informaciones y Memorias of the Society of Engineers of Lima, Peru, vol. viii, pp. 171–185, 1906, two accounts are given by Foster Hewett and José J. Bravo, respectively, of a remarkable vanadium occurrence at Minasragra, about 46 kilometers from Cerro de Pasco in Peru and 43 from the railway. The two accounts agree in all essential points that are common to both, though that of the Peruvian writer is much the more detailed as to the geography and geology of the region. The data immediately following are drawn from the publications referred to, and from additional information furnished by Mr. Hewett.

Cretaceous sedimentaries—shales, sandstones and limestones—dipping at about 45° have been intruded by two (Hewett) or three (Bravo) series of eruptive dikes, and at the point of greatest frequency of these intrusives occurs the vanadiferous deposit, which had as yet been opened up only very superficially by a few pits along an extension of 400 feet on the outcrop. The vanadiferous materials occur in vein formation and are three in kind, aside from alteration products that cover the surrounding surface. Under the hanging wall is a thickness of about eight feet of an amorphous material of complex mineral composition which will be designated hereinafter as the “ore.” Its color is dark, almost black (dark green like olivenite, according to Hewett, bright lead-gray with metallic luster on fresh surfaces but soon tarnishing, according to Bravo). Adjoining this material, without distinct line of demarkation beneath, is a singular hard coke-like carbonaceous matter, from eight inches to two feet in thickness, which blends on the farther side into a lustrous black substance of from four to six feet thickness, designated as asphaltite by both the above named writers, although it is a sulphur compound of carbon with very little hydrogen.

These three substances will now be considered in detail, beginning with the last, which from its unique position among carbonaceous mineral substances seems worthy of a specific name for the purpose of more ready separation from those bitumens and coals which it so strongly resembles in its superficial aspects. The name *quisqueite* is suggested by Mr. Hewett, after the settlement nearest to the locality of occurrence. The materials described in the following pages were

furnished by Mr. Hewett, and a portion of the chemical data published by him were based on incomplete preliminary tests by myself. The reason for examining them in detail in the laboratory of the U. S. Geological Survey is not only that they represent an occurrence and association so unique, but chiefly that an as yet undescribed association of vanadium and carbonaceous matter in eastern Utah presents some points of similarity with that of Peru, and by reason of the higher concentration in the latter they seem to offer a convenient stepping-stone to future research upon the North American occurrence.

As to the source of the materials composing this vein deposit, nothing can at present be said, nor is a satisfactory explanation at hand for the comparatively sharp separation, in what would seem to be one vein, of such unlike materials. Mr. Hewett remarks that "the appearance of the materials as well as their occurrence strongly suggests that they were forced into the shales in a plastic or even liquid condition. Subsequent metamorphism has altered the composition of the asphaltite and the condition of the sulphur in the sulphide material." It is conceivable that the injected material was originally homogeneous and that segregation took place after injection. Possible evidence in favor of this view is afforded by the fact that the rich vanadiferous ore contains several per cent of carbonaceous matter similar in composition to the quisquite, that the carbonaceous matter is itself vanadiferous, and that both are extremely rich in sulphur. In order to account for the coked matter between the two, it would seemingly be necessary to assume that the requisite heat came from the side of the vanadium sulphide ore. The adjacent dike undoubtedly played the chief rôle in this connection.

This is not the only known association of vanadium with carbonaceous matter, an association which is undoubtedly significant though we are as yet unable to explain it. Aside from the above mentioned occurrence in Utah, vanadium has been reported in numerous coals, in grahamite that probably came from West Virginia, and Mr. Hewett tells me that it is a constituent of the grahamite from Oklahoma. The enormously high proportion of vanadium in the Peruvian occurrence is of special interest, not only on that account but because it offers an opportunity to determine its state of combination in at least this particular case. It is possible that in some instances such sources may have furnished the vanadium of deposits of secondary minerals like those of the western United States.

Quisqueite.

This material, the asphaltite of Hewett and Bravo, though rich in carbon, is worthless as a combustible because of its

content in sulphur, which exceeds that of the carbon in the specimen examined. Mr. Hewett reports 45 per cent of sulphur and that, though not holding a flame, the material burns when heated with the blue flame of sulphur. It is brittle, with density 1.75 and hardness about 2.5. It is infusible and apparently not affected by the usual solvents for bitumen, except that carbon disulphide extracts much sulphur. It leaves a variable amount of highly vanadiferous ash—3.31 per cent, containing 0.544 V_2O_5 (Hewett), 0.80 per cent, likewise high in vanadium (Hillebrand). Much sulphur sublimes when the mineral is heated in a closed tube and later hydrogen sulphide is evolved. It is oxidized by long boiling with strong nitric acid. The following is the composition of the sample analyzed:

S soluble in CS_2	15.44
S combined	31.17
C	42.81
H	0.91
N	0.47
O by diff.	5.39
Moisture at 105°	3.01
Ash	0.80
	100.00

The ash afforded roughly: SiO_2 , 0.04; Al_2O_3 , 0.08; Fe_2O_3 , 0.10; NiO, 0.06; V_2O_5 , 0.52. These are, however, results of minor quantitative value because of the minute amount analyzed. It is practically certain, for reasons to appear later, that the vanadium, iron and nickel existed in the original material as sulphides, and, therefore, assuming that the main analysis is correct, that the oxygen reported is too low.

The composition of this material is, so far as my knowledge extends, unique, and there are no data known that throw light on its chemical structure.

The Coke-like Material.

The quisqueite seems to have been converted on its upper side into a sort of coke, though this differs markedly from artificial cokes. Its hardness is 4.5. Glancing blows of a hammer cause much sparking. It is somewhat vesicular, though without large cavities. The openings are mostly short thin contraction cracks without orientation, which are best observed under a lens. They are for the most part lined or filled with a thin brilliant pitchy black coating, often reticulated, of what appears to have been originally fused matter and to which the luster of much of the specimen when freshly broken open is due. There are also rather numerous minute blowholes lined with or some-

times loosely filled with the brittle pitchy matter just mentioned. Elsewhere the surface is rather dull and of a color having a suggestion of red when contrasted with the pitch black of adjacent parts. The texture is extremely fine-grained like that of steel and the fracture rather conchoidal. These peculiarities of texture often give rise to great unevenness on large fracture surfaces. In the closed tube there appears a sublimate of sulphur and then the odor of hydrogen sulphide.

The composition of the sample analyzed follows :

S soluble in CS ₂	0.64
S combined	5.36
C	86.63
H	0.25
N	0.51
O by diff.	4.64
Moisture	none
Ash	1.97

100.00

The ash is highly vanadiferous.

THE VANADIUM ORE.

The remainder of the deposit, about eight feet in thickness, is a complex mixture of mineral substances. The color in mass, as earlier mentioned, is dark, almost black, with perhaps a suggestion of green as stated by Hewett. It breaks for the greater part unevenly, but often somewhat smoothly along planes of weakness, portions of which show permanent brilliant metallic luster. This is due to a thin coating of presumably carbonaceous matter like that noticed in the coke-like material. Bravo reports enclosures of brilliant black "asphaltite" and also sulphur visible to the naked eye. No sulphur was to be seen in the samples at my disposal,* but there were many patches and points of a dull pyritous mineral, whiter than pyrite and usually of a faint reddish cast, apparently due to tarnish. These consist of an iron-nickel sulphide, of which more later, carrying vanadium and siliceous and titaniferous matter. Heated in the closed tube, the ore gives off sulphur copiously and then hydrogen sulphide. It does not melt.

The chief component was given in both the earlier publications as a vanadium sulphide, to which Hewett gave the name *patronite* and Bravo that of *Rizo-Patronita*, in honor of Senor Antenor Rizo-Patron, the discoverer of the ore and its vanadium contents. The paper of Hewett was published Sept. 1,

* Specimens received from Mr. Hewett since this was written do show free sulphur on some of the parting surfaces in the form of scales.

1906, and that of Bravo bears the date Aug. 31 of the same year, hence must have appeared a little later, although in the August number of the Boletin de la Sociedad de Ingenieros. Hewett's name, therefore, has the right of priority and being shorter is preferable, even though that given by Bravo may better conform to Spanish usage as to derivation, since it embodies the whole patronymic.

The following analyses given by those authors show the composition of the ore incompletely, since appreciable percentages of nickel and titanium were overlooked, and, moreover, they also show that it varies much in respect to the relative amounts of siliceous and sulphide components.

	Analysis by J. O. Handy (Pittsburg)	Analysis by H. Bunting (Lima)
SiO ₂	10·88	22·22
Al ₂ O ₃	3·85	8·32
Fe	2·45	1·98
V	16·08	15·36
MoO ₃	0·50	----
S soluble in CS ₂	6·55	41·81
S combined	54·06	
CaO	----	0·33
Moisture	trace	----
Undetermined	[5·63]*	9·98†
	[100·00]	100·00

Both I (in Mr. Hewett's paper) and Bravo reported the solubility of the vanadium in fixed caustic alkalies, and Bravo likewise in ammonia. I may say that ammonia does not act so quickly as the fixed alkalies. Bravo analyzed the alkaline extract for sulphur and vanadium, after first removing free sulphur, and reported 32·89 per cent vanadium and 67·20 per cent sulphur, corresponding approximately to the formula VS₂, the ratio as calculated by me from his values is 1:3·28).

The complete analysis of this ore is extremely difficult and in some respects the results given on p. 147 is lacking in precision. The following behavior threw light on the nature of the mineral components.

Repeated treatment in a Soxhlet extractor with carbon disulphide removed considerable sulphur. After thorough drying of the capsule and contents, hot water was passed through. The aqueous filtrate was blue-green and held a sulphate or sulphates of vanadium. This operation was followed by extraction with warm caustic soda as long as the filtrate came through colored. Hereby nothing but vanadium, sulphur and some of the siliceous components were taken out, and the

* Largely carbonaceous.

† Carbon.

solution was of a cherry-red color. In it the proportions of vanadium and sulphur were determined.

It may be said here that the analysis was of necessity made with interruptions, and it was noticed that the values obtained for free sulphur increased with lapse of time. The first determination gave 4.5 per cent, the second 5.5 per cent, and the third 7 per cent sulphur, each on a separate portion of the same sample. This seemed to indicate a progressive oxidation of the vanadium sulphide with liberation of free sulphur, or else that the ore contained insoluble as well as soluble sulphur and that the former on exposure of the powder to air underwent rather rapid conversion to the soluble modification. Heating the powder for some hours with a little carbon disulphide in a sealed tube in a steam bath did not result in an increased yield of free sulphur, nor did heating the powder to 60° for some hours in the air do so, hence the latter explanation seems improbable. To test the former the portion of powder that had afforded 7 per cent sulphur and had then been extracted by hot water was allowed to dry thoroughly and left exposed to air under an inverted beaker for three weeks, after which time it was again tested for free sulphur and sulphate, both of which were found, thus apparently confirming the supposition of oxidation. But the free sulphur found in this test was so far in excess of that converted to sulphate that it would seem as if the liberation of sulphur took place much faster than the oxidation of that which remained in combination with the vanadium (see page 148).

It was impracticable satisfactorily to examine the material remaining in the Soxhlet capsule after extraction by carbon disulphide and water, but separate portions of the ore, treated directly with alkali, were used in part. From the residue thus obtained strong nitric acid after a few minutes action took out all the iron-nickel sulphide together with most of the remaining vanadium, all the molybdenum and some titanite oxide, silica and alumina, besides acting to a slight degree perhaps on the carbonaceous component of the ore. The sulphur of the metallic sulphide was apparently wholly oxidized by the nitric acid. The solution was analyzed, but for more exact determination of the composition of the sulphide large amounts of the ore, only coarsely broken up, were thoroughly extracted by alkali, the black residue was dried and rubbed down gently with the finger, and from it the sulphide was extracted by an electromagnet and purified by repetition of the treatment.

The residue not dissolved by nitric acid is black and contains most of the carbonaceous matter of the ore besides the titaniferous and siliceous matters not removed by the foregoing operations. The carbonaceous material contains much sulphur and seems in this respect to resemble the quisquite

already described. On burning it off there is left a straw-colored residue in which nothing mineralogically definite was recognized except a few quartz grains. It is not unlikely that it consists chiefly of a clay-like substance and titanium dioxide in an amorphous state. Some vanadium in an oxidized form, perhaps a constituent of the clay, is also present.

It thus appears that the sulphur and vanadium exist in four different forms in the powdered ore. Mr. Hewitt states that lead, zinc, copper, arsenic, antimony, calcium, magnesium, silver, gold, and platinum were sought but not found. Uranium and germanium were looked for in vain by myself. Prof. B. B. Boltwood, who kindly examined for me both the vanadium ore and the quisquite, reports hardly any evidence of radio-activity.

Bulk Analysis of the Ore.

The results in the following analysis are not in all cases highly accurate, and the summation is affected by indeterminate errors, among which is too high water, because some of it is derived from the hydrogen of the carbonaceous matter. This error is to a large extent offset by the oxygen of the carbonaceous matter. The vanadium sulphide constitutes about two-thirds of the ore, the metallic sulphide over one-tenth. It is not only an ore very rich in vanadium and from which the latter can be very readily extracted, but it also carries a percentage of nickel that may prove commercially of much value, since it will be left wholly in the residues after extraction of the vanadium.*

S (total)	58.79 (4.5 free)
V "	19.53
Mo	0.18
Fe	2.92
Ni	1.87
C	3.47
SiO ₂	6.88
TiO ₂	1.53
Al ₂ O ₃ (P ₂ O ₅)	2.00
Fe ₂ O ₃	0.20
MnO	trace
Cr	trace?
Alk.	0.10?
H ₂ O	1.90
O from V. sulphate	0.38

99.75

* Specimens received from Mr. Hewett since this paper was written showed in some cases no visible metallic sulphide, in others but a few specks. Tests were not made to ascertain if the amount actually present is less than in the specimen first received.

Free Sulphur and Water-Soluble Extract.

Several determinations of the sulphur extractable by carbon disulphide were made at considerable intervals of time. The first gave 4.5 per cent, the second 5.5, and the third 7 per cent, thus, as already said, indicating a progressive liberation of free sulphur. The extractions were made in a Soxhlet apparatus tillan extract was found free from sulphur.

The first determination of the water-soluble extract gave 0.41 per cent SO_4 and the solution held vanadium, as shown by its blue-green color and by qualitative test. Much later, in another portion, there was found 1.23 per cent SO_4 and 0.92 per cent V, with ratio V to SO_4 of 1 to 0.71. The vanadium was in an intermediate stage of oxidation between V_2O_4 and V_2O_5 , as ascertained by direct titration and again after reduction by sulphurous acid.

When the powder that had served for the last test, and which had afforded 7 per cent free sulphur, was allowed to dry and left exposed to the air for three weeks and then again extracted by carbon disulphide and hot water in turn, there was found additional 0.81 per cent of SO_4 and 0.40 per cent of V, but the vanadium of the aqueous extract was all in the V_2O_4 state, for after titrating directly and then again after reduction by sulphurous acid, the results were identical. The ratio of V to SO_4 was not, however, the same as in the previous test, being 1 to 1.07. In this last test there was found 3.83 per cent of free sulphur in addition to the 7 per cent found at first, and since the sulphur in the SO_4 is but 0.27 per cent, or but one-fourteenth of the free sulphur formed during the three weeks, the ground will be apparent for the earlier remark (p. 146) concerning the greater rapidity of splitting off of free sulphur from the original sulphide than of oxidation of the lower combination of vanadium and sulphur that presumably resulted from this division. But the variation in the two ratios given above between vanadium and SO_4 has not been cleared up. These approximate very roughly to 1 to 1, which indicates a similar ratio in the lower sulphide, to whose direct oxidation the sulphate is supposed to be due, that is, VS. But much more knowledge is needed, based on numerous and varied tests, before the reactions involved in the changes above indicated can be written.

Patronite.

Several determinations of the sulphur and vanadium in the alkaline extract, after first removing free sulphur and the water-soluble constituents, gave the following results :

V	19.16	18.89	19.09	18.46
S	47.74	47.84	45.65	44.74
Ratio V : S	1 : 3.97	1 : 4.04	1 : 3.82	1 : 3.87

The determinations with the two highest ratios were earlier analyses in which least free sulphur was found and presumably least oxidation had taken place. They point to a formula VS_4 for the sulphide instead of VS_3 , as reported by Bravo, whose actual ratio was 3.28. A sulphide of this composition seems very singular and the possibility suggested itself that the compound might be ortho-sulphovanadic acid, but this would probably be soluble in water and an amount equal to that in the ore would need, moreover, above 1 per cent of hydrogen, whereas the total as represented by the water found is less than 0.20 per cent, and this unquestionably belongs largely with the siliceous and aluminous matter of the ore.

In the light of the observation relating to the splitting off of free sulphur from the sulphide, a process that is evidently connected with exposure to air, the possibility has to be considered that the free sulphur found in the test showing least may all have been originally combined with the vanadium to form a still higher sulphide than VS_4 . The ratio calculated on this basis is less than 1 to 4.5, indicating a formula not above V_2S_9 . Lacking, as we do, any knowledge regarding the higher sulphides of vanadium, speculation at present would be premature.

Whatever may be the true formula, the mineral is new and the name patronite may well be applied to it.

The Iron-Nickel Sulphide, a Highly Nickeliferous Pyrite.

The bulk analysis of the ore indicates a greater percentage of the iron-nickel sulphide than would be supposed by inspection, and than was obtained by separation in the manner already outlined. Much of it is evidently in a state of fine division and escapes in the washings. Indeed, it was sought to recover only the grains of some size. It was noticed after separation that while some of the larger grains especially showed the pyritous color on fracture surfaces, all were more or less covered with a black coating of what is assumed to be the carbonaceous material of the ore and that most of them were black throughout, apparently from the same cause since on solution in nitric acid a considerable carbonaceous residue was left. In a few instances apparent crystals, seemingly of octahedral habit, were observed, but otherwise the fragments were quite destitute of crystalline structure. The color is rather whiter than that of pyrite, as said before, becoming of a reddish cast by tarnish. The mineral is not attracted by a hand magnet but attaches itself readily to an electromagnet. The density of the material analyzed was 4.33, but this value is of little worth since, despite repeated purification, the frag-

ments contained a good deal of carbonaceous, siliceous and titaniferous matter in a state quite invisible to the eye. Heated in a closed tube much sulphur is evolved. The mineral is very insoluble in hydrochloric acid but is readily attacked by nitric acid with complete oxidation of the iron, nickel and sulphur. The other constituents remain more or less unattacked according to the duration of contact with the acid.

The results given below are for the four chief constituents the mean of concordant determinations. It is to be noted that if the vanadium was counted as the element, every analysis gave a summation of approximately only 97 per cent. This is accounted for in part probably by the extreme oxidizability of the mineral when exposed in powder form to the air, especially when wet. Hot water extracts from the powder ferrous and nickelous sulphates with only a very little vanadium. If the powder is left moist on the filter, relatively large additional quantities of iron and nickel can be extracted next day, and for several successive days, with very little vanadium. But the discrepancy cannot be apparently in large part thus accounted for. It seems necessary to assume that the vanadium is in an oxidized form, perhaps as a constituent of the siliceous-aluminous material. In this case its condition would be that of trivalency in all probability, a condition which also affords a more satisfactory summation than that of quinquivalency. Against its presence in combination with silica and alumina is its great excess over that in which it is known to occur in such forms in nature. On the other hand, the matter insoluble in nitric acid still contains some vanadium.

The following experiment seems to put it beyond question that the vanadium is not a constituent of the metallic sulphide.

	Mean	Atom. Ratio		Calc. to 100
S	45.06*	$\div 32.06 = 1.455$	$= 2.02$	52.31
Fe	25.38	$\div 55.9 = 0.454$	} $0.721 = 1.00$	29.46
Ni	15.70	$\div 58.7 = 0.267$		18.23
Co	trace			100.00
V	4.31	$= 6.33 V_2O_3$ or $7.66 V_2O_5$		
Mo	0.09			
C	0.47			
H ₂ O	1.38	(partly from H of carbonaceous matter)		
TiO ₂	0.93			
SiO ₂	1.93			
Al ₂ O ₃	2.45	(with a little P ₂ O ₅)		
				97.70

* This does not include the sulphur that may have been held by the undissolved carbonaceous matter.

When the powder was exposed over night in a covered platinum crucible to the action of strong hydrofluoric acid, nearly half the vanadium and much of the silica, alumina and titanium were extracted, but only about one twenty-fifth of the iron and nickel, these two showing exactly the ratio afforded by the main analysis below. Boiling with dilute sulphuric acid yielded results somewhat similar.

If the vanadium is disregarded, the iron-nickel sulphide has the formula $(\text{FeNi})\text{S}_2$ with iron to nickel as 1.70 to 1, or nearly 5 to 3. A pyrite with such a high proportion of nickel is unknown. But a single one of the analyses quoted in Hintze's Handbook of Mineralogy shows anywhere near 6 per cent nickel, this one, however, showing also about 3 per cent cobalt. The nearest approach to the present case is seen in the mineral gunnarite $3\text{FeS}_2 \cdot 2\text{NiS}$, incompletely described by Landström (Geol. Fören., ix, 368, 1887.) with density 4.3 and a tin-white color with a tinge of yellow, tarnishing yellowish brown. The present mineral would seem to be quite distinct from gunnarite and for the present is to be regarded as a highly nickeliferous pyrite. Should it seem proper to give it a specific name later, *bravoite* is suggested, after Senor José J. Bravo, the Peruvian writer on the vanadium occurrence at Minasagra.

The Carbonaceous Material of the Ore.

A determination of carbon and sulphur in 0.2459 gram of the residue insoluble in alkali and nitric acid gave 0.0475 carbon and 0.0254 sulphur, of which last 0.0036 was soluble in carbon disulphide. These figures indicate a similarity to quiskite, although the sulphur is lower.

The Oxidation Products of the Ore.

Oxidation products are reported to cover the surface of the ground in the vicinity of the vein outcrop. The specimen examined by me resembles porous limonite in appearance. There was found in it by a rough partial analysis about 45 per cent V_2O_5 , 14–15 Fe_2O_3 , 15 H_2O , 20 or more of siliceous gangue, nearly 1 of MoO_3 and a little SO_3 . Nickel is absent, or practically so. The material does not represent a single species, for it contains probably more than one vanadium compound, among them doubtless the minute micaceous scales, greenish sometimes and sometimes yellowish, that may be seen with a lens.

Lab. U. S. Geological Survey,
May 22, 1907.