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HEWETTITE, METAHEWETTITE AND PASCOITE, HYDROUS CALCIUM VANADATES.

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INTRODUCTION.

(Read April 25, 1914.)

Some years ago, Mr. D. Foster Hewett, in a paper[1] on the remarkable vanadium locality of Minasragra, Peru, described briefly certain oxidation products of the vanadium sulphide ore, patronite, which he was inclined to regard as vanadic acids, although the opinion of one of us (H.), based on preliminary analyses, was that two of the minerals were calcium vanadates.

Several years later the chief constituent of a certain red ore of vanadium from Paradox Valley, Montrose County, Colorado, was identified (H.) as a calcium vanadate, seemingly identical with one of those from Peru. Since then this red ore has been found over a wide area, extending into Utah. A good deal of additional chemical work has been done intermittently during the past three years upon material of both occurrences and it has been studied microscopically. It has developed that, although the minerals are deceptively alike in appearance and general behavior and have the same empirical formula, they seem to be specifically distinct, are probably in fact isomers. The Peruvian mineral, the first known and studied, we are pleased to name ***hewettite,*** after Mr. D. Foster Hewett, now of the U. S. Geological Survey, who has done so much to make the Minasragra occurrence known. Its isomer may appropriately be called ***metahewettite.*** It is probable that hewettite occurs also in Paradox Valley (see under metahewettite, pp. 37–38).

The detailed results of the several authors' work are submitted in the following pages, a preliminary announcement having appeared in the *Jour. Washington Acad. of Sci.*, *3*, 157, 1913.

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[1] *Trans. Am. Inst. Min. Eng.*, *40*, 291, 1909.

HEWETTITE.

Hewettite was rather abundant at the time of Mr. Hewett's visit to Minasragra. It is wholly of superficial occurrence, derived by oxidation from the vanadium sulphide, patronite. The principal specimen examined by us was a lump about the size of a small apple.

In the lumpy aggregates of pure mineral hewettite is deep red (mahogany red)[2] with a somewhat silky luster. Under the microscope the needles measure usually less than 0.01 mm. in width and 0.2 mm. in length. The extinction is parallel. The refractive indices measured by immersion methods could be only approximately found because of the extreme thinness of single blades and the lack of entire parallelism of the blades in a group. Also, β and γ were so high that slight heating was necessary to embed the mineral in the standard refractive media, thus causing expulsion of an unknown amount of water. For Li-light $\alpha = 1.77$, $\beta = 2.18$, $\gamma =$ about 2.35 to 2.4. Elongation is parallel to γ. Pleochroism is strong; γ dark red, α and β very light orange-yellow. The mineral is probably orthorhombic. A determination of density, made by Mr. E. S. Larsen, on air-dried material gave a value 2.618. A subsequent determination by one of the authors (M.), using material containing 9 molecules of water, gave 2.554. The apparent discrepancy between these two determinations is explained by the fact that the material used by Mr. Larsen was partially dehydrated.

The mineral when heated passes through various color changes (see p. 46) and melts readily, forming a dark red liquid; it is slightly soluble in water.

The composition of an almost pure specimen, on which the foregoing optical examination was made, is given under analysis 1 (p. 40). Analysis I*a*, in the footnote on pp. 40–41 (quoted by Mr. Hewett, loc. cit., p. 311), represents a lump of ore showing little evidences of crystallization but otherwise resembling closely the better specimen, although the microscope shows it to be far from homogeneous. In spite of the similarity in appearance of the two specimens, the

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[2] The specific color terms used in these descriptions are based on comparisons with Ridgway's standards. See "Color Standards and Color Nomenclature," Robert Ridgway, Washington, D. C., 1912.

analyses show quite different percentages of lime. This is not surprising if we conceive that the vanadium of the patronite has become oxidized to a polybasic acid of quinquivalent vandium, which then was gradually neutralized by calcium. It seems reasonable to expect that ores of all gradations occur from the sulphide patronite to the half neutralized salt hewettite and finally to the fully neutralized salt represented by pascoite (p. 49). Indeed, such intermediate stages are probably represented by a number of the specimens brought from Peru by Mr. Hewett and of which a few analyses are given in his paper. These ores are, for the most part, microcrystalline, though some show distinct evidences of crystallization, as Mr. Hewett pointed out. They are of varying colors, from red through greenish to the black of the original patronite. Some of the specimens are not fully oxidized[3] but contain vanadium in a lower state of oxidation than corresponds to quinquivalency, and even free sulphur. Some of them are characterized by high iron content and relative freedom from lime, as shown by the following analysis,[4] which seems to represent essentially a ferric vanadate.

V_2O_5	57.3
V_2O_4	4.8
MoO_3	3.3
Fe_2O_3	19.6
TiO_2	.1
SiO_2	.6
CaO	.7
H_2O	13.9
	100.3

Molybdenum is naturally a characteristic component of the oxidation products of patronite since it occurs in the patronite ore.

METAHEWETTITE.

Unlike the Peruvian mineral, the North American vanadate is an impregnation in sandstone, generally coating the sandstone grains, sometimes filling cavities and crevices. The specimens are almost

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[3] Analysis I indicates that oxidation is not yet quite complete in our best specimen.

[4] Made in 1907 in the laboratory of the U. S. Geological Survey and quoted by Mr. Hewett, *loc. cit.*, p. 311.

always friable, some falling to powder. Gypsum frequently accompanies the metahewettite and often encloses it, producing then the appearance of a distinctly crystallized red mineral. When pure the powder is dark red; gypsum present lightens the color. Even when free from gypsum the red vanadate is almost always associated with other minerals, partly residuals from the impregnated sandstone, although occasionally almost pure material is found, like that represented by analysis II (p. 40). The impurities interfered greatly at first with the precise determination of the composition of the vanadate, particularly as to its water content. For this reason no quantitative analysis of the mineral from Paradox Valley is given, although an abundance of the ore was at our disposal and one or more analyses of it were made before purer material, from Thompson's, in eastern Utah, was obtained. These analyses made evident, however, the chemical identity of the Paradox and Thompson's minerals.

The ore at our disposal from Thompson's differs somewhat from that of Paradox Valley by a greater variation in its shades of red, some of these being very bright in contrast with the usually duller shades of the ore from Paradox.[5] There are also associated with it at least two interesting minerals, both of which were also noticed later in ore from Paradox and the Henry Mountains.

One of these, gray in color, is a hydrous silicate of aluminum, trivalent vanadium and potassium. It is no doubt the same silicate that was first noted by one of us (H.) in carnotite ores and seems to be a constant associate of all the uranium and vanadium ores of western Colorado and eastern Utah, in some places constituting the chief vanadiferous component of the ore. In the ore from Thompson's it forms soft patches throughout the red mass, some of which are of sufficient size to permit of separation in a fairly pure state.[6] Per-

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[5] Ores of deep color have been found recently by Mr. Frank L. Hess, of the U. S. Geological Survey, in the Henry Mountains, Utah.

[6] The gray mineral accompanying metahewettite occurs in firm granules consisting of aggregates of very minute doubly refracting particles which cannot be isolated for microscopic study. The refractive indices of aggregates from various portions of the ore varied between 1.59 and 1.64, apparently indicating differences in composition. Some larger lath-shaped particles

haps the greenish tints of some of the Paradox ore specimens are caused by this or another related silicate, like the roscoelite from Placerville, Colorado.[7]

The second characteristic mineral is selenium, in amount up to one per cent. of the ore from Thompson's. It seems to be included as specks in the gray silicate. It is entirely absent from the specimens of Paradox ore first obtained, but is present in ore from the Henry Mountains, Utah, and in some small specimens seen recently that were said to come from Paradox Valley. The presence of selenium can be detected by heating the ore in a glass tube closed at one end, when a red sublimate (sometimes accompanied by a white one of selenium dioxide) appears when most of the water has escaped. The fact that the free element appears as a sublimate does not by itself prove the existence of the selenium in the free state in the ore, for there was enough organic matter present, in a state invisible to the eye, to reduce an oxygenated compound of selenium if present. But the weight of evidence points to its presence in the elemental state and not as a selenide or oxygenated compound.[8] No connection was observed between the presence of the selenium and the bright red color of some specimens of the ore. The differences in shades of red are attributed to differences in physical condition of the metahewettite and to the effect of associated minerals.

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were observed, possibly pseudomorphs, containing abundant dark inclusions of more or less prismatic shape arranged parallel to the laths. These laths are aggregates, but portions of them seem to have a definite orientation with respect to the outlines, extinguishing parallel and having γ parallel to their lengths. The inclusions were selenium and bituminous matter. This gray material is probably not roscoelite. For purpose of comparison a study was made of the properties of the roscoelite from Placerville, California, probably identical with that previously analyzed by Hillebrand (*Am. J. Sci.*, *7*, 351, 1899; Bull. U. S. Geol. Survey, No. 167, p. 70, 1900).

Optical properties of roscoelite: Color, deep green with almost metallic luster. 2E variable between 60° and 75° or more. Optical character—. $\gamma = 1.680\text{–}1.685$, $\beta = 1.675\text{–}1.680$.

[7] Hillebrand and Ransome, *Am. J. Sci.*, *10*, 120, 1900, Bull. U. S. Geol. Survey, No. 262, p. 18, 1905.

[8] The mineral presents deep red transparent prisms, up to 0.05 mm. long, showing parallel extinction. This characterization fits one of the known forms of selenium. Sublimation tests on a few specks indicated free selenium. It seems to be insoluble in carbon bisulphide. So far as known this is the first established occurrence of elemental selenium in nature.

Nearly all of our ore specimens from Paradox Valley, Thompson's and the Henry Mountains were free from uranium minerals, but the complexity of the metahewettite ores under special conditions is well illustrated by a very small specimen from Paradox. In addition to constituents indistinguishable to the eye, this showed in juxtaposition and much commingled, metahewettite, carnotite, a brownish material rich in uranium and resembling some forms of ferric phosphate, and jet black, lustrous bituminous or coaly matter. This last, if uraniferous, is perhaps the unnamed mixture of which a preliminary notice by Karl Kithil appeared in *Science, 38*, 625, 1913.

Fortunately several small lumps of very pure material from Thompson's were found. This material gave only a very faint reaction for selenium and was otherwise almost free from contamination. Upon it analysis II. is based.

Metahewettite crystallizing with 9 molecules of water occurs in two typical habits with intermediate forms. The purest material from Thompson's is a feebly lustrous, loose, earthy powder; that from Paradox Valley appears chiefly in compact aggregates of separable, shining blades, though the earthy variety also is found here. Both are deep red, but on account of the larger size of its bright reflecting surfaces the bladed variety appears lighter colored. When powdered the bladed variety is claret brown, the earthy variety is dark maroon. The color of the ores containing the mineral varies greatly because of admixed minerals; furthermore, variation of the water content of the mineral produces changes in color (see p. 46).

Microscopically the earthy variety consists of minute sharply bounded tables about .04 mm. long, piled in subparallel groups. The outlines and optical properties indicate orthorhombic symmetry. The compact variety consists of plates like those in the earthy variety, closely joined in parallel or radiating, more fibrous aggregates. The optical properties are more easily determined on these large aggregates. Pleochroism is strong in groups seen edgewise, but is scarcely noticeable in the plane of the tables. α is light orange-yellow, β deep red, γ deeper red. Two optic axes barely come into the field of a No. 12 objective over a condenser immersed in oil. 2E thus measured is about 135°. The plane of the optic axes is parallel to the elongation. The refractive indices α and β were determined with difficulty. α was obtained from groups of crystals seen edgewise; β is so high that it could barely be matched without heating by immersion in a mixture of tin iodide, methylene iodide and the compound of arsenic sulphide and methylene iodide. γ could not be obtained except after expelling water from the mineral by heat.

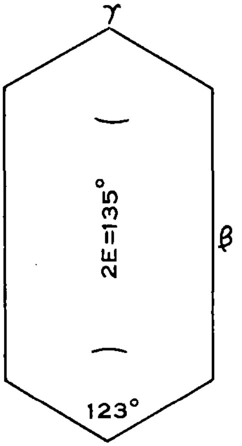

Fig. 1. Optical orientation of metahewettite.

For Li-light $\alpha = 1.70$, $\beta = 2.10$ and 2V (calculated) $= 52°$. α is the acute bisectrix. No measurable differences between the optical properties of specimens from different localities were found. Fig. 1 shows the optical and crystallographic relations. The axial ratio $a:b = .54:1$.

The density of the mineral containing 9 molecules of water—determined in xylol—is 2.511; after the loss of 6 molecules of water it is 2.942. The loss of this water is not accompanied by any perceptible breaking down of crystal structure. The same fact was observed with hewettite. Like hewettite, metahewettite melts readily and is slightly soluble in water. The solubility, slight as it is, affords a means, by the use of much boiling water, of separating from metahewettite the associated minerals mentioned on pages 34 and 35.

Differing strikingly in external aspect from the ores described above is a single specimen from Paradox Valley, shown us by Mr. Frank L. Hess, of the U. S. Geological Survey. This consists of a single bundle of interwoven fibers implanted on a layer of crystallized gypsum. This specimen, on account of its markedly fibrous structure, bears a closer resemblance to the best of the hewettite from Peru than does the mineral described above. Indeed, optical evidence shows that it is hewettite.

ANALYSES OF HEWETTITE AND METAHEWETTITE, AND THEIR DISCUSSION.

Long after the first analysis of hewettite was made, it was found that both it and metahewettite are extremely sensitive to atmospheric changes in humidity, especially within a certain narrow range. It was therefore essential that they be brought always to the same definite state of saturation with respect to water.[9] It was found by experiment that this condition could be satisfactorily attained by exposing the mineral powder at a definite temperature over sulphuric acid of vapor tension near that of pure water until equilibrium was established. The strength of acid over which the mineral was placed

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[9] Failure to observe this precaution may lead to serious error in establishing a probable formula for minerals with variable water content. For instance, if, as with hewettite and metahewettite, the mineral is analyzed in air-dry condition when the air humidity is high, a very different result will be obtained than when the air is dry. The variations in moisture content of these minerals when left exposed to the air may vary 8 or 9 per cent. between September and December in Washington. This is not efflorescence as usually understood, for although the reaction reverses itself with return of humidity the loss of water is not accompanied by breaking down of the crystal structure.

Calcio-carnotite from Colorado (the tyuyamayunite (?) of Nenadkevich) and probably also the original carnotite (essentially the potassium salt) show similar wide differences in water content at different seasons of the year. This may be and probably is true also of other minerals. If so, an explanation is afforded of some of the conflicting statements of different analysts in regard to the water content of certain minerals.

It is, further, important to make a series of exposures over sulphuric acid of increasing concentrations, up to the maximum, at a fixed temperature, and then to carry out tests at rapidly increasing temperatures, in order to detect, by the losses at each step, the number of hydrates that may exist, and also, if possible, what proportion of the water may be differentiated from water of crystallization or of absorption. The curves resulting from such tests with these minerals are shown in Fig. 2.

preparatory to analysis was chosen after a preliminary trial had shown about the range of highest vapor pressure over which little change in water content took place. Sulphuric acid of sp. g. about 1.105 (15°) was found to give the desired vapor pressure, about nine tenths that of saturation.[10] Two different temperatures were employed for establishing equilibrium over this acid in a thermostat, namely, 25° in winter and 35° in summer (temperatures most easily maintained).

At 25° the water-vapor tension of this acid is about 21.8 mm. or 2 mm. less than that of pure water at the same temperature, and 38.8 mm. at 35°, or about 3.5 mm. less than that of pure water. Upon material thus brought to a definite water content the analyses were made. One portion was used for studying the course of dehydration, first by exposing the mineral at 25° (or 35°) until equilibrium was reached, successively over sulphuric acid of concentrations that corresponded to lowering of the vapor tension by tenths approximately and finally over phosphorus pentoxide.[11] With the

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[10] The tables of Domke and Bein were used in this connection (*Z. anorg. Chem.*, *43*, 176, 1905).

[11] The value of conclusions deducible from such a series of fractionations on minerals of the kind in question depends on careful observance of certain precautions. In the first place, the mistake must not be made, as in the present case, of using different temperatures for the initial saturation. It was not expected that our tests would extend from winter into summer, as they did at intervals, thus necessitating the use of two temperatures. Of course, the vapor tension of an acid of given strength is markedly greater at 35° than at 25°. The initial water content of the mineral may therefore differ and the results of tests started at the two temperatures not be strictly comparable. For, although the mineral is under a greater water vapor tension of the acid at 35° than at 25° and might therefore perhaps take up more water than at the lower temperature, it is probable that the higher temperature will have its effect on the mineral also but in a quite indeterminate degree (see Fig. 2 and p. 44 of text, for an instructive illustration of one effect of temperature differences, as shown by curves I. and II.). In the second place, at the conclusion of any one test of a series the mineral must not be allowed to cool in the desiccator after removal of the latter from the thermostat, but must be taken out of it at once and inserted quickly into a capped weighing vessel before it has time to cool, for if allowed to cool before removal the final condition will approach that of room temperature and not be that of the experiment. Moisture may be condensed on the mineral and its containing vessel and the former may perhaps reabsorb water in.

lower vapor pressures a vacuum was employed. The loss observed at the end of the last exposure was practically identical with that occasioned by a temperature of 100° for a few hours in dry air. Then the fractionation was continued at temperatures above 100°. The results of some of these tests will be given later (pp. 44–45).

The following table of analyses does not show all the determinations that were made. In fact, the first complete analysis of hewettite is omitted, because it was made before the need for bringing the mineral to a definite saturation as to water content was realized. That analysis confirmed, however, in all other essentials than water, the data contained in analysis I. below.

ANALYSES OF HEWETTITE AND METAHEWETTITE.

	Hewettite,[12] Peru, in Equilibrium with Water-vapor Tension of 21.8 mm. at 25°.	Matahewettite, Utah, in Equilibrium with Water-vapor Tension of 38.8 mm. at 35°.	
	I.	II.	
V_2O_5	68.19	70.01	
V_2O_4	——	——	
V_2O_3	——	.35	
MoO_3	1.56	.13	
CaO	7.38	7.25	7.25
MgO	none	.03	
K_2O	none	.09	
Na_2O	.15	.08	
H_2O (total)	21.33	21.30	(mean of 21.24, 21.31 and 21.34)
Fe_2O_3, etc.	.11	.19	
SiO_2	——	.80	
Insol.	.17		
	100.10	100.23	

Trace Li in I., none in II. A very little Cl in I. and II. Trace P_2O_5 and Se in II. No Ba or Sr found in either. V_2O_4 and V_2O_3 assumed, their amounts measured by consumption of permanganate when the mineral was dissolved in dilute sulphuric acid (see discussion of molecular ratios, p. 41).

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addition to that condensed on its surface. In the third place, in cases when a vacuum is employed this should be relieved by air bubbling through acid of the same strength and temperature as that in the desiccator, if possible while the latter is still in the thermostat.

[12] An earlier analysis of more compact material from Peru, devoid of crystalline appearance, gave the following results:

MOLECULAR RATIOS.

In calculating molecular ratios for the minerals one is confronted with difficulties arising from the presence of vanadium of lower valence than 5, of molybdenum, and of small amounts of constituents other than calcium. These different problems will be taken up in order.

Vanadium.—In hewettite the presence of vanadium in the quadrivalent state may be regarded as probable in view of its existence in many of the specimens representing much less complete oxidation of patronite. In these cases it may be assumed with considerable probability that there exist vanadyl-vanadic oxides or salts, since artificial compounds of the kind are known. If a compound of this nature exists in hewettite, it demands a portion of the V_2O_5, and, if hydrated, a considerable percentage of water.

In metahewettite, however, there is great reason to believe that the vanadium of lower valence is trivalent. That it exists as a constituent of a silicate containing also aluminum and potassium was pointed out on p. 34. It will be so regarded. This stand is taken with full knowledge that a characteristic black ore from Paradox contains much of its vanadium in the quadrivalent state, as mentioned in our preliminary paper.[18]

Molybdenum.—The presence of molybdenum hampers some-

	I*a*. Per Cent.	Mol. Ratio,
V_2O_5	66.8	4.79
V_2O_4	.7	
MoO_3	2.8	.26
CaO	4.3	1.00
H_2O (100° —)	13.9	10.03
H_2O (100° +)	6.9	4.97
Fe_2O_3, etc.	3.3	
SiO_2	1.2	
	99.9	

This analysis is given chiefly to show how deceptive the evidence afforded by sharp molecular ratios may be, for microscopical examination showed the material to be very far from pure. It also serves to show what different compositions similar appearing materials may have.

[18] *Jour. Washington Acad. Sci.*, *3*, 158, 1913.

what the drawing of conclusions as to the formulas assignable to the vanadates, since we know nothing positive as to its chemical condition and whether foreign to the vanadate molecule or a part of it, nor, if foreign what part if any of the water is to be assigned to it. So much may, however, be affirmed with positiveness from careful microscopical examination, that the sample of hewettite analyzed represents essentially a single homogeneous mineral and not a mechanical mixture of different minerals. This belief is supported by the behavior of the mineral when it is gradually brought into complete solution by successive treatments with much hot water, for the solution of the molybdenum keeps pace with that of the vanadium. The molybdenum may perhaps best be considered as forming calcium molybdate which is held in solid solution. This assumption has been made because it seems called for by the varying proportions of molybdenum in different specimens and by the difficulty of deducing a probable formula under any other assumption.

Other Constituents.—The absence of any acidic constituent in hewettite to offset the sodium forces us to group this with the calcium as part of the vanadate molecule, unless perchance there be an admixture of a vanadyl-vanadate (see p. 41). In metahewettite the potassium may be referred with a high degree of probability to the silicate of which mention has been made. This silicate requires a small part of the water. There is no evidence of such a silicate in the Peruvian mineral. The sodium and magnesium of metahewettite are not accounted for, but in part at least may belong to the silicate mentioned or to another, except in so far as the chlorine present in small amount may claim some of the sodium (also in hewettite). The amounts reported for sodium may be subject to considerable error in both analyses, and if in error are too high. The iron oxide is no doubt admixed.

After deducting MoO_3 and its equivalent of CaO and neglecting V_2O_4, V_2O_3 and all other minor constituents except Na_2O in I., the molecular ratios deducible with employment of the 1913 atomic weights are:

	I.	II.
V_2O_5	3.06	3.00
CaO	1.00	1.00
H_2O	9.61	9.20

The value for V_2O_5 in I. becomes 3.00 if enough is deducted to form an equi-molecular compound with the V_2O_4.

Before discussing the formulas of the minerals we must present a number of considerations bearing on their specific differentiation, in the course of which certain experimental data essential to a proper understanding of the subject will be given.

EVIDENCES OF SPECIFIC DISTINCTION OF HEWETTITE AND METAHEWETTITE.

The evidence which impels us to give different names to the Peruvian and North American minerals, in spite of the fact that they seem to have the same empirical formula, will now be set forth.

Optical and Crystallographic Differences.—Metahewettite is

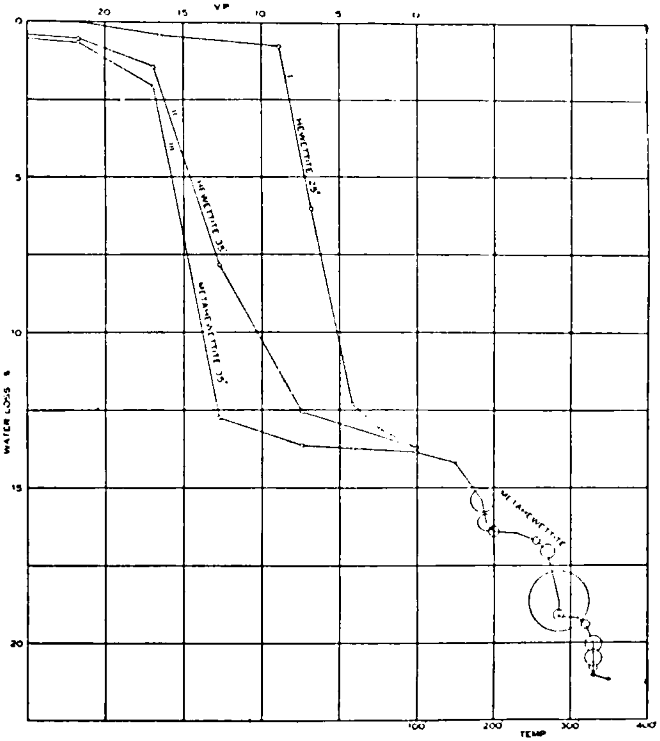

FIG. 2. Showing the course of dehydration of hewettite and metahewettite over sulphuric acid of different concentrations at room temperatures, and of metahewettite at temperatures above 100°.

darker red than hewettite and has two directions of strong absorption for light, while hewettite has only one. Metahewettite crystallizes in well-defined tabular forms or broad blades, hewettite in slender blades.

Loss of Water at Room Temperature.—There is a real difference in the behavior of the two minerals during progressive dehydration over sulphuric acid. Reference to Fig. 2 (curve III.) shows that at 35° metahewettite loses 10.65 per cent. of water in one drop from 17 mm. to 12.7 mm. vapor tension, nearly as much as hewettite loses in the two stages from 17 mm. to 7.4 mm. (curve II.). The points of observation shown in the several curves of the figure in almost all instances represent 24-hour exposures and are approximately equilibrium points. It was unexpectedly found that equilibrium at these points was practically attained in one day, for even after several days' exposure the losses in weight were seldom appreciably greater than after one day. This fact seems to support the argument that the curves indicate a real difference between the two minerals.[14] The curves shown are as a rule quite closely reproducible with different samples of mineral.

The very important effect of varying temperature at a fixed vapor tension of water in the desiccator is strikingly brought out by comparing curves I. and II. for hewettite. It is seen, for instance, that at 35° and 12.7 mm. vapor pressure the mineral loses nearly 8 per cent. of water against a little over half of 1 per cent. at 25° and the same pressure. Again, curve I. shows an equilibrium point at 6.05 per cent. water, curve II. at 7.85 per cent. To the question of why the two points do not appear in the same horizontal line if we are dealing with water of crystallization, two answers suggest themselves: Either (1) an intermediate hydrate which forms at 25° may not have appeared at 35° or, (2) the concentrations of acid used

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[14] The lines connecting points of observation in the figure do not signify that the rate of loss was uniform for each unit-lowering of vapor pressure for the interval between two points. The actual loss for each interval would probably be more correctly expressed by a vertical line corresponding to some vapor pressure intermediate between those of the actual points of observation. Just where this line should fall might be determined by making observations with acids of smaller variation of vapor pressures and allowing more time for the attainment of equilibrium.

were not sufficiently close together to indicate all the hydrates formed.

Loss of Water When Heated Above 100°.—Other differences become apparent when the minerals are heated up to the point of losing the last molecule of water. The experiments showing this were made at the geophysical laboratory, the heating being done in an oil or a nitrate bath, both in an open tube and in tubes which were evacuated from time to time, and the loss determined by weighing the tubes.

Metahewettite, after losing 13.8 per cent. (six molecules) of water over strong sulphuric acid, was first heated gradually from 100° up to 350° during one hour with weighings at frequent intervals. Water was expelled abundantly at three stages near the temperatures 185°, 275°, and 340°. The loss at each stage as determined by these weighings and by repeating the heatings and weighings on another sample at favorable temperatures, was found to correspond to about 2.3 per cent., or one molecule of water at each stage[15] (see Fig. 2, lower portion). The sizes of the circles represent the loss of water at each heating divided by the time of the heating. This is the rate of loss of the water.

Hewettite, on the other hand, exhibits only one well-marked loss in weight when heated rapidly. Near 250° a loss corresponding to two molecules of water was observed. Near 300° and 350° there are evidences of increased rate of loss if the temperature is increased rapidly in 30 minutes. These losses correspond to one-half molecule each. These data are not shown in the figures.

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[15] This method of rapid heating and frequent weighings affords surer indications of the existence of water in different stoichiometrical proportions than that of holding the mineral in dry air for a long time at successively increasing temperatures. By either method a rate of dehydration, not a condition of equilibrium, is measured. Fig. 2 shows two distinct breaks in the rate of water loss for metahewettite when it is heated rapidly as described in the text. The curves plotted for 5-hour periods of heating in a dry-air current (not shown in the figure) are without distinct breaks.

The temperatures at which water escapes most rapidly bear little relation to those employed in slow heating. Long heating results in a higher loss at a given temperature, and in complete dehydration at a much lower temperature, than very rapid heating.

Change of Color Due to Heating.—Metahewettite, dark maroon in color at first, becomes progressively darker red till the last molecule of water begins to escape, then the color becomes gradually lighter and finally yellow-brown. Concurrent with the last change is a breaking up of each crystal into a crystalline aggregate which retains the form of the original crystal.

Hewettite also darkens when water is lost. At the start, with nine molecules of water, it is mahogany red. The hydrate with three molecules is between carob-brown and liver-brown, the compound with one molecule chestnut-brown, and the anhydrous powder medal-bronze. No breaking down of structure was observed till the last molecule of water was lost.

Changes in Weight and Color after Dehydration.—The powders of both minerals were exposed after complete dehydration to sulphuric acid of sp. g. 1.10. Metahewettite from Utah, after dehydration by heating in air, regained its original weight and color in a few days, but after treatment under greatly reduced pressure the color was not restored, even after moistening, although the observed loss of weight had been the same in both cases. Hewettite, on the other hand, after heating to only 270° and while it still retained one molecule of water, neither regained its original color nor quite its original weight when placed in moist air. In one experiment, after heating to 350° and losing 20.75 per cent. in weight, it regained 19 per cent., but on again fractionating over the acids first used the rate of loss and the amount lost at each step were markedly different from those noted in the first fractionation.

PROBABLE FORMULA.

Manifestly the empirical formula indicated for metahewettite nearly saturated with water at 35° is $CaO, 3V_2O_5, 9H_2O$. What it may have been when the minerals were originally deposited can not at present be said, although from the curve for water content under varying hygrometric conditions at summer temperatures (Fig. 2), which shows only very slight changes when the humidity is high, it might be argued that the limit of hydration has been reached with nine molecules of water. The effect of low temperatures is, however, unknown, and it may be that the original water content was higher.

The same statements apply to hewettite, but here the excess of 0.6 molecule of water above nine molecules seems to be real, since it is by no means accounted for by the fraction of one per cent. represented by the nearly horizontal upper part of the curve, which fraction might be considered hygroscopic or absorbed water.[16] It is conceivable that this excess is connected with molybdenum, but much more likely that it has to do with a vanadyl-vanadic compound as already suggested (p. 41).

For the moment we will assume that the formula of both minerals, when holding the maximum amount of water, is $CaO, 3V_2O_5, 9H_2O$. Of what acid, then, are they salts?

The ratio of CaO to V_2O_5 shows that they cannot be salts of orthovanadic acid. Moreover, the known orthovanadates are very few in number and exhibit little stability, but pass readily into hexavanadates. From the fact that six of the nine molecules of water are quickly removable at ordinary temperatures in dry air and the others are much more firmly held, it might seem justifiable to assume six molecules of water of crystallization and three of constitution. Such disposition of them necessitates derivation of the minerals, as quarter-saturated salts, from the hypothetical acid $H_8V_6O_{19}$, an octobasic hexavanadic acid, a possible derivative of orthovanadic acid. We are confronted, however, with the fact that neither such an acid nor salts of it are known. Hexavanadates, however, derived from the tetrabasic acid $H_4V_6O_{17}$, also a derivative of orthovanadic acid, have been described and they resemble in general the two minerals in question, so far as can be determined from the meager data available.

Tetrabasic hexavanadic acid offers the possibility of two isomers of a salt of a bivalent metal. It seems then necessary to consider these minerals as acid salts of this acid, and the name metahewettite for one of them is not only justified but appropriate. If this reference is proper, only one molecule of water of constitution is possible

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[16] Not all of the hygroscopic or absorbed water was necessarily removed in the first part of the dehydration over sulphuric acid.

and the other eight are water of crystallization. Against two of the eight being regarded as water of crystallization might be advanced the difficulty of removing the seventh and eighth molecules, but this can not be considered a weighty argument. Neither can the fact that the water content is so markedly affected by outside humidity and is susceptible of repeated removal and restoration be brought as a conclusive argument against the assumption of water of crystallization, for it must be remembered that loss of water is not accompanied by rupture of the crystalline structure, as is usually the case with true hydrates. On the other hand, in favor of water of crystallization, as opposed to water of absorption, must be placed the breaks in the curves of dehydration observed when the minerals are rapidly heated above 100°, and the fact that the content of water at a fixed atmospheric temperature does not bear a continuous relation to the outside humidity.

On the whole we are disposed to adopt the view that eight of the nine molecules represent water of crystallization and to report the formulas of both minerals as examined by us to be $CaH_2V_6O_{17}\cdot 8H_2O$. Under natural conditions mixtures of this and another salt of much lower hydration may and do often occur.

Inspection of the formulas of the artificial alkali and alkaline-earth hexavanadates throws no light on this problem, since the range in number of molecules of water is very wide for the normal alkali salts and the number is reported as 14 for the normal barium salt and 9.5 for the normal magnesium salt. Acid salts of bivalent metals do not seem to have been prepared, unless Ditte's calcium "trivanadate" $CaO,3V_2O_5,12H_2O$, is such a salt, perhaps identical with one of the minerals described by us. Its description, however, does not fit our minerals, since it is reported as very soluble in water and as having the luster of gold. The evidence of the salts mentioned points, however, to the possibility that hewettite and metahewettite may have held more than nine molecules of water when formed, unless the fact that only slight changes occur in their water content with high atmospheric humidity at summer temperatures negatives such a possibility.

Under the name alaite K. A. Nenadkevich has given a very brief description[17] of a dark red, silky, soft and dense, moss-like mineral to which he assigned the formula V_2O_5,H_2O. The description fits hewettite very well in the main and it will be of interest to learn if on further study alaite may not prove to be a calcium vanadate related to, if not identical with, hewettite or metahewettite. Alaite is one of a number of vanadium and uranium minerals occurring in the Province of Ferghana, Russian Turkestan.

Pascoite.

Not observed in the surface deposit at Minasragra, Peru, but formed on the walls of an exploratory tunnel since its excavation, is a mineral representing a further stage of neutralization by calcium than is shown in hewettite. The specimens examined were among those brought from Peru by Mr. Hewett and the analysis given below was made several years ago in the laboratory of the U. S. Geological Survey. The name proposed, pascoite, is from Pasco, the province in which the locality of occurrence lies.

Crystallographically, this mineral is unsatisfactory, since it occurs only in minute grains and clusters of grains, arranged in a way indicative of a crustaceous deposit—as though they were secondary in origin and had been precipated as a crust about preëxisting masses. No well-developed crystals suitable for goniometric measurement were observed, and only here and there in the crystalline aggregates were minute crystal faces seen. No distinct cleavage was noted, although occasionally indications of an imperfect pinacoidal cleavage were observed in grains under the microscope. The fracture is conchoidal. In color this mineral ranges from dark red-orange to yellow-orange; the more homogeneous masses being uniformly red-orange throughout. In thin flakes it is translucent and the clearer individuals are vitreous to subadamantine in luster, especially on flat crystal faces which glisten here and there in the aggregate. The streak is cadmium-yellow and the hardness about 2.5. The specific gravity is about 2.457, determined in methylene iodide and benezene, on the clearest and most homogeneous material. This value may be slightly low because a crystalline aggregate, instead of a single crystal, was

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[17] *Bull. Acad. Sci. St. Petersburg*, p. 185, 1909.

used, and minute air spaces therefore may have been present between the grains.

In the powder form the grains are usually irregular in shape and colored more or less intensely in shades of orange, red, and yellow. Pleochroism is noticeable; $\alpha =$ light cadmium-yellow; $\beta =$ cadmium yellow; $\gamma =$ orange. Absorption $\gamma > \beta > \alpha$. The refractive indices were determined by the immersion method; mixtures of methylene iodide, arsenic tribromide and arsenic sulphide (realgar) being used for the purpose. Owing to the color of the mineral, however, the phenomena on which the refractive index determinations by this method rest were less sharply marked than usual, and the probable error is correspondingly larger.

$$\alpha = 1.775 \pm .005$$
$$\beta = 1.815 \pm .005$$
$$\gamma = 1.825 \pm .005$$

The birefringence is strong and gives rise to high interference colors, even in comparatively thin grains. By direct determination, $\gamma - \alpha$ was found roughly to be about .050. The optic axial angle was measured by the double screw micrometer ocular[18] on sections showing only one axial bar and also on a section normal to the acute bisectrix. For sodium light 2V was found to be $50^\circ.5 \pm 1^\circ$ or 2E is about 100°; for lithium red light 2V is about $56^\circ \pm 3^\circ$, or 2E, about 115°. The determination in lithium light was much less satisfactory and accurate than that in sodium light. The dispersion of the optic axes is very considerable with $2V_{Li} > 2V_{Na}$ and its effect is clearly marked in the interference figure. The appearance of the interference figure shows, moreover, remarkably strong crossed dispersion—so strong in fact that in white light a section normal to the acute bisectrix never extinguishes completely, but near the position of extinction for light of any wave-length shows abnormal interference colors in characteristic tones, especially of green and orange. On a section nearly normal to the acute bisectrix the position of total extinction for sodium light made an angle of about 8° with that for lithium light. This angle, $\gamma_{Li}{:}\gamma_{Na} = 8^\circ$, is only ap-

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[18] *Am. J. Sci.*, *24*, 317–369, 1907.

proximatetly correct, and may be several degrees in error, owing to the weakness of the lithium light source used, and consequent lack of sharpness of position of total extinction.

The above optical data indicate that this mineral is in all probability monoclinic in crystal system, with its optic axial plane normal to the plane of symmetry. To summarize, the determinative optical characteristics of this mineral are: Crystal system, probably monoclinic; axial ratio, unknown; cleavage, poor and probably after 010. H, about 2.5; sp. g., about 2.46. Color, dark red-orange to yellow-orange; luster, vitreous to sub-adamantine. Pleochroism, noticeable, $\gamma =$ orange; $\beta =$ cadmium-yellow; $\alpha =$ light cadmium-yellow. Absorption, $\gamma > \beta > \alpha$. Refractive indices, $\alpha = 1.775 \pm .005$; $\beta = 1.815 \pm .005$; $\gamma = 1.825 \pm .005$.

Birefringence is strong. $2V_{Na} = 50^\circ.5 \pm 1$. $2E_{Na}$ about 100°. $2V_{Li} = 56^\circ \pm 3^\circ$.; $2E_{Li}$ about 115°. Dispersion, crossed and strong, Optical character —. Plane of optic axes normal to plane of symmetry.

On the whole, the material is homogeneous and comparatively free from inclusions and suitable for chemical work. Here and there foreign material was observed, but in the material selected for chemical analysis it was not present in sufficient quantity to veil seriously the chemical relations.

Pascoite melts readily, forming a deep red liquid, and is easily soluble in water.

ANALYSIS OF PASCOITE.

	Per Cent.	Mol. Ratio.
V_2O_5	64.6	3.18
MoO_3	.3	——
CaO	12.6	2.00
H_2O 100° —	13.8	6.87
H_2O 100° +	7.8	3.88
Undet. and loss	.9	——
	100.0	

The ratios are not as satisfactory as could be desired. The values approach those required from the formula $Ca_2V_6O_{17} \cdot 11H_2O$, which calls for: V_2O_5, 63.76; CaO, 13.10; H_2O, 23.14. Very recent tests show that almost no loss of water occurs at room temperatures until the surrounding humidity is reduced practically to zero. When dehydrated over P_2O_5 the color is no longer orange but dirty yellow. After rehydration in moist air the color is much brighter yellow, but without any trace of the original orange.

As with hewettite and metahewettite, the amount of water evolved at and below 100° is almost exactly removable by exposure over strong sulphuric acid at room temperature for one or two months and much more rapidly in a vacuum. Above 100° further loss begins, but is complete only at a temperature of perhaps 300°. No experiments have been made as yet to trace the progress of dehydration at temperatures above 100°. Further tests on this mineral are needed and will be made if opportunity offers.

The arguments advanced (pp. 46–48) for hewettite and metahewettite with respect to their chemical classification apply to pascoite also. In this case, if the assumptions made for the former minerals are justified, we have normal calcium hexavanadate with x molecules of water, at least 11 when the mineral was formed.

ANALYTICAL PROCEDURE.

The methods of analysis need no special mention except as to the separation and determination of the vanadium and molybdenum. As a rule the portions used for water determinations served also for the other constituents. They were treated in a glass tube, with dry hydrochloric acid gas, after solution in nitric acid and evaporation to dryness in a porcelain boat on a hot plate. The brown vapors were collected in receptacles containing a little water. Two of these in series were sufficient, but a third was sometimes used, all so connected that no back suction of liquid was possible if the gas stream slackened. The material in the boat is attacked instantly the acid vapor reaches it, even without the aid of heat, but the reaction is not complete in one operation even when heat is applied after vigorous action ceases. It is necessary, usually, to remove the boat, to reconvert the contents to nitrates and to repeat the treatment with hydrochloric acid gas several times, and to wash out and dry the glass tube between each operation.

The molybdenum, less volatile than the vanadium, comes off only, or at least for the most part, during the later periods and upon heating. If present in some quantity it reveals itself by a white crystalline deposit in front of the boat.

The contents of the receptacles and of the tube were finally evaporated in porcelain with sulphuric acid, which was then heated till fumes arose. After dilution, the deep blue solution was transferred to a flask, saturated with hydrogen sulphide gas, and heated while the gas still passed. The flask was then stoppered and allowed to stand, over night as a rule, before filtering. The molybdenum sulphide was roasted to oxide.

The filtrate was brought to boiling in a flask while passing carbon-dioxide gas until hydrogen sulphide was wholly expelled, then titrated in the flask at 70°–80° with permanganate. The vanadium was again reduced, this time with sulphur-dioxide gas, which in turn was expelled by boiling in a current of carbon dioxide, and the vanadium was again titrated. If desired the operations of reduction and titration were repeated. The values obtained after successive repetitions of the reduction by sulphur dioxide agreed well but were always somewhat lower than after reduction by hydrogen sulphide. The difference is no doubt due to the presence in the one case of a little free sulphur from the hydrogen sulphide, which consumes permanganate at the high temperature of titration. If the molybdenum sulphide has been filtered through paper instead of a Gooch crucible, permanganate is also consumed by organic extracts from the paper.

SUMMARY.

Two apparently different calcium vanadates are described, which resemble each other very closely and have the same composition—$CaO \cdot 3V_2O_5 \cdot 9H_2O$—when holding their maximum water content at room temperatures. One of them—hewettite—occurs at Minasragra, Peru, and has been noticed on a single specimen from Paradox Valley, Colorado. The other—metahewettite—occurs at numerous localities in western Colorado and eastern Utah. Both minerals are sparingly soluble in water.

A third calcium vanadate—pascoite ($2CaO \cdot 3V_2O_5 \cdot 11 ?H_2O$)—is also described. This occurs with hewettite at Minasragra. It is very soluble in water.

The first and second minerals are regarded as hydrated acid hexavanadates—$CaH_2V_6O_{17} \cdot 8H_2O$—the third as a normal hexavanadate, $Ca_2V_6O_{17} \cdot 11\, ?H_2O$.

The reasons for specific separation of hewettite and metahewettite are set forth in detail. The two minerals are so sensitive to changes in atmospheric humidity that their water content varies within wide limits at different times of the year. The removal of all or nearly all the water does not result in breaking down of the crystal structure, and until this has occurred the water is wholly or in great part taken up again when opportunity is offered.

The importance is emphasized of bringing all minerals that behave in this way to a definite maximum water content before analyzing them and of following carefully the course of dehydration under prescribed conditions. Detailed directions are given for such tests and for avoiding several sources of error.

Attention is also called to two fairly constant associates of metahewettite. One of these (also a constituent of carnotite ores) is a gray hydrous silicate of aluminum, trivalent vanadium, and potassium. The other is elemental selenium, the existence of which as a mineral species seems now for the first time established.

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