

ART. XXXVI.—*The Occurrence and Properties of Sincosite, a New Vanadium Mineral from Sincos, Peru*; by WALDEMAR T. SCHALLER, U. S. Geological Survey, Washington, D. C.

*Introduction.*

Specimens of a green mineral found in a black carbonaceous shale from Sincos, Peru, were kindly furnished for investigation by Mr. W. Spencer Hutchinson of Boston, Mass. It was known to contain vanadium, calcium, and phosphorus, and as it could not be identified with any known mineral, was recognized by Mr. Hutchinson as probably a new species. A minute fragment of the same material had been tested qualitatively some time previously for Mr. D. Foster Hewett and determined to be a vanadium mineral of unknown composition and relationship. The better and more abundant material furnished by Mr. Hutchinson permitted of a more thorough study, with the result that the essential properties of the mineral were definitely established. A preliminary note was published in the *Journal*<sup>1</sup> of the Washington Academy of Sciences, giving a general description of the mineral, with an analysis, and general group relationship.

*Locality.*

The name sincosite is derived from the locality, the mineral being obtained close to the small Indian village of Sincos (Department of Junin), Peru, which lies on the eastern slope of the main range of the Andes, about halfway between the crest of the Andes and Mantaro River. Sincos<sup>2</sup> is about 160 kilometers (100 miles) east of Lima and about the same distance southeast of Quisque (Minaragra). The vanadium deposits of Minaragra, Yauli,<sup>3</sup> Llacsacocha, and Sincos, lie on a northwest-southeast line paralleling the crest of the Andes mountains and but a few miles east of the crest.

<sup>1</sup> Schaller, W. T., Sincosite, a new mineral. (Preliminary note): *Jour. Washington Acad. Sci.*, vol. 12, No. 8, April 19, 1922.

<sup>2</sup> Sincos is probably very close to the village given as Minto on the maps.

<sup>3</sup> Hewett, D. F., Vanadium-deposits in Peru; *Trans. Amer. Inst. Min. Engr.*, pp. 291-316, 1909.

The following notes on the locality and on the occurrence of sincosite were furnished by Mr. W. Spencer Hutchinson, who abstracted them from a report on the deposit made by Mr. Gragg Richards. The locality is described as follows:

The vanadium property of the *Compania Minera de Huancayo* is situated in Lat.  $11^{\circ}55'$  S., Long.  $75^{\circ}20'$  W. of Greenwich, in the district of Sincos, province of Jauja, Department of Junin, Republic of Peru, on W. side and some 500 m. above the Mantaro River and 3700 to 1400 m. above sea-level. The property is 8 km. from Sincos, a native pueblo on the Mantaro River, accessible in the dry season by fording the river from Matahuasi, a station on the *Ferro Carril Central del Peru*, 320 km. from Callao. (Matahuasi in midway between Jauja and Huaucayo.)

#### *Occurrence and Association.*

Together with the preceding notes on the locality, furnished by Mr. Hutchinson, are given the following details on the occurrence of the mineral.

“The vanadium-bearing shales occur as a syncline with a general strike of N.  $50^{\circ}$  W. mag. They are both underlain and overlain by limestones. The lower limestone carries nodules of chert, limonite, and calcite but no fossils were noted.

The shales are generally sandy and friable with varying amounts of carbonaceous material up to 20%, varying in color from gray or light yellow to black. The black carbonaceous shales, in general, occur in the middle of the bed, but the carbonaceous matter is weathered out at croppings up to depths of over 1 m. In places concretions of limestone, up to 0.5 m. in diameter, occur in the shale, the bedding planes passing through the concretions without interruption.

Thin beds of what appears to be volcanic ash are rather frequent in the shales but generally under 0.02 m. in thickness. They also occur in the lower part of the upper limestone.

Ammonites are plentiful throughout the shale beds, whether carbonaceous or not, reaching a diameter up to 0.2 m.

A basic dike, 6-8 m. wide, occurs at a point 5 km. southeast of the tunnel, cutting both the shales and underlying limestone with strike N.  $30^{\circ}$  W. The dike is decomposed at the outcrop and its composition uncertain. At a point 7 km. southeast of the tunnel another decomposed igneous mass is exposed on W. side of a gulch for about 20 m. No other intrusions were noted on the property.

Sincosite, the vanadium mineral, occurs in the main drift in emerald-green to brass yellow micaceous scales, rectangular in

outline. The scales tend toward radial arrangements along bedding and joint planes and with fossils in the black shales. Analysis of this material gave 14.00% V, 2.78% P and 9.66% CaO. In a seam of dust-like carbonaceous material, apparently this same mineral forms as spherules, the change in form, passing from the bedded shale to the powder, being traceable. Analysis of spherules gave 9.80% V, 4.45% P and 10.10% CaO. The rectangular micaceous scales suggest relation to some of the uranium phosphates.

Except for this mineral, the only indication of vanadium noted in the shales were occasional brownish and greenish stains. A yellowish mud, being deposited in the main drift, apparently by surface water, gave 0.80% V. In clayey peat at a spring at the camp, a blue amorphous mineral occurs along with limonite. This material gives a rather weak test for vanadium.

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The soft, black amorphous material from the main drift was examined under the microscope by Mr. Gillson and myself. Even under the highest powers with oil-immersion objective, this material still appeared as dust, though small, colorless, transparent scales, probably the vanadium mineral, were rather plentiful. No plant or other organic remains were to be found.

The irregular, narrow, coal-like seams in this amorphous material are non-conformable to the bedding of the enclosing shales and thus, with the absence of plant remains, suggest a petroliferous material which may have migrated rather than coal formed in place. In this relation it may be noted that the fossil ammonites are distributed throughout the shale beds irrespective of the carbonaceous content.

Vanadium occurs extensively in the shales and samples yield assays of 0.15 to 0.20% V. At one place a 0.3 m. bed of black powdery carbonaceous material with rich vanadium-bearing spherules, and containing crystals of sincosite, has been developed for a length of 125 feet by a tunnel and drift."

The following notes on the occurrence have no direct reference to the mode of occurrence in place but present the results of observations made in the laboratory on the available specimens. They may, therefore, be incomplete inasmuch as the suite of specimens available for laboratory study may not have included all the different modes of occurrence of sincosite in place.

The sincosite is found, as stated, in a black carbonaceous shale, probably of Cretaceous age as, at places in it, ammonites are present. Dr. T. W. Stanton was kind

enough to examine the specimens showing ammonites and has stated that they yielded "some fairly good looking small keeled ammonites, but as they are much flattened by pressure and fail to show any trace of sutures I have not ventured to attempt a generic determination, and the species is most likely undescribed. The general features which are preserved show that the fossils are either Cretaceous or Jurassic in age, and I think that the probabilities are strongly in favor of Cretaceous. Either better preserved or more definitely characteristic fossils are needed to determine the exact age." This shale is rather soft and earthy but when cut with a knife yields a smooth, lustrous surface. The original bedding planes are well preserved and the rock splits readily parallel to them.

Mr. Hutchinson states that a bed in the shales a third of a meter thick consists largely of nodules. These nodules average about from one to two centimeters in thickness and are fairly round, occurring either isolated or as coherent groupings of two, three, or even more. Many of these nodules, when broken open, show a crystalline appearance with a rude radiated structure. A faint concentric structure is occasionally present but most of the nodules do not show any characteristic concretionary structure. Some of the nodules show at best only a diffused radiating structure and others show none at all. The so-called "crystalline appearance" is due to a shining carbonaceous substance, resembling coal, which seems to be the main component and cause of the radiating members. It may be, however, that some other minerals, as gypsum, or even sincosite, were the cause of the radiating nodular structure. Some nodules seem to have broken down into a loosely coherent, structureless, dull earthy mass, with the disappearance of the bright shining compact material. A few such nodules, consisting in the center of only a loose dull earthy material, are surrounded by a narrow shell of greenish material which has a decided concretionary structure and easily breaks up into concentric shells.

The nodules on the average contain much sincosite, nearly one half. The dull earthy masses appear to be poorer in the mineral, which during the alterations of the shining material has probably become concentrated in the surrounding narrow greenish shell.

The sincosite is present in varying quantity in all the specimens of shale from this locality which have been examined. It seems to occur rather generally in the massive bedded shales but only in small quantities except where local concentration has taken place. These concentrations, however, appear to be rather abundant, judging from the half dozen or so specimens which were examined.

Four more or less distinct modes of such local concentrations were noted. The first and visibly most abundant mode is where the sincosite is developed in seams and cracks of the shale which probably are the original bedding planes. These seams vary in size from those so thin as to appear in cross section as a very fine green thread, to others almost a centimeter thick. Most of these seams of sincosite are regular and parallel, and in the smaller seams the flat crystals of sincosite lie closely compacted parallel to the direction of the seam, which they almost completely fill. Only where these seams diverge from the original bedding planes and apparently have become enlarged on account of the more irregular later fractures is there a relative abundance of the mineral developed in complete individual crystals. Other seams are more irregular in direction and in thickness and probably represent in part local fractures cutting across the original bedding planes of the shale.

The second mode of occurrence is in small seams (at least no large ones were seen on the specimen examined) cutting across the original bedding planes of the shale, in a typical example almost at right angles. The only difference from the first mode of occurrence is that the seams distinctly cut across the bedding planes and therefore show conclusively that they are of later origin. They are completely filled with scaly, compact masses of sincosite. They cut across the compact shale and the nodules (the fourth mode of occurrence) with apparently equal ease.

The third mode consists of irregular masses of sincosite plates lying embedded in the compact shale. These masses are about a centimeter across and show no clearly defined relation to any seam of sincosite, though such a minute seam may be present but obscured by the black shale. The plates of the mineral are closely compacted

and in places suggest a rudely radial structure. These three modes of local concentration of sincosite show many intergradations. The cases cited represent merely some of the more pronounced divergencies, but they are in no way to be considered as representing distinct modes of occurrence.

The fourth mode of local concentration is represented by the nodules. These consist of about 45 per cent sincosite, 5 per cent gypsum, and 50 per cent of "gangue" insoluble in acid. This 50 per cent of "gangue" is made up of ash 23 per cent, water 5 per cent (other than that contained in the sincosite and gypsum), and 22 per cent volatile matter (excluding all water). An analysis of these nodules is given with the analysis of the mineral. This analysis suggests the presence of some vanadate containing quinivalent vanadium in addition to the sincosite, as the analytical determinations show a slight excess of total  $V_2O_5$  over that corresponding to the  $V_2O_4$  due to the sincosite. Possibly a little hewettite or melanovanadite is finely disseminated through the material. A cold water extract of the nodules has a strong olive-colored appearance, whereas the pure mineral sincosite does not seem to be sufficiently soluble in cold water to impart to it a decided color, although but very little pure sincosite was available for such tests which are therefore not altogether conclusive.

The bright, shining nodules readily give a small sublimate of brick-red selenium when heated in a closed tube, especially if the material be heated very gently at first and all the water driven off. The dull-appearing nodules yield very much less selenium. It is not known in what form or in what mineral the selenium occurs. Molybdenum and nickel, present in the vanadium ores from Minaragra, could not be detected in the nodules from Sincos. Occasionally the shale is cut by narrow seams of a mixture of sincosite and a lustrous black organic substance, resembling hard coal. This material is very brittle, does not fuse when heated in a closed tube, and seems to approach a hard coal. The sincosite plates are scattered promiscuously through this material, in places apparently making at least half of the entire seam. The lustrous black substance resembles the bright shining radiated material of the nodules previously mentioned.

Occasionally on breaking a piece of shale along a pronounced seam, there is found a multitude of small clear gypsum crystals of ordinary habit and combination.

*Crystallography.*

The flattened rectangular crystals of sincosite average about one to two millimeters across, with a thickness reaching about one-fifth as much. The largest plates are less than a centimeter long. The crystals are tetragonal but show only the base  $c(001)$ , and the prism  $a(100)$ . The square base is equally striated parallel to its edges; the faces of the prism are very much rounded and striated horizontally and, on the reflecting goniometer, the prism faces begin to show reflections at about  $80^\circ$  inclination from the base. On crystals studied under the microscope, the presence of a form in the zone  $c \wedge m(110)$ , probably the prism  $m$ , was established on several crystals but the identity of the form could not be definitely determined. The crystals are often built up of many superposed plates nearly in parallel position. No terminal faces other than the base could be determined on any of the crystals. The value of the crystallographical vertical axis  $c$  is therefore not known.

The shape, habit, and mode of aggregation of the platy crystals of sincosite is the same as that commonly shown by autunite, torbernite, etc. In fact, except for a very slight difference in tint, the green crystals of sincosite resemble very greatly those of torbernite. This resemblance is also shown in the striations, cleavage, and optical properties.

*Physical properties.*

The crystals have a good basal cleavage, and thin sections show a second cleavage parallel to the faces of  $a(100)$ , and a third poorly developed cleavage parallel to  $m(110)$ . The crystals are brittle but break easiest along the cleavage planes. The hardness was not determined on the little material available but it is relatively low. The density is 2.84, approximately. Fusion and solubility are given under the heading Chemical Composition.

*Optical properties.*

The mineral is leek-green but varying in shade according to the condition of aggregation, and also apparently to a partial alteration (oxidation of the vanadyl vanadium?). Among the loose material submitted by Mr. Hutchinson and also on some of the specimens of black shale, are scales of sincosite that appear almost brass-like in color although this is in part due to the high reflection from their surface. Close inspection reveals a considerable quantity of green in their brassy color and no scales were seen that could be called yellow. But some change does occur in many of the scales, and along with this change the vitreous green sincosite crystals take on a decidedly yellowish shade and almost a submetallic luster. This change is well seen under the microscope, the greenish material becoming olive colored, due to the introduction of considerable brown. This addition of a brownish color generally takes place around the edges of the plates; occasionally a broad indefinite band crosses the crystal plate. An alteration is probably taking place, possibly a change in the vanadium from the quadri- to the quinivalent state. No appreciable difference could be detected in the value of the refractive indices or their orientation or relationships. The amount of chemical change, while sufficient to alter the color and luster of the mineral, is probably slight. Very rarely a group of sincosite plates was encountered that seemed to have undergone much more alteration. The plates have broken down to a cream-colored amorphous mass which only feebly retains the original square crystal outline. Not enough material of any of these alterations, however, was available for any quantitative chemical study or analysis.

The green mineral turns dark brown to black when heated in a closed tube, without regaining the green color on cooling. The powdered mineral (streak) is pale green. The crystals are not transparent as viewed on the matrix, but in small pieces are transparent as viewed under the microscope.

The rectangular crystals showing only the base and prism do not admit of a distinction between tetragonal and orthorhombic symmetry on crystallographical



grounds alone, but optically most of the crystals are uniaxial, showing the tetragonal symmetry of the substance. Some of the crystals, however, are decidedly biaxial,  $2E$  varying from nearly zero to an average of about  $50^\circ$ . Only a very few pieces show the larger axial angle. Uniaxial bands occur traversing biaxial material and biaxial areas (very hazy in outline) are found in uniaxial material. The bands of alternating uniaxial and biaxial material are always parallel to the edges of the crystal, to the pronounced striations on the base, and to the prominent prismatic cleavage. In the biaxial sections, the optical axial plane is always diagonal ( $45^\circ$ )

FIG. 1.

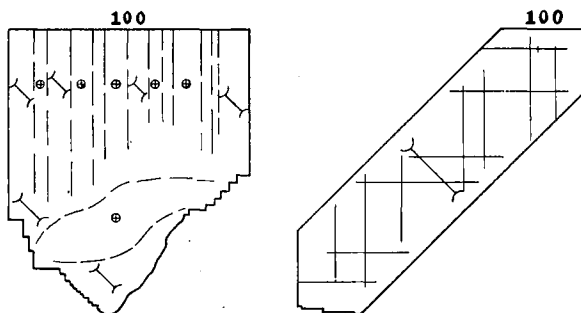


FIG. 1.—Alternating bands and areas of uniaxial and biaxial character in a crystal of sincosite.

FIG. 2.—Brassy yellow crystal of sincosite elongated parallel to one edge  $c(001):m(110)$ , with large axial angle.

to the edges of the crystal, never parallel to them or to the alternating bands of uniaxial and biaxial material.

The relationships are shown in Figure 1, the boundaries of the uniaxial and biaxial bands being much more indistinct and hazy in outline than the figure shows.

All the crystals, both uniaxial and biaxial, are optically negative. For the uniaxial crystals,  $\epsilon$  is about 1.655 and  $\omega$  about 1.680, both values varying slightly in different crystals. The values for the strictly biaxial plates are a very little higher, thus  $\gamma$  was determined as 1.685 and on other plates was found to go as high as 1.69 by Dr. Larsen. In these biaxial plates, the dispersion is strong  $\rho > v$ . Pleochroism is strong,  $\epsilon$  nearly colorless to pale

yellow and  $\omega$  gray-green. The writer is indebted to Dr. E. S. Larsen for verification of the optical constants, as given.

The greater bulk of the crystals are essentially uniaxial. A few are distinctly biaxial, a greater number contain areas and bands of both uniaxial and biaxial material. It is evident that at least two forms or modifications are present; one predominant, uniaxial, and a second one, biaxial, in much smaller quantity. The uniaxial or biaxial modification did not seem definitely to bear any relation to the color changes already noted, either to the olive-green or to the more brassy-appearing plates. It was noted that a few of the brassy crystals were considerably elongated parallel to one set of the  $m(110)$  faces and these were rather commonly biaxial, the relationship being as shown in figure 2. But many of the square greenish plates also are biaxial with  $2E$  the same size as in the brassy plates, and others of the brassy variety are uniaxial.

A re-examination of sincosite made (June 1924), two years after the first determinations, shows that a change in properties is slowly taking place. The material re-examined has been kept in a small vial, with a cork stopper, and has been opened several times at intervals for the removal of material. The small plates were immersed in oils of known index and studied microscopically. Viewed in the vial with a hand lens, no change in properties can be observed. The plates are still dark green in color with no suggestion of the brassy-appearing plates.

Nearly all of the crystals of sincosite are now definitely biaxial with  $2E$  medium to large, reaching a maximum measured value of  $83^\circ$ . No definitely uniaxial interference figure was encountered on testing several dozen different plates. The smallest axial angle measured ( $2E$ ) was  $16^\circ$  and there was a continued series of values up to the maximum of  $83^\circ$ . On a single rectangular crystal similar variations were observed, the smallest value (approaching uniaxiality) being on the border and the size of the axial angle increasing regularly to the center of the crystal, and then decreasing as the opposite border was reached. Together with the increase in size of the axial angle there was a pronounced increase in the dispersion. For the small axial angles no dispersion

was noticed. When the angle ( $2E$ ) was in the forties the dispersion was faintly perceptible,\* in the fifties it was moderate, in the seventies it was strong, and for the largest axial angle almost extreme. Many of the plates show under crossed nicols a uniform birefracting center (with maximum axial angle) surrounded by borders of alternating dark and bright indistinct bands, similar to those shown in figure 1. It is in this area of bands that the value of  $2E$  becomes a minimum. For all the plates the axial plane, as before, is at  $45^\circ$  to the edges (100) of the crystal.

The refractive indices have increased slightly over those of the uniaxial modification and for the decidedly biaxial crystals with large axial angle are about  $\alpha = 1.675$ ;  $\beta = 1.690$  (calc.),  $\gamma = 1.693$ . These higher values are in agreement with the results found by Dr. Larsen and already noted. He gives a value as high as 1.69 for the biaxial plates with strong dispersion. The pleochroism of the biaxial plates is similar to that of the uniaxial plates. Observed in oil, the color of the crystals shows variations in brownish-green, yellowish-green, grayish-green, and bluish-green. These variations were also noted previously on the original material, when first obtained. One crystal showed in one corner alternating bands of green and brown.

Chemically, such material is not sufficient for any quantitative determinations. A partial dehydration suggests itself and the mineral may be tending towards a lower hydration, possibly a four or even lower hydrate. Some of this biaxial material ( $\gamma = 1.693$ ) was placed in a desiccator over dilute sulphuric acid of density 1.105 over night, and the crystals were found to be changing back to the uniaxial modification, through the over night exposure in the desiccator had not been long enough to complete the change. Out of several dozen plates, only one retained the bright uniform interference color seen on the biaxial plates of high index ( $\gamma = 1.693$ ), one was completely and uniformly uniaxial ( $\omega$  was still higher than 1.68), two were almost completely uniaxial whereas twenty-three plates were optically very ununiform with irregular bright and dark areas, and in general with a

\* Using these defining terms as given by Larsen: The microscopic determination of the nonopaque minerals, U. S. Geol. Survey, Bull. 679, p. 161, 1921.

hazy axial angle of very low value as a maximum. These latter plates showed wavy extinction and a marked irregularity in their optical structure.

Bearing in mind the results given above, some of the "brass yellow" scales on the black shale were re-examined and found not to have changed during the last two years. They are all essentially uniaxial and where biaxial, the angle ( $2E$ ) is very small, from about  $10^\circ$  to  $20^\circ$  approximately. In oil, under a microscope, these "brass yellow" scales are of an olive color ranging towards the yellows and browns, but on crushing such a "brass yellow" crystal, many of the fragments are green rather than olive-green and more of these green fragments are biaxial with  $2E$  medium than the olive-green which, as stated, are almost uniaxial. The brassy-colored scales then do not represent the biaxial modification with higher indices and large axial angle but are more probably a stage in the oxidation of the vanadyl-vanadium of the mineral. Both the green and the brassy-colored plates may be either uniaxial or biaxial. The evidence seems to suggest that the biaxial modification is a lower hydrate, possibly with  $4H_2O$  and just as probable with only  $3H_2O$ , the mixture of the 3 and 5 hydrates giving an average value approximating to 4.

Twinning occurs not very frequently, and in the biaxial varieties is readily noticed by the traces of the axial planes of the two parts being normal to each other. The twinning plane is  $m(110)$ .

Inclusions of other minerals were noticed as being of two kinds, one red and the other black. The red prismatic inclusions were noticed near the edge of a brassy crystal and were mixed with bunches of much darker red (almost black) fibers which strongly resemble hewettite (or meta-hewettite). The red prisms suggest either selenium or thin hewettite crystals. The black inclusions are long black opaque crystals which occur in isolated prisms or in densely clustered groups of crystals in the sincosite usually near an edge. They may well be melanovanadite. Black irregular pieces of the carbonaceous shale also are abundantly present as inclusions. One specimen has some reddish material on it, resembling a red pencil mark. It is not individualized under the microscope and does not look like a natural product.

*Chemical Composition.*

The color changes in heating in a closed tube have already been given as changing from the green to a permanent dark brown to black, the mineral decrepitating and evolving water, and finally sintering to a dark-colored mass. A faint sublimation ring of reddish selenium is generally obtained. The mineral is readily soluble in dilute acids to a blue solution. In dilute sulphuric acid the crystals first become white and more opaque, probably due to the temporary formation of a mass of fine needles of gypsum. The water solution of the nodules (about half sincosite) becomes faintly yellow which color is lost on the addition of a little  $H_2SO_4$ . The pure mineral, however, is insoluble in water, using the expression as generally applied to minerals. The solubility seems to be about of the same general order of magnitude as that of hewettite.

Two analyses were made of the mineral on two differently selected samples. The first sample was carefully picked off the matrix of one specimen, and the second sample was selected from the loose material fallen off the specimen during transit from Peru. The first sample was more uniform and less mixed with the shale. The crystals were all of the green variety. The second samples contained some of the more olive-colored and brassy-looking material. Both analyses were made on small quantities of mineral, carefully hand-picked under a lens. The analysis of the first sample, composed of crystals picked from the one specimen and which were all of a uniform green color, gave the following results:

*Analysis of Sincosite from Peru.*

	Analysis.	Ratios.	Calculated $V_2O_5, CaO, P_2O_5, 5H_2O.$
$V_2O_4$ .....	36.3	0.218 or 1	36.57
$V_2O_5$ .....	0.0		
CaO .....	12.1	0.217 or 1	12.33
$P_2O_5$ .....	31.7	0.223 or 1	31.28
$H_2O$ .....	19.9	1.103 or 5.03	19.82
Insol. ....	0.3		....
	<hr/>		<hr/>
	100.3		100.00

The analysis yields the simple formula  $V_2O_4 \cdot CaO \cdot P_2O_5 \cdot 5H_2O$  and a comparison of the figures of the analysis with those calculated from the formula shows a close agreement. The analytical determination showed that all of the vanadium was present as  $V_2O_4$ . The water was determined as loss on ignition, with correction for the oxidation of the vanadium. Subsequent solution of the fused mineral grains in acid and actual determination of the state of valency of the vanadium in the fused mass, unfortunately could not be carried out on account of loss of the solution due to breakage of a beaker. The figure given, 19.9 per cent, was obtained as follows:

Loss at 110° . . . . .	1.8 per cent
Loss above 110° . . . .	14.6 per cent
O correction . . . . .	3.5 per cent
	<u>19.9</u>

The sample was very slowly ignited in an open crucible so as to allow for free access of air. It is, however, not conclusively proven that the mineral contains as much as 5 molecules of water. Other data suggest that perhaps only 4 molecules of water are present. The following data on the loss of water were obtained on 0.1070 gram of material. In a desiccator over dilute  $H_2SO_4$  of density 1.105, in a thermostat with a temperature of 25°:

After 2 days, total loss = 0.0002 gm. = 0.19 per cent

After 7 days, total loss = 0.0001 gm. = 0.09 per cent

In a desiccator over conc.  $H_2SO_4$ , in a thermostat at 25°:

After 7 days, total loss = 0.0003 gm. = 0.28 per cent

A check, using the same platinum dish, empty, showed a gain, after 7 days, of 0.0001 gm. The slight changes of a few tenths of a milligram noted are not over the errors of weight and of manipulation and the only conclusion that can be drawn is that a sample of sincosite neither increases nor decreases in weight over dilute or concentrated  $H_2SO_4$ . The same sample, heated in the open air to 110° to constant weight, showed a loss of only 0.0005 gm. = 0.47 per cent, considerably less than the loss of 1.8 per cent found on a different sample. The sample showing a loss of 0.47 per cent at 110° did not regain this weight in the balance on standing over night. It is possible, therefore, that the loss of 1.8 per cent is foreign to the mineral proper. If the vanadium was not

completely oxidized to the  $V_2O_5$  condition by the ignition in open air, then the correction applied, 3.5 per cent, is too high and coupled with the rejection of the 1.8 per cent lost at  $110^\circ$ , would reduce the water percentage and suggest that the true quantity of water present in the mineral is  $4H_2O$  and not  $5H_2O$ . This suggestion is partly verified by the partial analysis of the second lot of sincosite scales. This lot consisted of the loose debris found when the specimens were unwrapped and after most of the shale particles had been removed, consisted essentially of the green plates of sincosite similar to those comprising the scales of the first sample which were carefully picked off the matrix. This second lot, however, contained a number of the brassy-yellow scales and also others of an olive hue. The plates of sincosite were not as uniformly colored as those of the first lot and in general the sample did not look as homogeneous or as satisfactory as the first sample. The material, moreover, was obtained from half a dozen specimens instead of from a single one. Water was not directly determined in this sample; the value obtained by difference gives a ratio of  $4H_2O$  instead of  $5H_2O$ . The unhomogeneity of the sample, the small quantity of material available, and the fact that the "water by difference" is based on a summation of 100.0, whereas a summation of 102.0 for this kind of an analysis would by no means be too high, leads the writer to hesitate in placing too much emphasis on the fact that this second analysis gives a  $4H_2O$  ratio instead of a  $5H_2O$ . Although the latter figure is preferred and adopted, it is not considered final and other analyses on more material may well show that sincosite has the smaller quantity of water. It is considered as established though that practically all of the water of sincosite is retained at  $110^\circ$ . The second analysis is as follows:

*Analysis of Second Sample of Sincosite.*

	Analysis.	Ratio.	Calculated.	
			$V_2O_5, CaO, P_2O_5, 4H_2O.$	$V_2O_5, CaO, P_2O_5, 5H_2O.$
$V_2O_5$ ..	37.8	0.228 or 1.00	38.07	36.57
CaO ...	13.3	0.237 or 1.04	12.85	12.33
$P_2O_5$ ..	31.1	0.219 or 0.96	32.57	31.28
$H_2O$ ...	[17.1]	0.950 or 4.17	16.51	19.82
Insol. ..	0.7		....	....
	100.0		100.00	100.00

Checks made on both samples showed that in the first sample all the vanadium was in the  $V_2O_4$  condition, the consumption of permanganate being the same after reduction as in the first direct titration of the acid solution of the mineral. For the second sample, the titration after reduction was 0.1 c.c. greater. This corresponds to about 0.6 per cent  $V_2O_5$  in the sample, but the difference is too slight to place much emphasis on it and the value for  $V_2O_5$  is not reported in the analysis. From the character of the material of the second sample, however, it is not improbable that some oxidation has taken place in the mineral and the brassy appearance of some of the crystal plates may be due, in part at least, to a partial oxidation of the quadrivalent vanadium.

No arsenic, molybdenum, or nickel could be detected although traces of selenium were found in all the samples tested. The absence of molybdenum and of nickel, if verified by later work on larger samples, would be a chemical difference between this deposit and that of Minaragra where both these elements are common. It seems that no special search for phosphorus or for selenium has been made in the minerals from Minaragra. No sulphides were detected in any of the sincosite specimens though gypsum is abundant.

The analysis of the nodules, separated from the massive shale, as given below, shows them to consist of 45 per cent sincosite, 5 per cent gypsum, and about 50 per cent of gangue (shale) insoluble in acid. This 50 per cent of insoluble gangue is made up of ash 23 per cent,

*Analysis of Sincosite Nodules from Sincos, Peru.*

	Per cent.
$V_2O_4$ .....	15.67
$V_2O_5$ .....	0.33
CaO .....	8.81
$P_2O_5$ .....	14.72
$H_2O$ .....	14.51
$SO_3$ .....	2.32
Se .....	0.11
As, Mo, Ni .....	0.00
Insoluble ash .....	22.86
Insoluble volatile matter .....	21.68
	101.01



volatile carbonaceous matter 22 per cent, and water 5 per cent.

Thin sections of these nodules show them to consist of about half sincosite and half shale. The sincosite is in well developed rectangular scales with a greater or less quantity of shale inclusions scattered through the mineral. Some masses of these scales though are almost free from inclusions. The sincosite in the nodules seems to show a minimum of alteration and of deviation from strictly normal characters. The yellow and brown colors were not noted and the scales with the rectangular cleavages appear strictly isotropic. Nothing could be seen suggestive of any structural relationship between the sincosite and the shale.

A calculation of the ratios of  $V_2O_4 : CaO : P_2O_5$ , after deduction of gypsum and of enough CaO to satisfy the  $V_2O_5$  in the ratio of 2 : 3 (as in water soluble pascoite), gives 0.094 : 0.126 : 0.104. Some calcium may have been extracted from the insoluble ash, otherwise the ratios are sufficiently close to the 1 : 1 : 1 ratio of sincosite.

A calculation of the specific refractive energy,  $K$ , of sincosite, using the formula

$$K = \frac{n-1}{d},$$

gives a value of 0.236. The specific refractive energy,  $k$ , of  $V_2O_4$ , as calculated from the values of sincosite

$$(K = k_1 \frac{p^1}{100} + k_2 \frac{p^2}{100} + \text{etc}),$$

gives<sup>5</sup> a value of 0.22 if the mineral has  $5H_2O$  and 0.24 if the mineral has  $4H_2O$ . The value of  $k$  for  $V_2O_5$ , as given by Larsen,<sup>6</sup> is much higher, namely, 0.43.

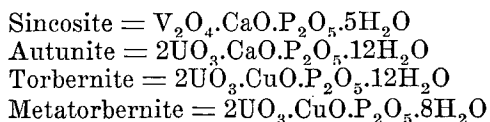
#### *Relationships.*

The square shape of the crystals of sincosite, with their striations and cleavages and uniaxial optical character, suggest a relationship to the minerals of the uran-

<sup>5</sup> This value of  $k$  for  $V_2O_4$  is verified by a value calculated from data obtained on minasragrite, namely 0.255. The data on the other vanadyl minerals, fernandinite and melanovanadite, are insufficient for any calculation of  $k$ .

<sup>6</sup> Larsen, E. S., The microscopic determination of the nonopaque minerals: U. S. Geol. Survey, Bull. 679, p. 31, 1921.

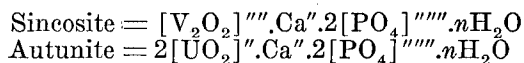
ite group. In fact the green crystals of sincosite so much resemble those of torbernite that they have been taken for that mineral. From a knowledge of the composition of sincosite, it may be at first thought that the absence of uranium would militate against any such relationship. The formulas of some of the minerals may be given:



All the known members of the uranite group have eight or more molecules of water and it may be questioned whether one (sincosite, for example) with less than eight molecules of water could belong to this group. A study of the literature of the minerals of the uranite group indicates, however, that for each species there are a set of hydrates, each one having different properties, and that although 12 is the maximum number of molecules possible for any one of the species, the minimum is not known. A tabulation of all published analyses of autunite, for example, shows that the water content ranges from 12 to 7 molecules. Artificially dehydrated autunites, however, contain as little as 2 molecules. It is debatable if carnotite belongs to the uranite group, but if it does, then it represents a species with but 2 or 3 molecules of  $\text{H}_2\text{O}$ .

It is believed that sincosite rightfully belongs to the uranite group although if so it is the one with the smallest molecular water content, unless carnotite also belongs here. Neglecting the water for the present, it still remains to show the chemical relationship of the formula of sincosite with that of autunite, for example. If such a relationship exists, then vanadyl-vanadium must function similarly to uranic-uranium. Both are base-forming, the vanadyl-vanadium, that is quadrivalent vanadium, as oxide,  $\text{V}_2\text{O}_4$ , reacts as the vanadyl group  $[\text{V}_2\text{O}_2]\text{O}_2$ , which functions chemically as the integral group  $[\text{V}_2\text{O}_5]$  with an unsatisfied valency of 4. Similarly, uranic-uranium, as oxide,  $\text{UO}_3$ , reacts as the uranyl group  $[\text{UO}_2]\text{O}$ , which functions chemically as the integral group  $[\text{UO}_2]$  with an unsatisfied valency of 2.

So in order to obtain equal valency, two groups of uranyl,  $[\text{UO}_2]^{++}$ , are equivalent to one group of vanadyl,  $[\text{V}_2\text{O}_2]^{++}$ . That is  $2[\text{UO}_2]^{++} = [\text{V}_2\text{O}_2]^{++}$  on a valency basis. And this is exactly the relationship which exists between sincosite and autunite.



It is therefore believed that sincosite is truly a member of the uranite group, even though it contains no uranium and its water content is lower than the lowest of any known species of the group.

A study is being made of the relationships of the different hydrates of the different species of the uranite group, and it is hoped to be able to point out enough of such relationships to enable one to place any new members of this group that may be found, such as sincosite seems to represent.