# WEINSCHENKITE, YTTRIUM PHOSPHATE DIHYDRATE, FROM VIRGINIA*

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## ABSTRACT

Weinschenkite, $YPO_4 \cdot 2H_2O$, hitherto known only from a single Bavarian locality, occurs in Rockbridge County, Virginia, where as in Bavaria it encrusts manganiferous limonite. This paper describes the occurrence of the mineral, gives its physical properties and chemical composition, with special attention to the spectroscopy of the rare earths present, and discusses the fluorescence, dehydration, and laboratory synthesis of the compound. It is suggested that a combination of biochemical processes involving forest growth and geochemical reactions of a diagenetic nature in the upper soil zone are the main factors that have resulted in the formation of weinschenkite.

## OCCURRENCE OF WEINSCHENKITE IN VIRGINIA

The Kelly Bank mine, where the weinschenkite occurs, comprises three small open pits at the west foot of the Blue Ridge, a mile east of the village of Vesuvius, Rockbridge County, Virginia. The mine was originally worked for limonite, but was briefly re-opened for manganiferous iron ore in 1940. The ore occurs mostly as large irregular lumps having botryoidal surfaces and embedded in yellow clay containing lenses and nodules of chert and silicified calcareous oölite. The clay occupies the stratigraphic position of the Tomstown dolomite (lower Cambrian) close to its contact with the underlying Antietam sandstone, which in this vicinity dips steeply northward. The clay with the contained ore (Fig. 1) was formed during or since early Tertiary time by weathering of the Tomstown beds beneath the valley-floor peneplain. In its relations to geologic structure, rock strata, and topography, the

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Kelly Bank mine does not differ in any obvious respect from the numerous other occurrences of iron and manganese ore that have been described in the Blue Ridge region.[1]

In the course of an examination of manganese ore deposits of the Virginia Blue Ridge country during 1941, H. D. Miser and M. M. Knechtel observed that specimens of manganiferous iron oxide from the

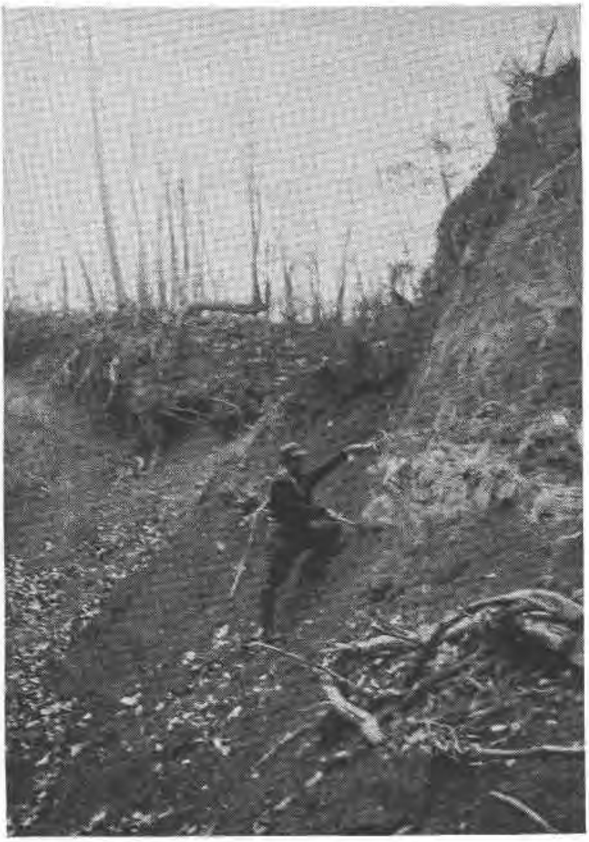

FIG. 1. View of Kelly Bank mine, Vesuvius, Virginia. The weinschenkite is restricted to a zone a meter thick and several meters wide, shown between the two picks.

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[1] Harder, E. C., The iron ores of the Appalachian region in Virginia: *U. S. Geol. Survey, Bull.* **380,** 235–237 (1909).

Stose, G. W., Miser, H. D., Katz, F. J., Hewett, D. F., Manganese deposits of the west foot of the Blue Ridge, Virginia: *Virginia Geol. Survey, Bull.* **17** (1919).

Knechtel, M. M., Manganese deposits of the Lyndhurst-Vesuvius district: *U. S. Geol. Survey, Bull.* **940.**

Kelly Bank mine were more or less coated with minute specks of a whitish material. Under a hand lens the specks were resolved into radially fibrous aggregates, the largest less than a millimeter across; the fibers themselves were white with a silky luster. The material proved to be the rare mineral weinschenkite, $YPO_4 \cdot 2H_2O$, hitherto known only from one occurrence, the Nitzelbuch mine in Auerbach, Bavaria, described by H. Laubmann[2] in 1923.

FIG. 2. Manganiferous limonite from Kelly Bank mine, Vesuvius, Virginia, showing specks of weinschenkite on surface of ore. Scale in inches.

The appearance of the mineral characteristically coating brown siliceous limonite, or black manganese oxide, is shown in Fig. 2. The indicated rectangular area, enlarged 12 diameters, is shown in Fig. 2. The hemispherical rosettes frequently have a dusty brownish surface;

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[2] Die Phosphatmineralien und Edelerden des Amberg-Auerbacher Erzkörpers: *Geognostische Jahreshefte* **53**, 193–204, Munich (1923).

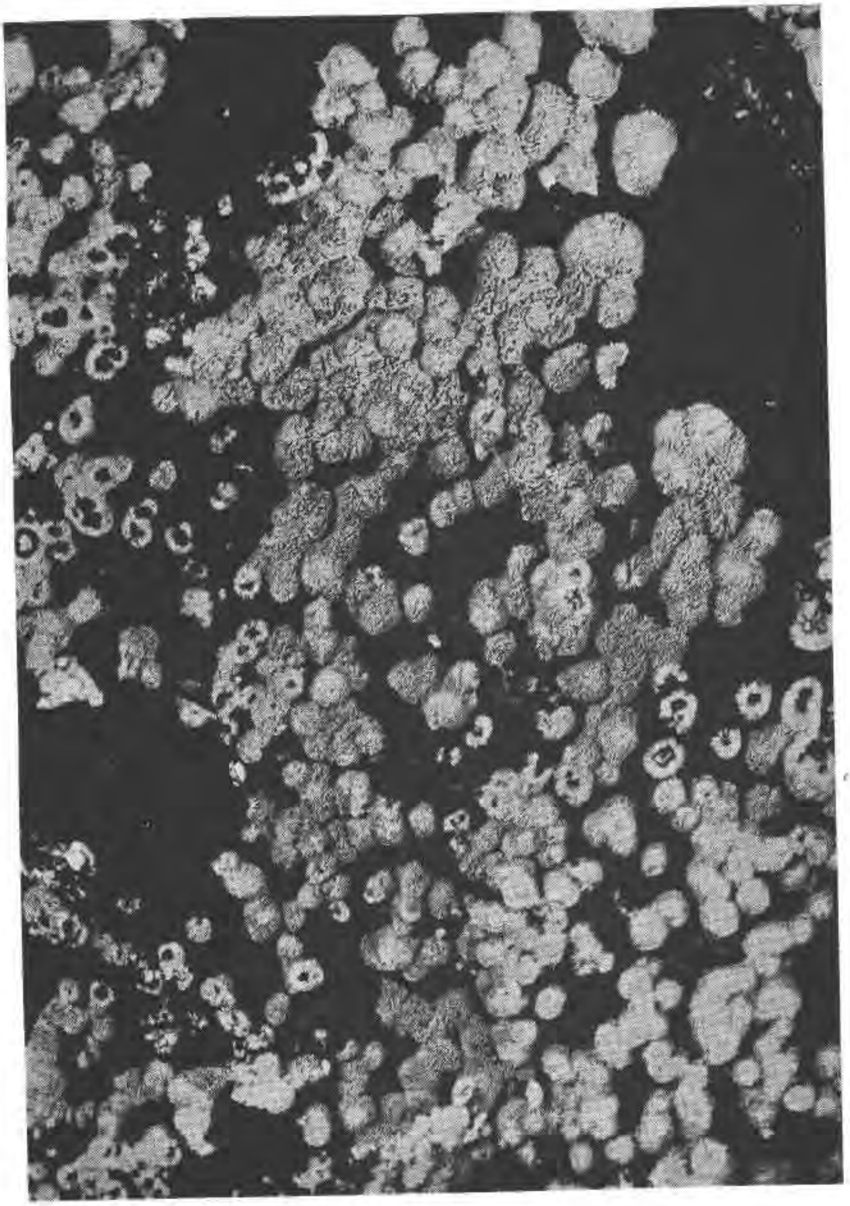

FIG. 3. The rectangular area in Fig. 1 is magnified 12 times and shows an area $\frac{1}{2}$ by $\frac{3}{8}$ of an inch. The spherulites showing radially fibrous structure are clearly seen, also the black cores and spherical shells of manganese oxide. The grey dusty exterior contrasts with the clean white interior, shown where the spherulites have been broken.

many of them, when broken, show concentric black zones or cores of manganese dioxide. In some of them the black oxide forms a ridge enveloping the lower part of a rosette; these features indicate overlapping of the weinschenkite and the last of the manganese dioxide deposition.

## PROPERTIES OF WEINSCHENKITE

This rare mineral was identified by qualitative chemical tests, optical properties, spectrographic analysis, and comparison of the $x$-ray diffraction pattern with that of the original weinschenkite from the type Bavarian locality (Nat. Mus. No. C-4350) kindly furnished by Dr. W. F. Foshag of the United States National Museum. In all instances the observed properties for the Virginian and Bavarian minerals were in substantial agreement.

### *Optical Properties*

For the Bavarian mineral there are two sets of optical data, one by Laubmann, given in the original paper, and a second set in Larsen-Berman,[3] presumably determined by Larsen and Berman; the present writers' data agree better with the latter.

The optical data are as follows:

| *Weinschenkite from Bavaria* | | *Weinschenkite from Virginia* |
|---|---|---|
| *Laubmann* | *Larsen-Berman* | *Milton-Murata-Knechtel* |
| $\alpha$=1.58 | 1.600 | 1.605 |
| $\beta$ .... | 1.608 | 1.612 |
| $\gamma$=1.63 | 1.645 | 1.645 |
| X=$b$, Z:$c$=30°± ; | X=$b$, Z:$c$=30°± | X=$b$, Z:$c$=35°± |
| Mono. laths‖010<br>elong.‖$c$ | | Fibers or laths‖$c$ |
| Dispersion "normal" | | Marked dispersion of bisectrices. |

Laubmann calls attention to the difficulty of making precise optical determinations because of the minute dimensions of the particles, other than length along $c$. His remarks on this point are justified, and it was found necessary to view the laths immersed in oil under high magnification to obtain a definite image of the terminations of the laths, so that $\alpha$ and $\beta$ could be measured. Even so, the very definite dispersion of the bisectrices introduced further difficulties in determining at which position the refractive index of the oil matched that of the grain (using white light). Consequently, the figures cited must be considered as uncertain in the third decimal, but exact enough for the purpose of identifying the mineral.

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[3] *U. S. Geol. Surv., Bull.* **848,** Microscopic Determination of the Non-opaque Minerals, Washington (1934).

## *X-Ray Diffraction Pattern*

The $x$-ray powder patterns of weinschenkite are shown in Figs. 4($a$), ($b$) and ($c$). Measurements on the photographs show that the cell volumes of the two natural minerals differ by less than 0.2% and the cell volume of the artificial mineral which gives a more diffuse pattern is smaller than that of either natural mineral by less than 0.6%. Since the uncertainty in density determinations is greater than these variations, calculated densities are based on Strunz's values of the cell constants.

POWDER PATTERN DATA

| *Weinschenkite (Virginia)* | | *Gypsum* | |
|---|---|---|---|
| Spacing | Intensity | Spacing | Intensity |
| 7.51 | vvs | 7.7 | 0.50 |
| 4.18 | vvs | 4.29 | 1.0 |
| 3.74 | m | 3.81 | 0.15 |
| 3.01 | vvs | 3.06 | 0.63 |
| 2.82 | m | 2.87 | 0.63 |
| 2.60 | mw | 2.68 | 0.50 |
| 2.39 | mw | 2.48 | 0.20 |
| 2.164 | ms | 2.22 | 0.20 |
| 2.042 | mw | 2.07 | 0.50 |
| 1.965 | mw | | |
| 1.855 | mw | 1.88 | 0.25 |
| 1.825 | mw | | |
| 1.774 | s | | |
| 1.755 | m | | |
| 1.638 | mw | | |
| 1.594 | mw | | |
| 1.530 | w | | |
| 1.503 | w | | |
| 1.438 | mw | | |
| 1.344 | w | | |
| 1.248 | w | | |
| 1.214 | w | | |
| 1.124 | mw | | |
| 1.118 | s | | |
| 1.045 | w (b) | | |
| 0.999 | vw (b) | | |

The weinschenkite pattern was made with iron radiation, and the weaker lines are omitted. The data for gypsum are from the *ASTM-NRC* card file.

(b) indicates a broad line.

## *Cell Constants and Density*

Strunz,[4] studying the Bavarian mineral whose composition is given

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[4] Strunz, H, Isotypy between $YPO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$. Abstract in *Chemical Abstracts*, **36,** 2813 (1942).

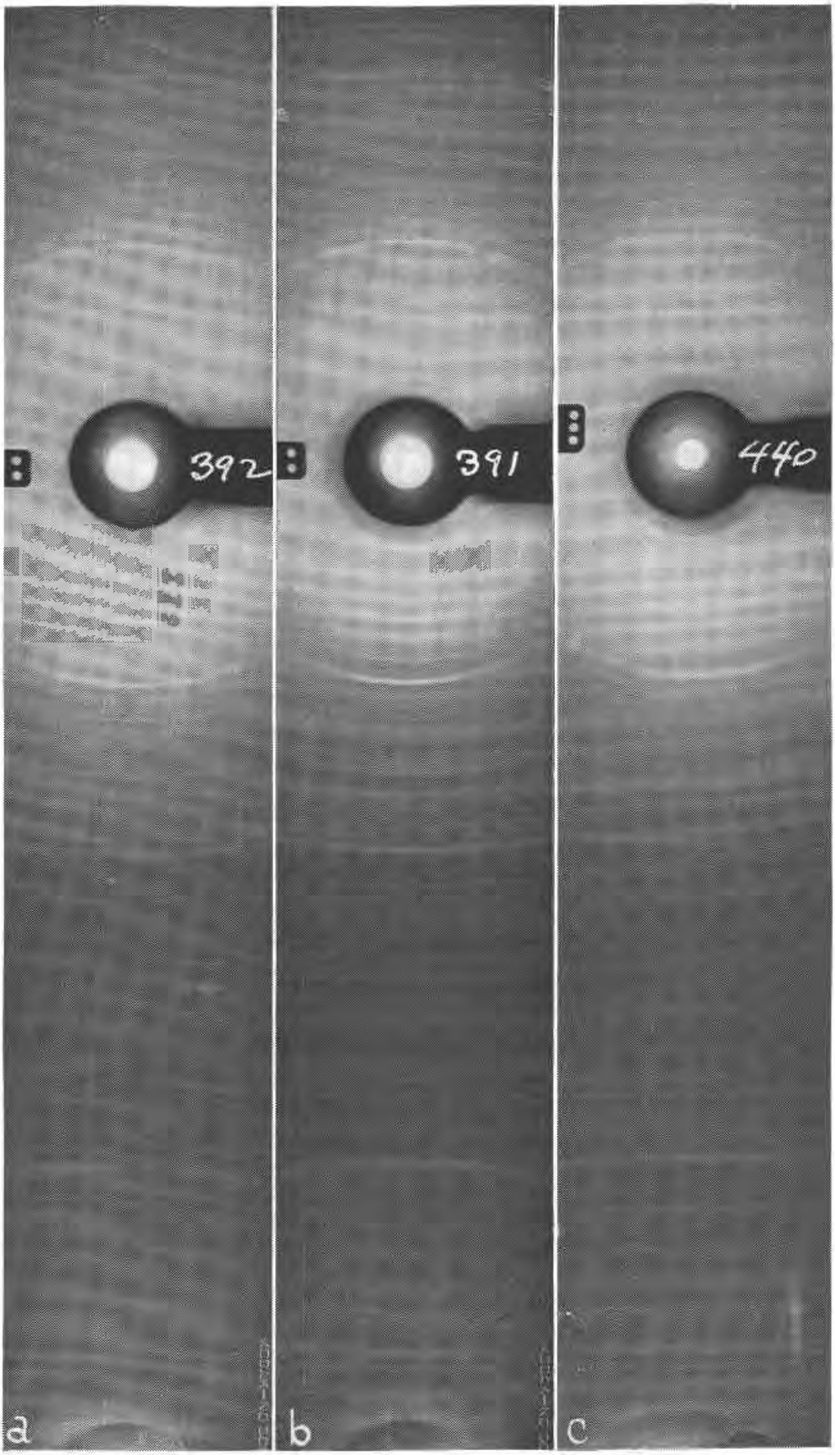

FIG. 4. *X*-ray diffraction patterns. (a) Weinschenkite, Auerbach, Bavaria, (b) Weinschenkite from Vesuvius, Virginia, (c) Synthetic $YPO_4 \cdot 2H_2O$ (artificial weinschenkite).

as $(\mathrm{Y, Er})\mathrm{PO_4 \cdot 2H_2O}$, found the lattice constants (powder and rotation diagrams around (001) and goniometric measurements) to be:

$a = 6.48$ Å $\quad b = 15.12$ Å $\quad c = 6.28$ Å

$a:b:c = 0.429:1:0.415 \quad \beta = 129°24'$

space group $C^6_{2}\gamma - A\,2/a$ (?) Z = 4 mols. per unit cell,

cleavage angle $(\bar{1}01)/(001) = 60°30' \pm 30'$. Density determined = 3.10.

These data of Strunz's, together with the value of the mean atomic weight of the mixed rare earth metals (100.05) of the Bavarian mineral determined by Henrich,[5] may be used to calculate the density of the Bavarian weinschenkite. The density

$$\mathrm{D} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{\dfrac{4\text{ Molecular weights}}{\text{Avogadro's Number}}}{a\ b\ c\ \sin\beta}$$

where $a = 6.48$ Å, $b = 15.12$ Å, $c = 6.28$ Å,

$\beta = 129°24'$, $\sin\beta = 0.772734$

whence $a\ b\ c\ \sin\beta = 475.5$ Å$^3$.

Using chemical atomic mass units and assuming that Strunz's values are based on the "crystal Ångstrom" scale,

N (Avogadro's Number) $= (6.0596 \pm 0.0016) \times 10^{23}$ [6] and

$$\mathrm{D} = \frac{4\mathrm{M}}{6.0596 \times 10^{23} \times 475.5 \times 10^{-24}} = 0.01388_4\ \mathrm{M}$$

for $\mathrm{M_{RPO_4 \cdot 2H_2O}} = 231.06$

$$\mathrm{D_{Bavarian\ weinschenkite}} = 3.208.$$

The mean atomic weight of the rare earth elements of the Virginia mineral was determined (by weighing the anhydrous sulphate derived from a weighed quantity of oxide) to be 104.5. For the Virginia mineral, therefore, $\mathrm{M_{RPO_4 . 2H_2O}} = 235.5$, and the density of the Virginia weinschenkite is calculated as 3.270. Actual determination by floating in a methylene iodide-acetone mixture and weighing the matched liquid in a pycnometer gave 3.263. Finally, a similar determination made on synthetic weinschenkite gave 3.17. These several values for the density, with some other computed results, are tabulated in Table 1.

The determined and calculated values for the Virginia mineral are in reasonable agreement and indicate approximately four times as much yttrium phosphate as the heavier rare-earth phosphates (ytterbium, erbium, etc.). The discrepancy in the values for the synthetic material

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[5] Henrich, F., *Jour. prakt. Chemie*, **142**, 1–5 (1935).

[6] This value is obtained from a recent paper by J. A. Bearden, Evaluation of the Avogadro number, N, and the charge on the electron, 3, by *x*-rays: *Jour. Applied Physics*, **12** (395–403), May (1941).

For a discussion by W. Schlecht of Avogadro's number in reference to crystallographic calculations, see page 108 of this issue.

TABLE 1. DETERMINED AND CALCULATED DENSITY OF WEINSCHENKITE AND OTHER RARE-EARTH PHOSPHATES

| | *Determined* | *Calculated* |
|---|---|---|
| Bavarian | 3.10 (Strunz) | 3.208 |
| Virginian | 3.263 | 3.270 |
| Synthetic | 3.17 | — |
| Pure $YPO_4 \cdot 2H_2O$ | — | 3.05 |
| $CdPO_4 \cdot 2H_2O$, $DyPO_4 \cdot 2H_2O$, $ErPO_4 \cdot 2H_2O$, $YbPO_4 \cdot 2H_2O$ | — | 4.04–4.23 |

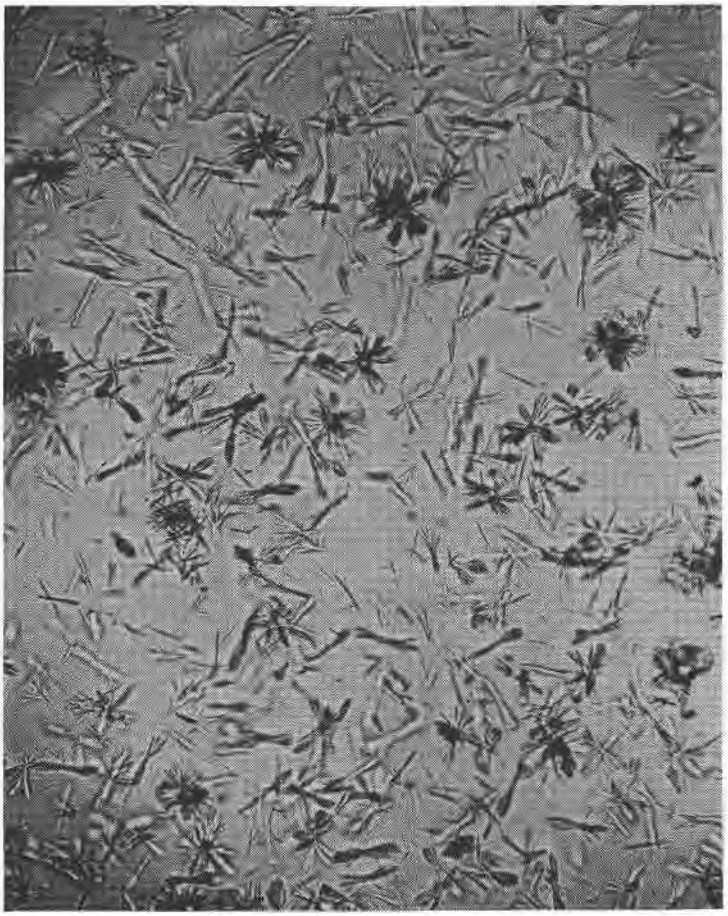

FIG. 5. Synthetic weinschenkite, $YPO_4 \cdot 2H_2O$. Note tendency to spherulitic development. ×250.

arises from the fact that the yttrium salt used in preparing the compound contained some of the heavier rare-earth elements as is readily seen in its spectrogram. It is possible that Strunz's determination for the Bavarian mineral is somewhat low, the tendency of the felted needles to retain trapped air being a likely source of error.

## SYNTHESIS OF WEINSCHENKITE

Some artificial weinschenkite was made from a sample of yttrium nitrate, in the form of pink deliquescent crystals, manufactured by E. deHaën, Hannover, Germany. Solution in water of the nitrate was followed by precipitation with tribasic sodium phosphate, and washing with water to remove the excess precipitant and sodium nitrate from the yttrium phosphate formed. The precipitate was apparently amorphous, probably crystalline, but so fine-grained as to be "statistically isotropic." On standing in water for several weeks, however, the yttrium phosphate crystallized as shown in Fig. 5; and optically, and by *x*-ray examination as shown in Fig. 4, was evidently identical with the natural weinschenkite.

## SPECTROGRAPHIC ANALYSIS OF WEINSCHENKITE

Spectrograms of weinschenkite from Virginia and from Bavaria were taken adjacent to each other on the same plate. Carbon electrodes of special purity were used and the spectrograms taken with the Gaertner medium-size quartz spectrograph. The two spectra are practically identical. Strong lines of phosphorus and of the yttrium group elements are present; lines of Fe, Al, Si, Mg, and Ca are very faint; those of Ti, As, Ag, Bi, Cd, Pb, Sb, Sn, Zn, Cu, Ba and Sr, also B, Be, and Ge are absent. The only notable difference between the two spectra is that the lines of ytterbium are stronger for the Virginian weinschenkite. A few faint manganese lines given by the Bavarian mineral are due to impurities, as are the faint lines of Fe, Al, Si, Mg, and Ca mentioned above.

A spectrogram made of the rare earths isolated from the Virginian weinschenkite was examined in detail between the wavelengths 2400–6000 A.U. The rare earth lines were identified by comparison with spectrograms of known rare earth elements on the Dietert projection comparator, and also by determining the wave lengths of the lines and consulting *Harrison's*[7] *Wavelength Tables*, with the following results.

Major elements: Y (predominant), Yb, Er, Dy, Gd.
Minor elements: Nd, Sm, Eu, Ho, Tm, La (trace).
Not found: Th, Sc, Ce, Pr, Tb, Lu.

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[7] Massachusetts Institute of Technology Wavelength Tables compiled under the direction of G. R. Harrison. New York, Wiley & Sons (**1939**).

F. Henrich[8] has estimated the relative amounts of the rare earths in the Bavarian weinschenkite from the intensity of the $L_\alpha$ $x$-ray lines as follows:

> Y 10, Gd 4, Dy 4, Er 4, Ho 3, Tb and Yb traces and small traces of the cerium earths, mainly neodymium. If the amount of Nd in the cerium earths be taken as 10, then Sm=4, Eu=2, Pr=1. Atomic weight of the mixed earths is 100.05.

The kind and amount of rare earths in the weinschenkite from Virginia and in that from Bavaria are very much the same except for the larger amount of ytterbium in the Virginian mineral. The composition as determined spectrographically for the weinschenkite is interestingly compared with the grouping of the rare earths by Mellor:[9]

| | | | Atomic Number |
|---|---|---|---|
| Cerium family<br>Insoluble K-sulphates | | (Thorium Th) | |
| | | (Scandium Sc) | |
| | | Lanthanum La | 57 |
| | | Cerium Ce | 58 |
| | | Praseodymium Pr | 59 |
| | | Neodymium Nd | 60 |
| | | Samarium Sm | 62 |
| Terbium family<br>Moderately soluble<br>K-sulphates | | Europium Eu | 63 |
| | | Gadolinium Gd | 64 |
| | | Terbium Tb | 65 |
| Yttrium family<br>Readily soluble<br>K-sulphates | Erbium sub-family | Dysprosium Dy | 66 |
| | | Holmium Ho | 67 |
| | | Erbium Er | 68 |
| | | Thulium Tm | 69 |
| | Ytterbium sub-family | Yttrium Y | 39 |
| | | Ytterbium Yb | 70 |
| | | Lutecium Lu | 71 |

Of the cerium family, only a trace of lanthanum and small amounts of neodymium and samarium were found. Gadolinium in moderate amount and europium in small amount represent the terbium family. All of the yttrium family, except lutecium, are present with yttrium by far the most abundant.

Excluding yttrium, the rare earth elements present as major constituents have even atomic numbers, and this relationship, though based on a rough visual estimation of the intensities of spectral lines, is in agreement with what has been found in extensive geochemical studies

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[8] Loc. cit.

[9] Mellor, J. W. *Comprehensive Treatise on Inorganic and Theoretical Chemistry,* vol. **5,** page 495. London (1924).

by Goldschmidt[10] and others, and with the general rule that among the lanthanum series of rare earth elements (atomic numbers 57–71) those with even atomic numbers are more abundant than those with odd atomic numbers.

## FLUORESCENCE AND DEHYDRATION STUDIES

Both weinschenkite and the artificially prepared yttrium phosphate dihydrate do not fluoresce under the mercury vapor lamp provided with the Corning 986 filter. On being gently heated, they both show a moderately strong pink fluorescence, the artificial compound more strongly than the natural mineral. Strongly ignited, both cease to fluoresce.

A dehydration study was made on 0.0912 grams of the air-dried synthetic material; the results are presented in Table 2.

TABLE 2. DEHYDRATION OF WEINSCHENKITE

| Temperature °C | Heating Time Hours | Total Loss % | Theoretical Loss % | Fluorescence Color |
|---|---|---|---|---|
| 110 | 24* | .5 | — | none |
| 180 | 42 | 12.8 | $-1\frac{1}{2}\ H_2O=12.29$ | faint pink |
| 180 | 48 | 13.5 | — | faint pink |
| 250 | 48 | 14.6 | — | faint pink |
| 345 | 15 | 15.3 | — | faint pink |
| 450 | 20 | 15.9 | — | strong pink |
| 900 | 1 | 16.8 | $-2\ H_2O=16.39$ | none |

* Reached constant weight.

The water lost at 110° is probably absorbed moisture. The loss of water at the higher temperatures is very slow, the most rapid loss occurring when the sample is first heated to 180°. This relatively rapid loss of twelve per cent of water suggests a dehydration to the hemihydrate, similar to the behavior of gypsum. A faint pink fluorescence appears at this stage and persists as the temperature is raised, until at 450° it becomes markedly enhanced and the sample turns gray. Ignited at 900°, the sample turns white again and becomes non-fluorescent.

The only other study of the fluorescence of yttrium phosphate that has come to our attention comprises some experiments made by Crookes,[11] who tested his material inside of a cathode ray tube. He states:

> "Yttrium phosphate precipitated, washed, and dried at a heat below redness, and introduced into the radiant matter tube. It phosphoresced faintly, giving the citron band hazy

[10] Goldschmidt, V. M. Geochemische Verteilungsgesetze der Elemente. IX. *Skrift. Norske Vid. Akad. Oslo, I. Mat.-Naturv. Klasse*, **1937**, no. 4. Oslo, 1938.

[11] Crookes, W., *Select Methods in Chemical Analysis*, 3rd ed., page 92. London (**1894**).

> and faint, extending from about 3010 to 3060 (frequency squared). The red bands were faint, and the green bands, especially the first one, were stronger than usual. The salt was now removed from the tube aud heated to redness. It became of a grey colour, and now phosphoresced with a beautiful green light. . . . Heating the phosphate before the blowpipe made little change in the character of the phosphorescence."

The difference in the fluorescence behavior of yttrium phosphate as reported by Crookes and found by us may be due to the different methods of excitation used. This seems very probable from the fact that yttrium sulphate is unresponsive to our lamp, whereas Crookes invariably obtained a strong luminescence from it under the action of cathode rays.

## ORIGIN OF THE WEINSCHENKITE

The paragenesis of the Bavarian and Virginian deposits is very similar. The weinschenkite occurs in both as coatings on manganiferous limonite and in neither deposit is there any indication of igneous activity. The mineral was evidently deposited by meteoric waters. Other phosphates, such as wavellite, cacoxenite, apatite, beraunite, dufrenite and pseudowavellite, accompany the weinschenkite in Bavaria, but careful search of the Virginia material has failed to show any other phosphate mineral.

It might be considered that yttrium was an original constituent of the ore-forming solutions and at some later time was extracted and precipitated as the phosphate weinschenkite, in cracks and fissures in the ore. The chemical complexity of many manganese oxide ores, containing cobalt, barium, and lithium, together with the commoner elements, suggests that small quantities of rare earths may be present though overlooked in manganese oxides. Rare earths have not been reported, however, so far as known, in manganese oxides, and so far as known none of the other Appalachian deposits contain weinschenkite or other rare-earth minerals. There is apparently no definite evidence, therefore, to prove or disprove the hypothesis that the yttrium of the weinschenkite is derived from the original manganese oxide by diagenetic processes.

Another possible origin of the weinschenkite, involving cold meteoric waters but a source of the yttrium other than the ore itself, is concentration from the seldom-regarded but almost omnipresent yttrium in soils. Although the quantity of the rare-earth oxides in soils is so little as generally to preclude the formation of rare-earth minerals, it might be that under special conditions, as suggested below, an effective concentration and fixation as a definite mineral species, such as weinschenkite, could be effected. There are many recorded observations on the presence of yttrium and other rare-earth oxides in soils. Part of the rare-earth content is in such more or less common detrital minerals as xenotime, yttrium phosphate, and monazite, a cerium-earth phosphate with minor yttria. Rare earths may also be present as isomorphous replacements of the usual elements in the common minerals of soils. The total rare earth content of the lithosphere is considerable; as, for example, in the Netherlands East Indies Van Tongeren[12] cites the following averages: $La_2O_3$ 0.0023%, $Ce_2O_3$ 0.0029–0.0040%, $Nd_2O_3$ 0.0021–0.0024%, $Y_2O_3$ group "one or a few thousandths of a percent."

Locally, as in areas of alkalic rocks, there may be as much as ten times these quantities.

Goldschmidt[13] gives 0.0034% as the abundance of yttrium in the earth's crust. The figure for zirconium is 6 times this amount, namely 0.020%, and that for gold, 1/6000 that for yttrium. In other words, there is 6000 times as much yttrium in the earth's crust as the widely distributed gold, and, ubiquitous as the common mineral zircon is, zirconium is only six times as abundant as yttrium.

Although these figures refer to overall percentages and do not necessarily imply a universal distribution, comparable quantities of rare earths may be present generally. In rock and soil analyses, if the rare earths are not specifically sought, they will be counted as alumina. One reason for believing in widespread distribution is the recent work of Robinson, Whetstone and Scribner[14] and others, who have found considerable concentrations of rare earths in tree leaves from various localities in which no deposits of a specific rare-earth mineral are known. For example, Scribner finds in dried hickory leaves from Rockville, Maryland, 0.17% of rare earths; hickory leaves from Amelia, Virginia, a rare-earth mineral locality, have but slightly more, 0.20%. He also cites A. A. Drobkov[15] to the effect that phosphorites may contain as much as 0.8% of rare earths.

An examination was made of fallen leaves from a chestnut tree growing immediately above the Virginia weinschenkite locality, and a rare earth content, largely yttria, by spectroscopic analysis, of 0.06% of the dry leaves, or 1.29% of the ash, was obtained. Approximately eight times as much manganese was present. No yttria was found in oak leaves from the same place.

An analysis was also made of the whitish clay in which the wein-

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[12] Van Tongeren, W., *On the Occurrence of the Rarer Elements in Netherlands East Indies*, p. 172, Amsterdam (**1938**).

[13] Goldschmidt, V. M., The principles of distribution of chemical elements in minerals and rocks: *Jour. Chem. Society* (**1937**).

[14] Robinson, W. O., Whetstone, R., and Scribner, B. F., The presence of rare earths in hickory leaves: *Science* **87,** 470 (1938).

Scribner, B. F. *Proc. 6th Summer Conference on Spectroscopy*, pp. 10–13, Wiley & Sons, New York (**1939**).

[15] Drobkov, A. A., *Compt. Rend. Accad. Sci. U.R.S.S.*, **17,** 265–267 (1937).

schenkite-bearing manganiferous iron oxide occurs. Leaching the clay with hot 1:1 HCl yielded 0.08% of $Y_2O_3$, and 0.12% $P_2O_5$. In the compound $Y_2O_3 \cdot P_2O_5$, the weight ratio $Y_2O_3:P_2O_5$ is about 8:5. Apparently, then, much of the $P_2O_5$ present in the clay, possibly all of it, is not there combined with $Y_2O_3$ as the mineral weinschenkite. This compound may or may not be present in the clay.

In any event, there is a very minor concentration of yttrium in the local clay, a larger one in the residual ash of the chestnut leaves, and finally a major concentration as weinschenkite associated with the manganiferous iron oxide.

From the foregoing, it seems reasonable to consider a secular extraction of yttrium from the clay, or local soil, by the growing chestnut and other forest vegetation of the region. As percolating ground waters leach the soil and subsoil, yttrium is to some degree absorbed by the root systems, carried in the sap to the leaves, and thereby concentrated. A single leaf may contain the yttrium originally present in many cubic inches of soil. The humus formed from the leaves may contain yttrium or other rare earths in substantial quantity, perhaps well in excess of what the existing forest growth can utilize in its vital processes, though far too little to permit the formation of recognizable rare-earth minerals. A further agency of concentration is required and this, it is suggested, may be the manganese and iron ore minerals.

Many limonite and psilomelane deposits show a gel-structure, indicative of a present or past colloidal state. Both iron oxide and manganese oxide as they occur subaerially in nature undergo changes in the state of oxidation, with attendant changes in solubility. In general, they are fixed in the higher state of oxidation as limonite and psilomelane, but under reducing conditions, in an acid environment, they tend to dissolve. In a soil environment in a wet season the tendency would be to solution, and in a dry season the minerals would tend to re-form in, at first, a colloidal state. This cycle might repeat itself annually. Of course, it is not implied that the deposit will show these changes en masse, but the surfaces exposed to soil solutions may pass through such a cycle.

This active surface of the ore body may adsorb yttrium ions from the soil solutions, enriched as they are by the action of the regional forest growth, until a concentration is reached sufficient to furnish a visible precipitate with phosphate ions. In the absence of a body of iron-manganese oxide, yttrium ions in the upper soil zone would re-enter the crystalline or colloidal components of the soil, where they would be "trace" elements, and in no way, except perhaps spectroscopically, be detectable. Only at the contact with the ore body are conditions different;

there the yttrium ions, unable to re-enter soil minerals, undergo adsorption on the chemically-active surface of the ore.

In summary, the presence of weinschenkite in the Kelly Bank deposit may be the result of three necessary conditions: first, the biochemical extraction of minute quantities of rare earth metals by trees, especially chestnut and hickory, from the rare earths generally present sparingly in soils, followed by the annual shedding of the leaves in which the rare-earths are concentrated; second, a geological condition of the region such that the forest soil floor remains intact over a long period of time, permitting extended concentration and accumulation of yttrium earths in the humus layer; and, third, the presence of an outcrop of iron-manganese oxides, possibly once, if not now, phosphatic, which may have precipitated the weinschenkite.

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