THE AMERICAN MINERALOGIST, VOL. 48, SEPTEMBER–OCTOBER, 1963

# AN APPARENTLY TRICLINIC DIMORPH OF CRANDALLITE FROM A TROPICAL SWAMP SEDIMENT IN EL PETÉN, GUATEMALA

URSULA M. COWGILL, G. E. HUTCHINSON, *Osborn Memorial Laboratory, Yale University* AND OIVA JOENSUU, *Institute of Marine Science, University of Miami.*[1]

ABSTRACT

A mineral is described from clay sediments about 3 m below the surface of the Bajo de Santa Fé, El Petén, Gautemala, a large swamp forest. It occurred as powdery material and small masses not exhibiting crystal faces, up to 5 mm across, mainly associated with gypsum filling cavities of decayed roots, but also at one level dispersed in the clay. It is buff yellow, slightly translucent, with a waxy luster, H 3, G 2.50, biaxial (+) with 2V 70°–75°, $\alpha$ 1.602 $\pm$ 0.002, $\beta$ 1.607 $\pm$ 0.002, $\gamma$ 1.615 $\pm$ 0.005 (calc.). Some grains show cleavage perpendicular to *z* and some exhibit multiple twinning. *X*-ray powder pattern with four largest peaks at 2.97, 2.18, 5.75, 3.53 Å. The general pattern resembles that of the alunite-crandallite series, but without a conspicuous peak at 4.8 Å. Cell parameters, *a* 7.010 Å, *b* 9.819 Å, *c* 9.697 Å, $\alpha$ 103° 10′, $\beta$ 91°14′, $\gamma$ 90°34′, taken as triclinic rather than hexagonal as in candallite. Analysis indicates a calcium, strontium, lead, aluminum basic phosphate, with some substitutions of rare earths, corresponding to $(Ca, Sr, Pb)_2Al_7(OH)_{16}(PO_4)_3 \cdot 3H_2O$. Thermal analysis suggests that three water molecules are lost successively below 350°C without change in structure; at about 350°C the lattice collapses producing a white amorphous material which crystallizes at or above 900°C. The material must be of biogeochemical origin, possibly formed from material liberated in the decay of roots of one of the Melastomaceae such as *Miconia*.

## OCCURRENCE

The mineral here described was encountered in a study of the sediments of the Bajo de Santa Fé, a large seasonal swamp forest to the east of the ancient Maya city of Tikal, El Patén, Guatemala. A full account of the stratigraphy and geochemistry with a discussion of their ecological and archaeological significance will be given in a later paper.

The mineral was obtained from a pit just over 5 m. deep about 5 km east of Tikal that was dug by one of us (UMC) in order to elucidate the stratigraphy of the Bajo. The sediments prove to be a relatively pure clay, mostly montmorillonite with a small admixture of metahalloysite. Flint nodules and finely divided quartz occur in the clay and there is also at some levels a considerable amount of gypsum. Much of the latter replaces decayed roots of trees and shrubs. Associated with some of this gypsum in root casts between 293 and 318 cm at the sampling point, and also dispersed in the clay at a depth of 330 cm, where analyses indicated much strontium and rare earths, there was a small amount of the mineral present either as an earthy powder or in small masses up to 5 mm across.

[1] Contribution from Department of Biology, Yale University and Contribution No. 478 from the Marine Laboratory, Institute of Marine Science, University of Miami.

Some material was found between or on the surface of good gypsum crystals and had clearly formed after the deposition of the latter. No specimen has exhibited any crystal faces.

## Physical Properties

Color buff yellow to yellowish white, slightly translucent, lemon yellow when wet, streak yellowish white, lustre waxy. Moderate yellowish white fluorescence under ultraviolet. H 3. G 2.50 (pycnometer at 25° C.).

Sign +; biaxial with 2V moderately large (70°–75°), $\alpha = 1.602 \pm 0.002$, $\beta = 1.607 \pm 0.002$, $\gamma = 1.615 \pm 0.005$ (calc.); indices obtained with newly calibrated liquids, with temperature corrections and monochromatic light. Some grains have weak cleavage perpendicular to Z. Some grains but not all exhibit multiple twinning. Quartz is a minor contaminant. (Optical data by H. Winchell.)

## *X*-ray Crystallography

Powder patterns were obtained from two samples (field labels K 305 cm and N 307.5 cm) after dispersing the surrounding clay with sodium carbonate and dissolving the gypsum in 1N ammonium acetate at pH 6.5. A very small amount of quartz appears to be the only contaminant. Measurements were made with Ni-filtered Cu radiation at 50 kv 20 ma potential, scanning speed of 2° 2 theta per minute with 3° beam slit and 0.2 detector slit and 0.2° 2 theta per minute with 3° beam slit and 0.02 detector slit using a G. E. XRD 5 diffractometer. All peak positions were obtained by counting with a Geiger counter, 3 individual 100 sec. counts with the goniometer operated manually.

The major spacings correspond in a general way with those of the alunite-crandallite group of sulfates and phosphates, with the important exception that the second peak of crandallite at 4.80–4.82 Å corresponding to the 4.99 Å spacing of alunite, indexed by Pabst (1947) as 012, is almost absent. The published data on crandallite, and an *x*-ray diffractometer tracing (Fig. 1a) from a specimen from a locality (Grube Carolina, Salzbach, Bavaria, Brush Collection, Yale University) hitherto not studied in this way, all agree in having this spacing of fair intensity. The difference is particularly striking in view of the great similarity of the *x*-ray diffraction spectra of minerals of the most diverse chemical constitution in the alunite-crandallite group.

The observed spacings differ slightly from those of crandallite and taking only those of intensity over 10, corresponding to the crandallite spacings recorded by other authors (McConnell, 1942; Owens *et al.* 1960) it has not been possible to index our data satisfactorily on the assumption of hexagonal symmetry. However, if all our data are considered, includ-

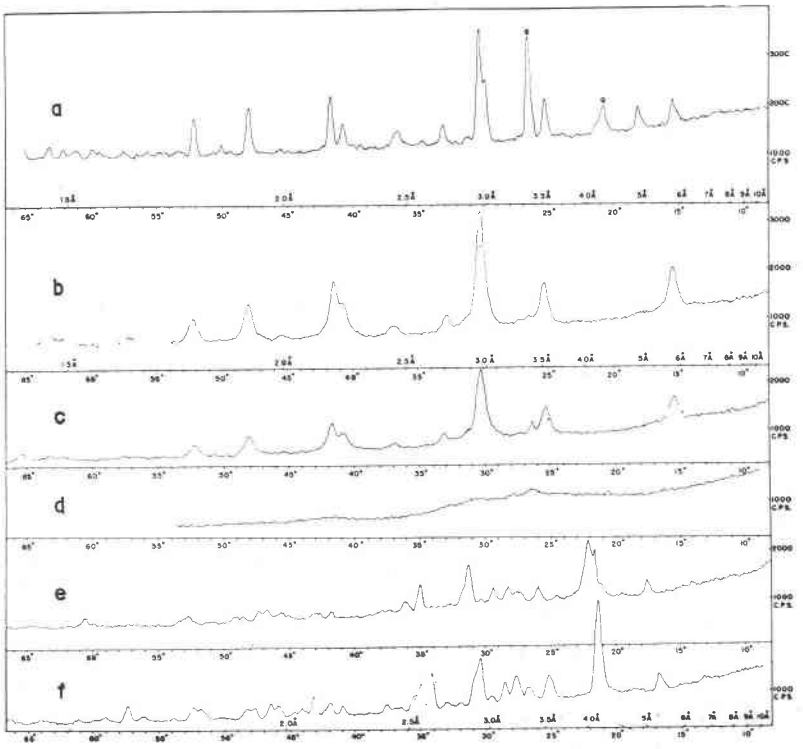


FIG. 1. *X*-ray tracings of crandallite, a, from Salzbach, untreated powdered mineral; b, from the Bajo de Santa Fé, untreated powdered mineral; c, the same heated to 350° C; d, heated to 525° C; e, heated to 950° C; f, healed to 1100° C.

ing a number of very weak peaks that hardly show on the tracing but can be identified by counting, and indexing is performed by Ito's (1950) method, followed by the Delaunay (1933) transformation, all our sixty-five observed peaks can be satisfactorily indexed on the basis of a triclinic cell. The observed and calculated spacings, intensities, indices and cell parameters are given in Table 1. While it has not been possible to ascertain the relationship of our triclinic cell to the conventional alunite crandallite structure, the agreement between our observed and the computed spacings based on our cell, suggests that there are really slight structural differences between our mineral and previously studied specimens of crandallite.

## ANALYSIS

Two samples, one from a bag marked K and the other from a bag marked N were analyzed. $SiO_2$ was determined gravimetrically, $P_2O_5$ by

TABLE 1. *X*-RAY DIFFRACTOMETER SPACINGS AND INTENSITY MEASUREMENTS, UNTREATED MINERAL FROM THE BAJO DE SANTA FÉ

| hkl | Observed dÅ | Computed dÅ | $I_{REL}$ |
|---|---|---|---|
| 010 | 9.45 | 9.56 | 1 |
| 100 | 7.00 | 6.82 | 1 |
| 011 | 6.51 | 6.60 | 2 |
| $\bar{1}10$ | 6.24 | 6.27 | 1 |
| $10\bar{1}$ | 5.75 | 5.63 | 36 |
| 101 | 5.47 | 5.54 | 3 |
| $1\bar{1}1$ | 5.37 | 5.34 | 1 |
| 110 | 5.06 | 5.04 | 2 |
| 020 | 4.77 | 4.78 | 1 |
| $\bar{1}20$ | 4.42 | 4.42 | 1 |
| $02\bar{2}$ | 3.53 | 3.52 | 35 |
| 200 | 3.42 | 3.41 | 6 |
| $12\bar{1}$ | 3.40 | 3.40 | 7 |
| 022 | 3.30 | 3.30 | 3 |
| 030 | 3.19 | 3.19 | 1 |
| $1\bar{3}0$ | 3.16 | 3.18 | 1 |
| $1\bar{3}1$ | 3.08 | 3.07 | 5 |
| $\bar{1}31$ | 2.97 | 2.97 | 100 |
| $21\bar{1}$ | 2.88 | 2.89 | 9 |
| 122 | 2.79 | 2.79 | 4 |
| 202 | 2.77 | 2.77 | 4 |
| $1\bar{3}2$ | 2.73 | 2.73 | 13 |
| $1\bar{2}3$ | 2.68 | 2.67 | 2 |
| 023 | 2.60 | 2.60 | 1 |
| 032 | 2.58 | 2.59 | 1 |
| $12\bar{3}$ | 2.45 | 2.46 | 8 |
| 041 | 2.29 | 2.29 | 2 |
| 300 | 2.27 | 2.27 | 3 |
| $02\bar{4}$ | 2.21 | 2.22 | 27 |
| $2\bar{4}1$ | 2.18 | 2.18 | 46 |
| 114 | 2.15 | 2.15 | 10 |
| 230 | 2.10 | 2.11 | 2 |
| $1\bar{4}3$ | 2.01 | 2.00 | 4 |
| $2\bar{4}2$ | 1.970 | 1.973 | 1 |
| 124 | 1.951 | 1.951 | 2 |
| 005 | 1.936 | 1.938 | 4 |
| $21\bar{4}$ | 1.917 | 1.919 | 11 |
| 043 | 1.900 | 1.899 | 29 |
| 034 | 1.872 | 1.872 | 5 |
| $2\bar{5}0$ | 1.858 | 1.858 | 2 |
| $\bar{2}34$ | 1.756 | 1.756 | 18 |
| 151 | 1.694 | 1.694 | 1 |
| $1\bar{5}2$ | 1.667 | 1.665 | 1 |
| $\bar{3}24$ | 1.643 | 1.644 | 1 |
| $1\bar{6}0$ | 1.636 | 1.636 | 2 |

TABLE 1—(*continued*)

| hkl | Observed dÅ | Computed dÅ | $I_{REL}$ |
|---|---|---|---|
| $01\bar{6}$ | 1.612 | 1.610 | 5 |
| $2\bar{6}0$ | 1.589 | 1.589 | 1 |
| $2\bar{4}4$ | 1.579 | 1.578 | 1 |
| $11\bar{6}$ | 1.560 | 1.559 | 1 |
| $41\bar{2}$ | 1.545 | 1.545 | 1 |
| $\bar{4}1\bar{3}$ | 1.535 | 1.535 | 1 |
| $4\bar{4}1$ | 1.531 | 1.534 | 1 |
| 116 | 1.517 | 1.518 | 2 |
| 403 | 1.494 | 1.498 | 6 |
| 062 | 1.483 | 1.485 | 5 |
| $24\bar{4}$ | 1.473 | 1.473 | 8 |
| $05\bar{4}$ | 1.453 | 1.456 | 3 |
| 126 | 1.437 | 1.440 | 15 |
| $1\bar{5}5$ | 1.421 | 1.422 | 4 |
| $33\bar{4}$ | 1.411 | 1.411 | 1 |
| $\bar{1}70$ | 1.400 | 1.402 | 1 |
| 162 | 1.390 | 1.390 | 1 |
| 145 | 1.385 | 1.385 | 1 |
| 154 | 1.376 | 1.373 | 1 |
| $06\bar{4}$ | 1.372 | 1.372 | 1 |
| *a* | 7.010 | 103°10′ | |
| *b* | 9.819 | 91°44′ | |
| *c* | 9.697 | 90°34′ | |
| V | 649.50 Å³ | | |
| *a*:*b*:*c* | 0.7139:1.0000:0.9876 | | |

use of the colorimetric method suggested by Truog (1930) and $Al_2O_3$ by the procedure proposed by Jackson (1958) in both samples after fusion with sodium carbonate. In sample K all other determinations are by emission spectrography (O. J.). In the other sample $Fe_2O_3$ and $TiO_2$ were determined with Tiron following Jackson (1958), and the alkalies and alkaline earths by flame photometry.

All percentages are expressed relative to the mineral dried at 110° C. as the water lost below this temperature is almost certainly mainly nonessential.

Since a little quartz is present in all our preparations and some grains appear more orange than others, doubtless due to staining with haematite, we conclude that the $SiO_2$ and $Fe_2O_3$ are contaminants, and have treated the small amount of alkalies and titanium in the same way. Considerable difficulty was encountered in obtaining a good estimate of

essential water from loss on drying at 110° C. and ignition to 600° C., because, as is indicated by differential thermal analysis, it is probable that some essential water begins to be lost between 100° C. and 110° C. The values for $H_2O+$ are therefore a little low. Part of the deficiency in the summation of the analyses is due to neodymium, which existed in about one third the amount of lanthanum, and of praseodymium present in about one ninth of the lanthanum. Europium is present but in very small amounts.

The density and unit cell volume taken with the analysis indicate three phosphorus atoms per unit cell. The formula may therefore be written

$$(Ca, Sr, Pb)_2Al_7(OH)_{16}(PO_4)_3 \cdot 3H_2O$$

which may be compared with the extreme formulae between which the known crandallites appear to lie (Palache, *et al.*, 1951)

$$Ca_2Al_6(OH)_{10}(PO_4)_4 \cdot H_2O$$
$$Ca_2Al_6(OH)_{14}(PO_4)_3 \cdot H_2O.$$

There is some deficiency in divalent metals, for which in part rare earth atoms presumably substitute in some of the unit cells. The mineral differs chemically from known crandallite not only in the presence of strontium, reported already in some specimens and replacing all the calcium in goyazite, and of lead, but also in the lower phosphate and higher water content. The last difference is confirmed by the low density. It has been suggested (McConnell, 1942) that $(OH)_4$ substitutes for $PO_4$ in the crandallites deficient in phosphorus. It is in the present case tempting to speculate as to whether some aluminum may not substitute for phosphorus in tetrahedral coordination. It is evident that a more complete study of the phosphorus-deficient crandallite minerals is needed before any clear idea of the relationship of the phosphate, hydroxyl and water in the structure can be obtained.

The low content of yttrium is interesting since in the clay of the Bajo the yttrium and lanthanum contents are of the same order of magnitude. The results of chemical analyses are presented in Table 2.

## Thermal Decomposition

The DTA curve of Fig. 2 was obtained with a Hoskins furnace set vertically, heating at the rate of 10° C. per minute with a C.A.T. control and Leeds and Northrup electronic equipment. Platinum, platinum 10 per cent rhodium thermocouples were used, temperatures being read with a Leeds and Northrup millivolt potentiometer. The sample holder is a covered cylinder of No. 308 steel with two wells, the reference well being filled with calcined $Al_2O_3$. The control thermocouple is situated

TABLE 2. CHEMICAL ANALYSIS

| | K | N | Mean | Molecular Proportions | Molecules Per Unit Cell |
|---|---|---|---|---|---|
| $Li_2O$ | n.d. | 0.13 | (0.13) | 0.0045 | |
| $K_2O$ | n.d. | 0.23 | (0.23) | 0.0024 | |
| MgO | 0.22 | 0.39 | 0.31 | 0.0077 | 1.139 |
| CaO | 6.0 | 6.46 | 6.23 | 0.1111 | |
| SrO | 4.0 | 3.93 | 3.97 | 0.0383 | 0.518 = 1.657 R''(OH) |
| BaO | 0.16 | n.d. | (0.16) | 0.0010 | |
| PbO | 2–4 | n.d. | (3) | 0.014 | |
| MnO | n.d. | 0.0 | (0.0) | 0.0000 | |
| $Fe_2O_3$ | 1.0 | 0.0 | 0.5 | 0.0038 | |
| $Al_2O_3$ | 35.51 | 35.59 | 35.55 | 0.3485 | 3.386 |
| $Y_2O_3$ | 0.19 | n.d. | (0.19) | 0.0008 | |
| $La_2O_3$ | 2.0 | n.d. | (2.0) | 0.0062 | 0.128 = 7.028 R'''$(OH)_2$ |
| $Ce_2O_3$ | 1.9 | n.d. | (1.9) | 0.0061 | |
| $SiO_2$ | 2.26 | 1.65 | 1.96 | 0.0326 | |
| $TiO_2$ | 0.075 | 0.12 | 0.098 | 0.0012 | |
| $P_2O_5$ | 21.61 | 22.25 | 21.93 | 0.1544 | $1.500 = 3PO_4$ |
| $H_2O+110°$ | 17.54 | 20.83 | 19.19 | 1.0649 | $10.346 = 11H_2O$ (see text) |
| | 94.47±1 | | 97.35 | | |
| $H_2O-110°$ | 4.11 | 4.47 | 4.29 | | |

G calculated 2.48, measured 2.50

between the two wells, the bead of which is in exactly the same level as that of the reference and sample thermocouples.

The DTA curve indicates three endothermic reactions (I, II, III) between 100° C. and 350° C., which we interpret as the successive losses

of three water molecules. Diffractometer tracings (Fig. 1c) of material heated at 350° C. for twenty minutes show some evidence of loss of crystallinity but no change in the characteristic pattern although 4.4 $H_2O$ per cell had been lost between 110° C. and 350° C. Presumably the loss of $3H_2O$ causes little change in structure, which however collapses with further dehydration. The heated mineral is a little browner after this treatment. Above 350° C. there is a steady endothermal reaction during which the structure collapses completely (Fig. 1d); the mineral is now greyish white. At 865° C. there is a striking endotherm. After this, the material becomes crystalline. The *x*-ray data (Fig. 1e, f) for the material heated to 950° C. and 1100° C. are given in Table 3. There are some differences perhaps due to melting and recrystallization between these temperatures. $AlPO_4$ having the cristobalite structure is probably present

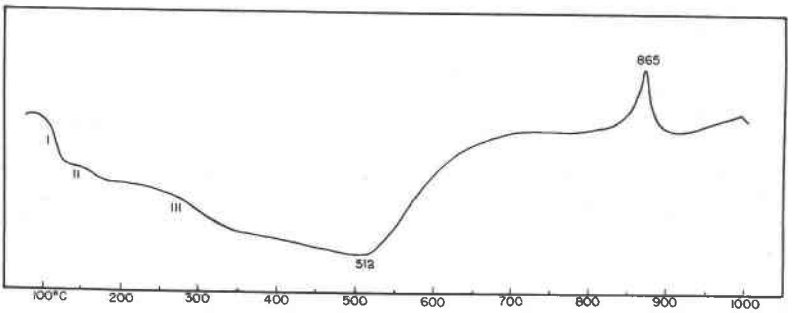


FIG. 2. Differential thermal analysis curve.

but in view of the likelihood that the material is a fairly complex mixture we have not attempted further interpretations.

## POSSIBLE MODE OF GENESIS

The clay of the deposit contains about 40 mg per kg strontium and similar amounts of rare earths. The only conceivable mechanism of concentration of the rarer elements in the mineral is biogeochemical. We suspect that the mineral was deposited from a solution of the products of decay of the roots of some plants in which rare earths, strontium and lead accumulate. *Miconia ciliata* grows in the Bajo (Lundell, 1961) though not in the vicinity of the pit. A specimen of this species from British Honduras had accumulated aluminum and strontium but not rare earths; the family Melastomacea, to which the genus belongs, are in fact generally aluminum accumulators (Hutchinson and Wollack, 1943). Rare earth elements with some aluminum are accumulated by the hickory (*Carya glabra* and *C. ovalis*) (Robinson and Edgington, 1945) so

TABLE 3. *X*-RAY DIFFRACTOMETER SPACING AND INTENSITY MEASUREMENTS OF MINERAL FROM THE BAJO DE SANTA FÉ AFTER HEATING TO 950° AND 1100° C.

| dÅ | 950° C. $I_{REL}$ | dÅ | 1100° C. $I_{REL}$ |
|---|---|---|---|
| 6.75 | 8 | 6.70 | 5 |
| | | 5.94 | 3 |
| 5.34 | 23 | 5.30 | 21 |
| | | 4.95 | 5 |
| 4.79 | 4 | 4.74 | 5 |
| 4.41 | 19 | | |
| 4.31 | 77 | | |
| 4.21 | 100 | 4.15 | 100 |
| 3.77 | 8 | | |
| 3.57 | 27 | 3.54 | 24 |
| 3.36 | 15 | 3.35 | 13 |
| 3.28 | 23 | 3.23 | 26 |
| 3.14 | 27 | 3.13 | 21 |
| 3.05 | 8 | 3.04 | 8 |
| 2.95 | 62 | 2.94 | 50 |
| 2.84 | 4 | 2.80 | 5 |
| | | 2.72 | 5 |
| 2.63 | 42 | 2.63 | 39 |
| 2.55 | 15 | 2.57 | 29 |
| | | 2.53 | 18 |
| 2.47 | 8 | 2.46 | 8 |
| 2.43 | 4 | 2.43 | 8 |
| 2.37 | 4 | 2.40 | 11 |
| 2.21 | 12 | 2.20 | 11 |
| 2.15 | 12 | 2.15 | 13 |
| | | 2.09 | 21 |
| | | 2.07 | 3 |
| 2.05 | 8 | 2.06 | 11 |
| 2.03 | 12 | 2.03 | 5 |
| 1.984 | 19 | 1.980 | 13 |
| 1.955 | 15 | 1.955 | 16 |
| 1.913 | 8 | | |
| | | 1.909 | 11 |
| 1.890 | 8 | 1.886 | 11 |
| 1.823 | 4 | 1.823 | 3 |
| 1.767 | 15 | 1.763 | 11 |
| | | 1.748 | 13 |
| | | 1.700 | 3 |
| | | 1.638 | 5 |
| | | 1.607 | 16 |
| 1.567 | 4 | 1.564 | 5 |
| 1.552 | 15 | | |
| | | 1.515 | 5 |
| 1.462 | 4 | 1.452 | 5 |
| | | 1.424 | 3 |
| 1.403 | 8 | 1.407 | 8 |
| | | 1.376 | 11 |
| 1.309 | 4 | | |

that the mechanism suggested is by no means impossible though what plants may be involved are unknown. We hope to examine this matter in a later work.

## Acknowledgments

We are deeply indebted to Dr. Horace Winchell for the optical data, for a specimen of crandallite and for continued help and encouragement throughout the investigation. The study of the Bajo was supported by the National Science Foundation (Grant No. 17831). The first field investigation was supported by the Henry L. and Grace Doherty Charitable Foundation, Inc. We are also grateful to the authorities of the University Museum, University of Pennsylvania and of the Tikal Project for the opportunity to make the field study.

## References

Delaunay, B. (1933) Neue Darstellung der geometrischen Kristallographie. *Zeit. Krist.* **84,** 109–149.

Hutchinson, G. E. and A. Wollack (1943) Biological accumulators of aluminum. *Trans. Conn. Acad. Arts Sci.* **35,** 73–128.

Ito, T. (1950) *X-ray Studies on Polymorphism.* Maruzen Co., Ltd., Tokyo.

Jackson, M. L. (1958) *Soil Chemical Analysis.* Prentice-Hall, Inc. Englewood Cliffs, N. J.

Lundell, C. L. (1961) Plantae Mayanae II. Collections from Petén and Belice. *Wrightia* **2,** 111–126.

McConnell, D. (1942) *X*-ray data on several phosphate minerals. *Am. Jour. Sci.* **240,** 649–657.

Owens, J. P., Z. S. Altschuler and R. Berman (1960) Millisite in phosphorite from Homeland, Florida. *Am. Mineral.* **45,** 547–561.

Pabst, A. (1947) Some computations on svanbergite, woodhouseite and alunite. *Am. Mineral.* **32,** 16–30.

Palache, Charles, H. Berman and C. Frondel (1951), *The System of Mineralogy.* Vol. II. John Wiley & Sons, Inc. New York.

Truog, E. (1930) The determination of the readily available phosphorus in soils. *Jour. Am. Soc. Agron.* **22,** 874–882.

Robinson, W. O. and G. Edgington (1945) Minor elements in plants and some accumulator plants. *Soil Sci.* **60,** 15–28.

*Manuscript received, October 3, 1962; accepted for publication, May 16, 1963.*