SECONDARY PHOSPHATES FROM BINGHAM, UTAH[1]

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ABSTRACT

Turquois, vivianite, and wavellite have been found as secondary minerals in the Utah copper mine, Bingham, Utah. Dense, bluish turquois veinlets up to an inch wide with associated pyrite are present in quartzite and granite porphyry. Spectrochemical analysis shows less than 0.01 per cent iron, indicating that the turquois is the pure aluminum end member of the series turquois-chalcosiderite. Well-developed elongated crystals of vivianite up to 5 cm in length are found along open cracks in silicified limestone. They are deep purple; when broken, the centers of the crystals are colorless and transparent but upon exposure rapidly oxidize to a deep purple. Analysis indicates a composition of $Fe_{2.98}Mg_{0.02}(PO_4)_2 \cdot 8H_2O$. Pale yellow wavellite occurs as radial botryoidal crusts in open cracks and vugs in granite porphyry and quartzite.

The three phosphates occur in zones along the north edge of the pit with vivianite farthest west, turquois in the center, and wavellite toward the east. The phosphate is believed to have been derived from the fossiliferous Tilden Limestone. The positions of vivianite and turquois appear to correspond to the iron and copper zones of the pit. Aluminum was likely derived from the aluminum silicate minerals of the stock. X-ray and differential thermal analysis data are in good agreement with those previously published for these minerals. Infrared spectra shows characteristic curves expected in the 2.5–3 and 9–10 micron regions.

INTRODUCTION

For some time vivianite and turquois have been found in the copper mine at Bingham, Utah. Wavellite was first found by Stringham during his studies in the pit in 1948. None of these phosphates from Bingham have been noted or described in the literature. It is probably necessary to state that in collecting these minerals the element of luck and chance plays a major role. Exposures are made by shovel cuts and the best samples are generally collected by either shovel operators or their helpers when exposures are made. Occasionally exposures are reported by the mine workmen and during the brief interval when no shovel cutting is done one may go into the pit and collect at the designated position. However, visitors are not allowed in the pit except when accompanied by responsible company personnel.

OCCURRENCE AND PHYSICAL PROPERTIES

The vivianite seems to be more or less concentrated in areas in the northwestern part of the pit; whereas turquois is found near the center and bottom while the wavellite is found occasionally on the northeast benches of the pit (Fig. 1). Vivianite occurs in open cracks in slender, sometimes radiating crystals up to 5 cm maximum length and are always

megascopic in size varying from the smallest about 1 millimeter long to slender or blade like crystals as much as 5 cm in length. (A large crystal 8.75 cm long was mounted as a tie clip by one of the mine workmen.) The 010 cleavage is well developed. Colors range from deep blue to colorless on freshly broken surfaces.

The turquois fills seams 1 mm to 1 cm wide and is massive in appearance with subconchoidal fracture and a light turquois blue color and dull earthy luster. Individual crystals are so minute they are difficult
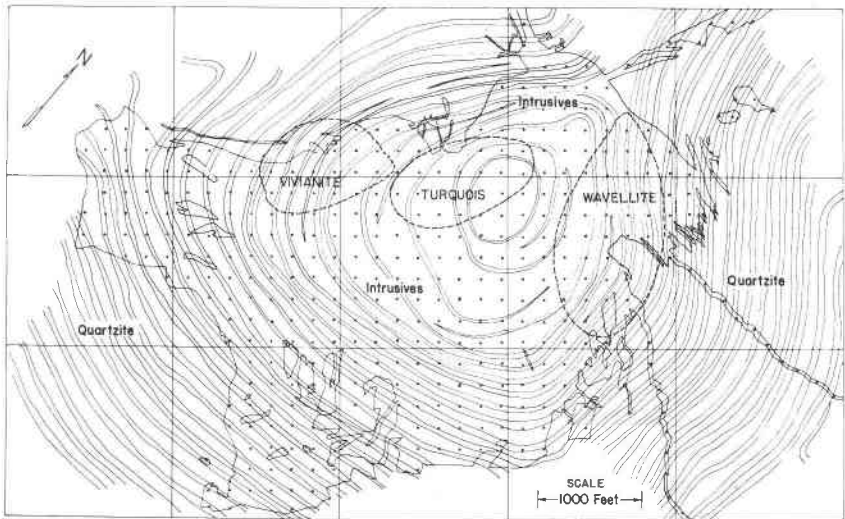

FIG. 1. Sketch map of Bingham copper pit showing areas where the phosphates are found.

to resolve with the highest power of the microscope. Locally small pyrite crystals are present in the same vein with the turquois.

Wavellite characteristically fills irregular vugs in altered granite as a lining. The honey yellow botryoidal form is always present with the spherical surface or ends of the crystals showing a velvety lustre. Individuals have been measured from 1 mm to slightly over 1 cm in diameter. When broken the units show crystal radial arrangement and the 101 and 010 cleavages are readily apparent.

In none of the three occurrences will the minerals be found in large quantities. An undamaged specimen thus discovered is usually quite carefully preserved.

CHEMICAL COMPOSITION

A spectrochemical analysis of the turquois showed less than 0.01 per cent iron. Therefore, it is very near the pure aluminum end member of

the aluminum iron series turquois-chalcosiderite. Other elements, Ca, Cr, K, Mg, Mn, Na, Si, Ti(?) and V(?), were found in trace amounts by spectrochemical analysis.

A partial wet analysis of the vivianite gave an atomic iron-magnesium ratio of $99.4 \cdot 0.6$ indicating a formula of $(Fe_{0.994}Mg_{0.006})_3(PO_4)_2 \cdot 8H_2O$. Spectrochemical analysis showed the following elements to be present in trace amounts: Be(?), Ca, Co, Cu, In, K(?), Li, Mn, Ni, Si(?), Ti, and V. The ferric-ferrous ratio was not determined, but was assumed to be low inasmuch as the purple color of the vivianite crystals was a surface effect only, presumably caused by oxidation of the ferrous ion near the surface. For instrumental analyses, the clear transparent center portions of the crystals was used, but on grinding, however, the initially white powder of the clear transparent vivianite, oxidized within a few minutes to a deep purple color.

Spectrochemical analysis indicates that wavellite, like the other secondary phosphates from this locality, exhibits little, if any, isomorphous substitution. However, the following elements were found in trace amounts: Ca, Cr, Fe, Mg, Si, Ti and V.

OPTICAL PROPERTIES

Optical measurements were made employing the universal stage. Indices were determined with freshly mixed oils, checked at the time of measurement, on an Abbé refractometer.

Vivianite: $\alpha = 1.582$, $\beta = 1.605$, $\gamma = 1.632$, $2V = 84°(+)$, $X = b$, optic plane $\perp(010)$, $Z \wedge c = 26°$, $v > r$ not strong, pleochroism of the colored varieties, $\alpha =$ blue, $\beta =$ light blue, $\gamma =$ colorless, uncolored varieties $\alpha =$ very pale blue, β and γ colorless.

Turquois: Individual crystal units are so small that only one index could be determined $n = 1.612 \pm .002$. Thick plates may be pale blue, whereas thin plates are colorless.

Wavellite: $\alpha = 1.522$ $\beta = 1.530$ $\gamma = 1.547$, $2V = 68°(+)$, orthorhombic, $X = a$, $Y = b$, $Z = c$ with (110) cleavage as reference, colorless in all directions.

X-RAY DATA

X-ray data for wavellite and vivianite were taken with a Norelco high angle diffractometer utilizing $CuK\alpha$ radiation. A pulse height analyzer was used to eliminate iron fluorescence from the vivianite pattern. Data for the turquois and supplemental data for the wavellite are from powder photographs taken with a 57.3 mm. radius camera.

X-ray data are in good agreement with data published on A.S.T.M. cards. Differences of line intensities between the Bingham phosphates and previously published data are probably due to orientation effects. Even

with great care, it was impossible to completely avoid some orientation in mounts of the fibrous wavellite. The vivianite pattern also possibly shows slight orientation effects.

Differential Thermal Analyses

Differential thermal analyses were run individually in a block of the type designed by Gruner (Manly, 1950). The furnace was Kanthal wound and a motor driven variable transformer used as a program controller where a heating rate of 12° C. per minute was maintained with thermocouples of chrome-alumel. Differential output was preamplified and curves recorded with a recording potentiometer. These are shown in Fig. 2.

The Bingham turquois gave a strong endothermic reaction at 350° C. and a weak exothermic reaction at 740° C. Manly (1950) obtained temperatures of 380° C. and 840° C. for these reactions on a sample from New Mexico.

The vivianite gave a weak endothermic reaction at 183° C. and a strong one at 211° C. Exothermic reactions were at 631° C. and 766° C. Manly (1950) noted a stepwise dehydration of vivianite from Keystone, South Dakota with a loss of five, two, and one molecules of water at 260°, 330°, and 380° C. respectively. Only two water loss peaks were noted on the DTA curve of the Bingham vivianite. The iron in the Bingham vivianite, however, oxidized at 631° C. with a sharply defined peak. Although Manly does not discuss them, his vivianite curve has two additional exothermic reactions, one occurring just under 700° C., the other occurring at a temperature slightly greater than 800° C. The Bingham vivianite has a small exothermic reaction at 766° C.

The wavellite gave endothermic reactions at 270° and 329° C. and exothermic reactions at 705° and 745° C. Manly obtained endothermic reactions at 275° and 315° C. on wavellite from Montgomery, Arkansas. The Montgomery wavellite gave an exothermic reaction at 710° C. whereas a sample from an unknown locality gave an additional exothermic reaction at 770° C.

The DTA curves of the Bingham turquois and wavellite are very similar to those of these same minerals published by Manly (1950). Differences in temperatures of reactions between the Bingham minerals and those run by Manly are probably due to slight differences in composition between the two sets of samples. This study did not confirm the three-step dehydration of vivianite described by Manly. No explanation is apparent for the differences between the DTA curves of the vivianites. It is interesting to note that turquois and wavellite, both hydrous basic phosphates with both hydroxyl and water of crystallization, have simpler
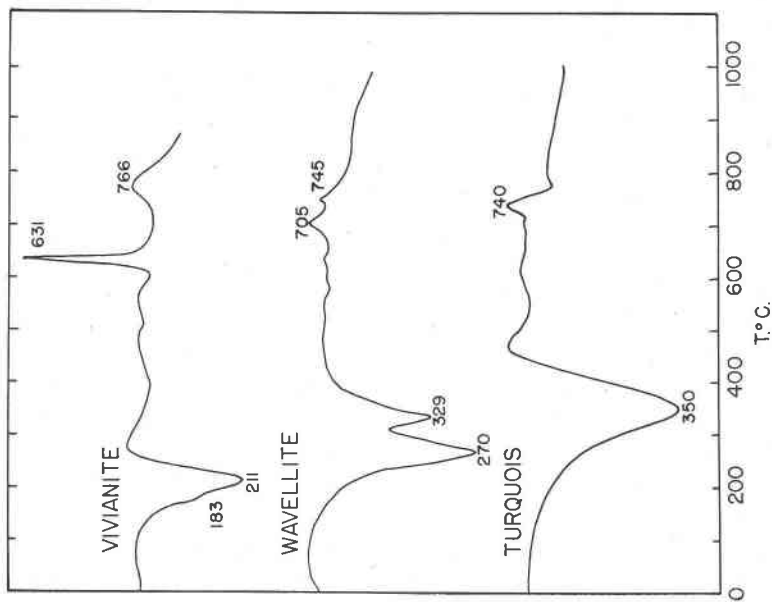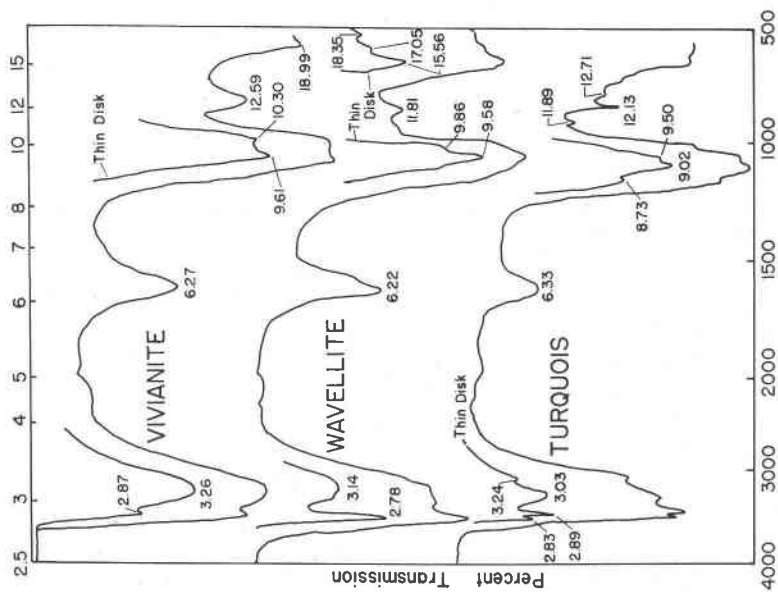
FIG. 2. (left) Differential thermal analysis curves of Bingham phosphates.
FIG. 3. (right) Infrared absorption spectra of Bingham phosphates.

water loss reactions on their DTA curves than does vivianite, a mineral with only water of crystallization.

INFRARED ABSORPTION

Infrared absorption spectra were taken on a Perkin Elmer Model 421 double beam spectrophotometer using grating optics thus running the spectra from 2.5 to 18 microns or slightly higher (Fig. 3). The finely powdered minerals were mixed with infrared grade potassium bromide in a mechanical agitator. Discs were pressed in a standard die at 7,000 lbs total load under vacuum where 500 mg of KBr were used. Another disc of the same mineral was prepared using 175 mg of potassium bromide under 6,000 lbs load. Each disc contained 0.25% of the mineral. Reference 505 mg pure potassium bromide discs were prepared in the same manner. Two runs were made on each mineral, one employing the thicker disc and scanning the full spectra while in the second run the thin disc was used in various wave lengths. Two more runs were made using the same discs in the same regions but with a decreased scale factor to 0.25. The advantage of this procedure is that when a peak is reached the wave number is read directly from the slow running counter thus establishing the wave length of the peak without interpolation from curves. This allows close identification of the peak but of course does not indicate amplitude. Many peaks are resolved by the reduced scale factor method which are shown generally as plateaus or small humps on a run of the normal scale. Thus, the new machine has a great advantage in accurately placing each peak at its proper wave length or wave number. The data shown in Fig. 3 are direct tracings from the curves of 2 reduced scale runs. The peak wave lengths are from direct observation of the reduced scale factor (0.25) run.

It can be seen from these data that infrared absorption spectra are useful for identification of the phosphates. The absorption bands between 2.83 and 3.25 microns represent O-H stretching. The absorption of longer wave lengths probably represent externally bonded water or O-H bonding and in the regions of shorter wave lengths is represented water of crystallization and hydroxyl. As shown in Fig. 3, the O-H stretch bands of turquois and wavellite both with hydroxyl ions in their crystal structure as well as water of crystallization, are more complex than that of vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$ which has water of crystallization only.

The band between 6 and 7 microns represents O-H bending. According to Cambridge and Lowe (1954), maxima in the 9.5 micron region represents ionic P-O stretching while those in the 10 micron region represent other modes of P-O stretching. From Fig. 3, it is apparent that turquois and wavellite show more ionic character than vivianite.

Origin

Copper and iron from pyrite, chalcopyrite, and bornite and aluminum from feldspars are readily available in the minerals of the pit. The problem arises as to the origin of the phosphate. Hansen (1961) reports that the Tilden formation of Upper Pennsylvanian age occurring in the district has a 12-foot fossiliferous limestone bed which could have supplied the phosphate for the formation of the three minerals. Detailed studies recently carried out by Welch (1961) and others indicate that this and some phosphatic nodules in the lower Pennsylvanian (Welch, pers. comm.) are probably the only phosphatic sources in the district.

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