

NOTES AND NEWS

"HEWETTITE" AND "METAHEWETTITE"

W. H. BARNES, *Division of Physics, National Research Council, Ottawa, Canada.*

The investigation of the structures of "hewettite" and "metahewettite" (Barnes & Qurashi, *Am. Mineral.*, **37**, 409, 1952) has been hampered, not only by the poor quality of single crystals of these minerals, but also by their hydration characteristics. In an attempt to establish reference standards for "wet" and "dry" material, a systematic *x*-ray diffraction powder investigation has been undertaken. Briefly the procedure has been to take up crushed specimens in capillary tubes (Matthews, *Anal. Chem.*, **26**, 619, 1954; Barnes & Sheppard, *Bull. on Narcotics, U. N. Dept. Social Affairs*, **6** (2), 27, 1954) and then (*a*) fill with distilled water, seal with Household (Duco) Cement or collodion, and take photographs at intervals until no change in the powder pattern was observed, on (*b*) store over P_2O_5 in a desiccator, remove at intervals, seal, photograph, open the seal, restore to the desiccator, and repeat until a constant pattern was obtained. Similar tests have been made starting with "wet" samples from (*a*) and drying as in (*b*), and commencing with dry samples from (*b*) and saturating with water as in (*a*). Individual samples also have been subjected to repeated cycles of hydration and dehydration.

The following specimens¹ have been employed:

1. Metahewettite, in conglomerate, Cactus Rat mine, Yellow Cat district, Grand Co., Utah (Harvard 98019).
2. Hewettite, Yellow Cat (Webber, U.S.G.S.).
3. Hewettite, Jo Dandy mine, Montrose Co., Colorado (MNG/4/49, U.S.G.S.; Sherwood-analyzed material).
4. Metahewettite, Montrose Co., Colorado (Harvard 95445).
5. Metahewettite, East Paradox Valley, Montrose Co., Colorado (Harvard 93306; type material from Dr. W. F. Foshag, U. S. National Museum).
6. Metahewettite, on gypsum with carnotite, Hummer mine, East Paradox Valley, Montrose Co., Colorado.
7. Hewettite, with pascoite in patronite, Minasragra, Cerro de Pasco, Peru (Harvard 96258; type locality).
8. Synthetic sodium vanadate (Marvin, U.S.G.S.; Magin-analyzed material).

The following results have been obtained:

A. The powder patterns of specimens 2, 3, 5, 6, and 7 vary with the degree of hydration of the material. Identical patterns, however, are

¹ I am indebted to Professor Clifford Frondel for specimens 1, 4, 5, and 7, and to Mrs. Alice D. Weeks for specimens 2, 3, and 8. Specimen 6 was obtained from Minerals Unlimited; it is completely different in general appearance from specimen 5.

obtained from all of these specimens (including the typical "hewettite" and the typical "metahewettite") after dehydrating "to constant pattern" over P_2O_5 ; this "dry" phase undoubtedly is the trihydrate, $CaO \cdot 3V_2O_5 \cdot 3H_2O$ (Hillebrand, Merwin & Wright, *Proc. Am. Phil. Soc.*, **53**, 31, 1914). On the addition of water to the samples, the powder pattern changes but the final "constant" pattern frequently is not precisely the same (especially in the region of small 2θ values) for samples from different specimens, and even for the same sample after repetition of the dehydration-hydration cycle; no regularities, however, have been observed to suggest any basis for distinction between the behaviour of "hewettite" and "metahewettite." In all cases the pattern of the hydrated samples returns to the standard one for "dry" material after dehydration over P_2O_5 . The fully-hydrated phase presumably is $CaO \cdot 3V_2O_5 \cdot 9H_2O$ (Hillebrand, Merwin & Wright, *loc. cit.*) and the small differences among the spacings and relative intensities observed in different patterns for the "wet" samples may result from the manner in which water molecules enter the lattice. Although little attention so far has been directed to possible intermediate stages of hydration in the present investigation, the patterns obtained during hydration and dehydration of the samples are not composed simply of those given by the "dry" and "wet" phases; there is no doubt that at least one intermediate hydrate exists. Hillebrand, Merwin & Wright (*loc. cit.*), largely on the basis of hydration-dehydration characteristics, came to the conclusion that hewettite and metahewettite are specifically distinct isomers. The present results, however, indicate that they are structurally identical. It seems unnecessary, therefore, to retain the name "metahewettite" unless it is employed to designate one of the hydrate phases, as in the case of rossite ($CaO \cdot V_2O_5 \cdot 4H_2O$) and metarossite ($CaO \cdot V_2O_5 \cdot 2H_2O$) (Foshag & Hess, *Proc. U. S. Nat. Museum*, **72**, art. 11, 1927).

B. Specimen 1 (Harvard 98019) from the Cactus Rat mine was the source of the crystals from which preliminary structural data for "metahewettite" were obtained (Barnes & Qurashi, *loc. cit.*). The structure, however, is *not* water-sensitive, and one of the "vanadium" peaks on the ($h0l$) electron-density map ($\frac{1}{2}$ cell) is rather low for V but of about the appropriate height for Na, while the peak tentatively identified as Ca could be V, at least insofar as height is concerned. Recently a sodium analogue of hewettite, $Na_2O \cdot 3V_2O_5 \cdot 3H_2O$, has been found in the Cactus Rat mine by Mrs. A. D. Weeks (Weeks & Thompson, U. S. Geol. Survey, Bull. **1009-B**, 1954, summarized by Fleischer, *Am. Mineral.*, **39**, 1038, 1954), and a sodium vanadate of this composition has been synthesized at the U. S. Geological Survey. The synthetic material gives the same

powder pattern as the natural (Na) specimen except for slight differences in intensity (private communication from Mrs. A. D. Weeks). The powder pattern of the synthetic sodium vanadate (specimen 8 of the present study) is identical with that of specimen 1, except for a diffuse band (not present in photographs of the latter) along the small- 2θ edge of the strongest line, and it is not affected by drying the sample or saturating it with water. Finally, a Beckmann flamephotometer determination, kindly made by Mr. J. C. Bartlet, Food and Drug Laboratories, Ottawa, on ~ 2 mg. hand-picked blades of specimen 1 showed 6.5% Na; this is in very good agreement with the theoretical value of 6.95% Na for $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, particularly in view of the small size of the sample and the difficulty of ensuring complete removal of adhering fragments of other minerals. For comparison it may be noted that a similar measurement on blades from specimen 3 (Jo Dandy, water-sensitive $\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) was negative ($< 0.2\%$ Na). There is little doubt, therefore, that specimen 1 (Harvard 98019) is, in fact, identical with Mrs. Weeks' sodium analogue of hewettite.

C. The status of specimen 4 (Harvard 95445) is not yet clear. The exact locality in Montrose County, Colorado, from which it was obtained is unknown (private communication from Prof. C. Frondel). It consists of long, red blades closely resembling the Jo Dandy material (specimen 3) in appearance, together with very finely-divided red powder, on, and impregnating, sepiolite and quartz. On the basis of powder photographs of wet and dry samples, however, the structure is not water-sensitive and, in this respect, it resembles specimen 1, but the powder pattern is markedly different from that of specimen 1. A flamephotometer measurement by Mr. J. C. Bartlet on < 1 mg. of hand-picked blades showed 3.7% Na. It is possible, therefore, that it is a mixed (Ca, Na)-analogue of hewettite.

Thus at present there appear to be three types of material variously labelled "hewettite" or "metahewettite," namely, (I) hewettite, $\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (comprising both the "hewettite" and the "metahewettite" of Hillebrand, Merwin & Wright), which exists in at least three hydrate forms with $n = 3, 6$ (probably), and 9, (II) the unnamed sodium analogue of hewettite in the trihydrate form, $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, reported by Mrs. Weeks, the structure of which is not water-sensitive, and (III) the material, also insensitive to hydration and dehydration, and possibly a mixed sodium-calcium variety of the sodium analogue, represented by specimen 4 (Harvard 95445).

Mrs. H. M. Sheppard and Mr. B. J. Cowick have assisted in taking the powder photographs and measuring many of the patterns.