# OBSERVATIONS ON HYDROHETAEROLITE

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## ABSTRACT

Hydrohetaerolite from Leadville, Colorado, is of tetragonal symmetry, space group *I4/amd*. The unit cell of dimensions $a=5.73_5$, $c=9.00_5$ Å contains $4HZnMn_{2-x}O_4$, where $x$ is approximately 0.4 and represents vacant cation positions. Decomposition into oxides of the constituent elements occurs on heating, and the recombination of these oxides to form hetaerolite, $ZnMn_2O_4$, at higher temperatures indicates hydrohetaerolite is a separate mineral species distinct from the former. A method of density determination for fibrous minerals is described.

A distinction between hetaerolite, $ZnMn_2O_4$, and the hydrous equivalent hydrohetaerolite was first made by Palache (1929), and was retained in the monograph on Franklin and Sterling Hill (Palache, 1935). An $x$-ray study of the two minerals has since been made by Frondel and Heinrich (1942), to which reference may be made for a revision of the relevant literature. From the hydrohetaerolite described by Ford and Bradley (1913) they obtained an $x$-ray powder pattern similar to that of hetaerolite, of which all but five weak lines indexed on a tetragonal cell of dimensions $a=5.72$, $c=9.05$ Å. Their $x$-ray single crystal photographs, stated to be of poor quality, were in agreement with the geometrically tetragonal cell. However these photographs were not sufficient to define a tetragonal symmetry, which was assumed in deducing a "partial space group" $I4/a-d$. Frondel (1953) has described hydrohausmannite, of composition $Mn_3(O,OH)_4$, and indicated the analogy to hydrohetaerolite.

The present investigation of hydrohetaerolite was made on a portion of the type material of Ford and Bradley (HMM92151) obtained through the courtesy of Professor Clifford Frondel. The specimen consists of a radiating aggregate of finely acicular crystals growing out from a core of finely granular crystals. The fibres show a number of cleavages parallel to the fibre axis, and are slightly twisted along this axis.

## $X$-RAY CRYSTALLOGRAPHY

A number of minute fibres which showed substantially no twisting were selected for the $x$-ray single crystal investigation. After several trials a crystal was obtained which gave small sharp spots on an $x$-ray rotation photograph. It was not possible to orientate the crystals by an optical goniometer to within less than 2° to 3°. Final exact orientation was therefore made on the $x$-ray goniometer, for which a method, essentially a variation of that described by Bairsto (1948), was developed.

Clear, sharp rotation and zero and first layer Weissenberg photographs were obtained for rotation about the axis of elongation of the fibre. The rotation photograph gave a period of 8.12 ± 0.01 Å along the fibre axis, and from the zero layer Weissenberg the parameters of the rectangular lattice perpendicular to the fibre axis were measured as $9.00_5 \pm 0.01$, $8.10 \pm 0.01$ Å. The symmetry $C_{2l}$ of both the zero and first layer Weissenberg photographs allows of tetragonal symmetry for the fibre axis the [100] or [110] directions. A Laue photograph of the fibre taken with the incident *x*-ray beam parallel to the direction of period $9.00_5$ shows this direction to be a fourfold axis of symmetry, and thus the tetragonal *c* axis, and establishes tetragonal symmetry. A photograph of the *hk*0 reciprocal lattice plane obtained on a Buerger precession camera likewise shows the fourfold symmetry.

TABLE 1. *X*-RAY POWDER PATTERN OF HYDROHETAEROLITE, $HZnMn_{2-x}O_4$
Tetragonal, *I*4/*amd*; $a=5.73_5$, $c=9.00_5$ Å; Z=4. Fe radiation, Mn filter

| *I* | *d*(*meas.*) | *hkl* | *d*(*calc.*) | *I* | *d*(*meas.*) | *hkl* | *d*(*calc.*) |
|---|---|---|---|---|---|---|---|
| ½ | 4.82 | (011) | 4.837 | tr | 1.387 | "(411)" | 1.375 |
| ½ | 3.34 | — | —* | ¼ | 1.312 | (305) | 1.311 |
| 7 | 3.02 | (112) | 3.013 | tr | 1.299 | (332) | 1.295 |
| 4 | 2.87 | (200) | 2.867 | tr | 1.283 | (420) | 1.282 |
| 8 | 2.66 | (103) | 2.659 | 3 | 1.263 | (413) | 1.262 |
| 10 | 2.47 | (211) | 2.467 | ½ | 1.155 | (316) | 1.156 |
| 1 | $2.25_4$ | (004) | 2.251 | ½ | 1.153 | — | —† |
| 1 | 2.13 | — | —* | tr | 1.131 | (431)(501) | 1.138 |
| 2 | 2.03 | (220) | 2.028 | | | (008) | 1.126 |
| 1 | 1.773 | (204) | 1.771 | ½ | 1.117 | (424) | 1.114 |
| 2 | 1.723 | (105) | 1.718 | 1 | 1.102 | (415) | 1.101 |
| 2 | 1.686 | (312) | 1.682 | ½ | 1.093 | (512) | 1.092 |
| 1 | 1.613 | (303) | 1.612 | 3 | 1.074 | (433)(503) | 1.072 |
| 5 | 1.570 | (231) | 1.566 | 1 | 1.060 | (521) | 1.058 |
| 7 | 1.508 | (224) | 1.507 | 3 | 1.015 | (440) | 1.014 |
| 4 | 1.434 | (400) | 1.434 | 1 | 1.003 | (523) | 1.004 |
| ¼ | 1.412 | (314) | 1.412 | | | | |

* Extraneous lines, varying in intensity among the *x*-ray powder patterns.

† Indexed as (334) by Frondel and Heinrich, a diffraction extinguished by the *d* glide-plane.

The smallest tetragonal cell has $a=5.73_5 \pm 0.01$ Å, $c=9.00_5 \pm 0.01$ Å, and for this orientation the fibre axis is the [110] direction. A partial diffraction symbol of *I*4/?*md* is given by the *hkl* diffractions present only for $h+k=2n$ and *hhl* diffractions present only for $2h+l=4n$ on the Weissenberg photographs. The further extinction condition of diffractions present only for $h=2n$ and $k=2n$ on the $hk0$ precession photograph leads to the complete diffraction symbol of $4/mmmI-/a-d$, allowing $I4/amd$ as the only possible space group. The $x$-ray powder pattern, Table 1, indexes for the above cell dimensions with excellent agreement between measured and calculated lattice spacings.

## DENSITY

A determination of the density of a 5 mg. portion of the specimen was made with a Berman torsion balance. The value obtained, 4.64 gm./cc., is in close agreement with the maximum value of 4.65 measured by Frondel and Heinrich. However, it has been thought that the measurement of volume and hence of density of this fibrous material by displacement of a liquid such as toluene may be in error.

As an aid in checking the density a direct volume measurement was made of a fibre of known mass. For this determination a fibre of dimensions $1.4\times0.4\times0.2$ mm. was selected, and its mass determined on a Becker microbalance as $0.294\pm0.003$ mg. The volume of the fibre was then determined by measuring the area of parallel serial cross-sections at known distances apart. To obtain such sections the fibre was mounted in a transparent catalyst setting plastic. A reference surface was ground and polished perpendicular to the axis of the fibre. Serial sections from tip to tip of the fibre at intervals of 0.05 to 0.18 mm. were then obtained by repeated grinding and polishing on surfaces kept parallel to the reference surface. The area of each cross-section of the fibre was calculated from the area of the magnified image on the focussing screen of a Leitz Panphot microscope, the area being measured by a polar planimeter. The position of each cross-section was determined with a screw micrometer by its distance from the reference surface.

The calculation of the volume from these measurements could not be made by Simpson's rule as the sections were not spaced at equal intervals. Each cross-sectional area was therefore assumed to be the average for a segment of the fibre extending halfway to each adjacent cross-section. Calculated in this manner, the sum of the volumes of the twelve segments along the fibre is $6.94\times10^{-5}$ cc., with an error estimated as not greater than 7%. This, together with the measured mass of 0.294 mg., gives a density of $4.3\pm0.3$ gm./cc. Within the limits of error this determination agrees with the value of 4.64 measured on the torsion balance; the density certainly cannot be much higher, and is well below the density 5.18 gm./cc. of hetaerolite.

The errors in the direct measurement of volume arose mainly from the cross-sections being obtained by hand grinding and polishing. Although the average spacing of the cross-sections was 0.12 mm., occasional overgrinding produced 50% larger intervals, with a marked reduction in overall accuracy of determination of the volume. Furthermore the hand polishing, completed on billiard cloth, produced distinct relief between the hydrohetaerolite and its enclosing plastic, which made the exact outline of the mineral difficult to locate. Mechanical equipment to produce constantly spaced, smaller intervals, and attainment of a relief free polish would substantially improve the accuracy of this method of density determination.

## POLISHED SECTION

In reflected light hydrohetaerolite is creamish-gray in color, with a reflectivity estimated as 15–20% by visual comparison with minerals of known reflectivity, and is distinctly anisotropic. The absorption index of the mineral, translucent in thin flakes, is very small, and, considering it as zero, the reflectivities in polished section calculate as $R_0 = 15.0\%$, $R_e = 12.5\%$, from the refractive index measurements $n_o = 2.26$, $n_e = 2.10$ of Berman (Palache, 1929). In comparison the reflectivities of hetaerolite calculate as $R_0 = 16.1\%$, $R_e = 13.1\%$ in good agreement with the values 17.7%, 13% measured by Orcel and Pavlovitch (1931) in white light. The properties in reflected light correspond closely with the description of hetaerolite from Sterling Hill by Orcel and Pavlovitch. However hydrohetaerolite is tarnished by 30% $HNO_3$, which does not affect hetaerolite although conc. $HNO_3$ has a positive reaction with the latter.

## HEAT TREATMENT

There is a clear although slight distinction in physical properties between hydrohetaerolite and hetaerolite. The essential difference in chemical composition is the presence of about 4% water in the former. A series of heating experiments was therefore made to find if hydrohetaerolite transformed to hetaerolite by loss of water at elevated temperatures.

Powdered 0.2 mg. portions of the Leadville hydrohetaerolite were heated in air for 2 hours at $400 \pm 5°$ C., $600 \pm 5°$ C., and $860 \pm 30°$ C. Heating at 400° C. produces no change in the $x$-ray powder pattern or in appearance. The product of heating at 600° is however distinctly lighter brown in color than the initial dark brown powder. The $x$-ray powder pattern reveals decomposition of the hydrohetaerolite to manganosite, $MnO$, and zincite, $ZnO$, together with the formation of a small amount of hetaerolite. Although $Mn_2O_3$ is the stable oxide of manganese at this temperature (Mason, 1943) none of its diffraction lines are present in the $x$-ray pattern. A portion of this mixture was heated for 2 hours at $850 \pm 5°$ C. in air. An $x$-ray pattern shows that most of the $ZnO$ and

MnO of the mixture combines at the higher temperature to form hetaerolite.

The product of heating at 860° gave a strong $x$-ray powder pattern of hetaerolite, together with a few additional, weak lines. This pattern indexes for a tetragonal cell with $a=5.73$, $c=9.24$ Å, in comparison with the parameters 5.72, 9.24 measured for pure artificial $ZnMn_2O_4$ by Mason (1947), and 5.75, 9.17 obtained for Sterling Hill hetaerolite by Frondel and Heinrich.

Thus in air hydrohetaerolite remains unaltered at temperatures of 400° and lower. Above a temperature between 400° and 600° it decomposes to a mixture of ZnO and MnO. At 600°, and more readily at higher temperatures, this mixture of oxides combines to form anhydrous $ZnMn_2O_4$, hetaerolite. Hydrohetaerolite thus has a different stability range from that of hetaerolite, and is a solid phase distinct from the latter. Accordingly, it is to be regarded as a separate mineral species distinct from the anhydrous hetaerolite.

## UNIT CELL CONTENTS

The close similarity of the $x$-ray powder patterns and cell dimensions of hydrohetaerolite with those of hetaerolite and hausmannite, all of the same space group, shows that these minerals are isostructural. The atomic contents of the unit cell should accord with the ideal structure determined for hausmannite by Aminoff (1926), which contains 16 oxygen ions approximately in cubic close packing in this cell. There is thus not sufficient space to geometrically fit more than 16 oxygen ions into the cell of hydrohetaerolite, which is distinctly smaller than that of hausmannite. Moreover the symmetry of the space group is such that each set of equivalent positions in the unit cell contains either four atomic positions or a multiple thereof.

The cell contents calculated for the measured density are listed in Table 2 for the analysis by Bradley, 1, Bradley's analysis assuming the $SiO_2$ present is due to admixed hemimorphite, 2, and for the analysis by Palmer 3 (Wells, 1937). In the second calculation the density is taken as 4.85 gm./cc. in allowance of the assumed 10.7% of hemimorphite of density 3.50. The oxygen content of the unit cell is close to 16, and the cell contents and required density for 16.00 oxygen ions in the cell are also given.

The unit cell contains close to $H_4Zn_4(Mn, Fe, Si)_{8-y}O_{16}$. The structural formula of hydrohetaerolite is thus $HZnMn_{2-x}O_4$, with $x$ about 0.4, and the presence of a deficiency of cations is revealed. A similar deficiency has been found in artificial hausmannite-like preparations by Dubois (1934), who prepared a compound of composition $Mn_2O_3$ but with an $x$-ray pattern closely resembling hausmannite, $Mn_3O_4$. Verwey and de Boer (1936) showed this can be described as $Mn_{3-1/3}O_4$ with 4/3 vacant cation positions per unit cell, analogous to $\gamma-Fe_2O_3$. The analysis of hydrohetaerolite indicates a greater proportion of vacant cation positions.

A variably hydrated manganese oxide isostructural with hausmannite has been prepared by Dubois (1934) and by Feitknecht and Marti (1945), and occurs naturally as the mineral hydrohausmannite, Frondel (1953). In analogy with the structure of hausmannite, the unit cell of hydrohausmannite contains 16(O,OH). A higher anion content is geometrically improbable. Moreover Verwey and de Boer (1936) show that the structure and electrical conductivity of hausmannite indicate $Mn^2_2Mn^4$ as the cations rather than $Mn^2Mn^3_2$. On this basis the analysis of hydrohausmannite (backstromite) from Långban, Sweden, by Mauzelius (Aminoff, 1919) gives a unit cell contents of $4\times(Mn^2$,

TABLE 2. ANALYSES AND UNIT CELL CONTENTS OF HYDROHETAEROLITE

ANALYSES

| | 1 | 2 | 3 |
|---|---|---|---|
| ZnO | 37.56 | 30.30 | 37.66 |
| $Mn_2O_3$ | — | — | 54.93 |
| MnO | 50.34 | 50.34 | — |
| O | 5.99 | 5.99 | — |
| $Fe_2O_3$ | — | — | 0.67 |
| $SiO_2$ | 2.69 | — | 2.91 |
| $H_2O$ | 4.36 | 3.55 | 3.78 |
| Hemimorphite | — | 10.76 | — |
| Total | 100.94 | 100.94 | 99.65 |
| G(meas.) | 4.64 | 4.85 | 4.64 |

| | CALCULATED UNIT CELL CONTENTS | | | UNIT CELL CONTENTS FOR O=16 | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| Zn | 3.80 | 3.58 | 3.86 | 3.91 | 3.47 | 4.07 |
| Mn | 5.84 | 7.42 | 5.77 | 6.00 | 7.19 | 6.08 |
| Fe | — | — | 0.07 | — | — | 0.07 |
| Si | 0.39 | — | 0.40 | 0.40 | — | 0.41 |
| H | 3.98 | 3.80 | 3.50 | 4.10 | 3.68 | 3.68 |
| O | 15.55 | 16.50 | 15.17 | 16.00 | 16.00 | 16.00 |
| G(calc.) | | | | 4.77 | 4.72 | 4.89 |

1. Hydrohetaerolite, Leadville, Colorado; Ford and Bradley (1913).
2. The same, considering the $SiO_2$ is in admixed hemimorphite.
3. Hydrohetaerolite, Leadville, Colorado; Palmer (Wells, 1937).

Mg)$_{1.42}$Mn$^4_{1.00}$O$_{4.00}$H$_{1.16}$, excluding $H_2O-130°$. The alternative cation valencies correspond to a cell contents of $4\times$(Mn$^2$, Mg)$_{0.42}$Mn$^3_{2.00}$O$_{4.00}$H$_{1.16}$. The density of hydrohausmannite with these atomic contents in a cell of dimensions $a=5.79$, $c=9.49$ Å (Frondel, 1953), calculates as 4.13 gm./cc., much below the density 4.84 gm./cc. of hausmannite.

The difference in cell dimensions of hydrohetaerolite and hetaerolite is greater than the differences in the variants of hausmannite, Table 3.

TABLE 3. CELL DIMENSIONS OF HYDROHETAEROLITE AND RELATED STRUCTURES

| | $a$ | $c$ | Cell Contents/4 | Reference |
|---|---|---|---|---|
| Hydrohetaerolite | $5.73_5$ | $9.00_5$ | $HZnMn_{2-0.4}O_4$ | (Present study) |
| Hetaerolite | 5.73 | 9.24 | $ZnMn_2O_4$ | (Present study) |
| Hydrohausmannite | 5.79 | 9.49 | $Mn_{3-0.6}(O, OH)_4$ | Frondel (1953) |
| Hausmannite | 5.79 | 9.44 | $Mn_3O_4$ | Aminoff (1926) |
| $\gamma$-$Mn_2O_3$ | 5.7 | 9.4 | $Mn_{3-1/3}O_4$ | Verwey and deBoer (1936) |
| Magnetite | 5.94[1] | 8.40 | $Fe_3O_4$ | Hagg (1935) |
| Maghemite | 5.90[1] | 8.34 | $Fe_{3-1/3}O_4$ | Hagg (1935) |

[1] Dimensions of the structural unit which corresponds to the unit cells of the other minerals, and is half the volume of the cubic cell.

The slight increase in cell dimensions of hydrohausmannite relative to hausmannite, and the strong (002) diffraction in the $x$-ray powder pattern of the former have no parallel in hydrohetaerolite. The presence of cation vacancies in hausmannite and in magnetite, of similar structure to hetaerolite, results in only a slight decrease in the cell dimensions.

In structures of the hausmannite type (Aminoff, 1926) the oxygen ions are in a distorted cubic close-packing. The oxygen ions in layers parallel to 001 are in a close packed arrangement with but little separation beyond the normal ionic radius, and the distortion is in the $c$ axial direction as a separation of these layers beyond the ionic distance in the 001 planes. This distortion is distinctly smaller in hydrohetaerolite than in hetaerolite, and the reduction may arise from the position of the hydrogen in the structure, and the nature of the hydrogen bond.

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