Hydrohetaerolite from Maruyama mine, Hokkaido, Japan

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Hydrohetaerolite, Zn$_2$Mn$_4$O$_8$•H$_2$O, was found in the oxidation zone of Maruyama copper-lead-zinc-manganese mine, southwestern Hokkaido. This is the second occurrence reported in Japan.

The mineral is brownish black. X-ray powder diffraction pattern shows that it is tetragonal with $a_0$ 5.72, $c_0$ 9.09Å, and space group $I_4_1/amd$. Wet chemical analysis gives an empirical formula of (Zn$_{1.62}$Mg$_{0.56}$)$_2$Mn$_{3.88}$O$_{8.00}$•11.13H$_2$O.

Introduction

A distinction between hetaerolite, ZnMn$_2$O$_4$, and the hydrous equivalent hydrohetaerolite, Zn$_2$Mn$_4$O$_8$•H$_2$O, was first made by Palache (1929), and was retained in the monograph on Franklin and Sterling Hill (Palache, 1935). The first X-ray study of hydrohetaerolite was made by Frondel and Heinrich (1942). Later X-ray works by Wadsley (1955) and McAndrew (1956) have shown that hydrohetaerolite is tetragonal, space group $I_4_1/amd$ with $a_0$ 5.75, $c_0$ 9.05Å (Wadsley) or $a_0$ 5.735, $c_0$ 9.005Å (McAndrew).

The first occurrence of hydrohetaerolite in Japan was recorded from Kawazu mine, Shizuoka Prefecture (Kato, 1973). However, the mineralogical data have not been published.

During the course of the study of manganese oxide minerals, one of us (E.K.) collected a brownish black mass of manganese oxide from the oxidation zone of Maruyama copper-lead-zinc manganese mine, Southwestern Hokkaido. The mineral was identified as hydrohetaerolite by X-ray studies and chemical analysis. This is the second occurrence of hydrohetaerolite reported in Japan. In this paper, the chemical, physical and optical properties of the mineral are presented together with the X-ray powder data.

Occurrence

The Maruyama mine is located at Kam-inokuni Town, Hiyama District about 60 km south-west of Hakodate City, Hokkaido (Fig. 1).

The ore deposits are epithermal veins cutting Paleozoic formation, consisting
Hydrohaetaerolite from Maruyama mine

mainly of slate with some intercalations of sandstone and chert, and Miocene rhyolitic welded tuff (Saito et al., 1967). The ore minerals are composed of sphalerite, galena, chalcopyrite and rhodochrosite associated with subordinate pyrite, tetrahedrite and some minor minerals. Gangue minerals are quartz and small amounts of carbonates such as dolomite, ankerite and kutnahorite.

In this mine, numerous species of secondary minerals of copper, lead, zinc, manganese and iron are found in the oxidation zone. They are goethite, cryptomelane, nsutite, birnessite, todorokite, chalcophanite, amorphous MnO₂, smithonite, cerussite, aurichalcite, malachite, hydrozincite, greenockite, anglesite, linarite, pyromorphite and mimetite.

Hydrohaetaerolite occurs as massive mass in the oxidation zone, associated with cryptomelane, goethite, cerussite and quartz.

**Physical properties**

Hydrohaetaerolite occurs as an aggregate of finely granular crystals. The color is brownish black and streak dark brown. The specific gravity, 4.35, is slightly lower than the reported value 4.64 of Leadville material by McAndrew (1956).

In reflected light hydrohaetaerolite is yellowish gray in color, with lower reflectivity than the cryptomelane*, and distinctly anisotropic (Fig. 2).

![Fig. 1. Map showing the location of Maruyama mine.](image)

![Fig. 2. Photomicrograph of polished section of hydrohaetaerolite from Maruyama mine.](image)

* Reflecting power in green light in air is 27.9% (Roy, 1962).

**X-ray Studies**

The X-ray diffraction pattern of hydrohaetaerolite was obtained by Rigaku-Denki X-ray diffractometer using Fe radiation with Mn filter. The pattern was compared with that of Leadville material (McAndrew, 1956) and indexed in terms of tetragonal cell as in Table 1. The lattice dimensions of the hydrohaetaerolite from Maruyama mine were calculated from the powder pattern as follows:

\[ a_0 = 5.72 \text{Å}, \quad c_0 = 9.09 \text{Å}. \]
Table 1. X-ray diffraction patterns of hydrohetaerolite (Fe radiation, Mn filter)

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>d_{calc}</th>
<th>d_{obs}</th>
<th>d_{calc}</th>
<th>d_{obs}</th>
</tr>
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<tbody>
<tr>
<td>001</td>
<td>4.800</td>
<td>4.820</td>
<td>4.807</td>
<td>4.820</td>
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<tr>
<td>004</td>
<td>2.670</td>
<td>2.680</td>
<td>2.672</td>
<td>2.680</td>
</tr>
<tr>
<td>022</td>
<td>2.020</td>
<td>2.020</td>
<td>2.020</td>
<td>2.020</td>
</tr>
<tr>
<td>006</td>
<td>1.779</td>
<td>1.780</td>
<td>1.773</td>
<td>1.773</td>
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<tr>
<td>012</td>
<td>1.733</td>
<td>1.735</td>
<td>1.723</td>
<td>1.723</td>
</tr>
<tr>
<td>012</td>
<td>1.735</td>
<td>1.735</td>
<td>1.723</td>
<td>1.723</td>
</tr>
<tr>
<td>003</td>
<td>1.633</td>
<td>1.634</td>
<td>1.613</td>
<td>1.613</td>
</tr>
<tr>
<td>014</td>
<td>1.562</td>
<td>1.562</td>
<td>1.561</td>
<td>1.561</td>
</tr>
<tr>
<td>024</td>
<td>1.515</td>
<td>1.513</td>
<td>1.507</td>
<td>1.508</td>
</tr>
<tr>
<td>006</td>
<td>1.429</td>
<td>1.429</td>
<td>1.434</td>
<td>1.434</td>
</tr>
</tbody>
</table>

* Calculated on the basis of a₀ 5.72, c₀ 9.09A.
** Calculated on the basis of a₀ 5.735, c₀ 9.005A.
*** Extraneous lines, varying in the intensity among the X-ray powder patterns.

Chemical Composition

The material used for chemical and thermal analyses was purified by the Frantz isodynamic separator and heavy liquid. The X-ray examination of the purified material indicated the contamination of small amounts of goethite, cerussite, and quartz as impurities. About 200 mg of purified material was analyzed by the normal wet method.

Palache, Berman and Frondel (1944) reported the general formula Zn₃Mn₄O₈·H₂O, and considered that the Si reported in the analyses was due to contamination. Wadsley (1955) gave the formula Zn₄Mn₃+62/3O₁₂ (OH)₄, and McAndrew (1956) gave 4HZnMn₂-XO₄ with X about 0.4. They indicated the presence of a deficiency of cations. All the formulas are fairly in good approximations.

The results shown in Table 2 are calculated into the empirical formula (Zn₁.₆₂Mg₀.₅₆)₂.₁₈Mn₃.₈₈O₈.₀₀·1.₁₃H₂O as 8(O) after the deduction of CO₂ and PbO as cerussite, Fe₂O₃ as goethite and SiO₂ as quartz. This is close to the general formula Zn₃Mn₃O₈·H₂O. On the other hand, the formula calculated on the basis of 4(O, OH) is H₀.₉₉(Zn₀.₇₁Mg₀.₂₅)₀.₉₆Mn₁.₇₀O₄.₀₀, which is very close to the formula HZnMn₉₋ₓO₄ with X about 0.4 by McAndrew (1956). The hydrohetaerolite from Maruyama mine shows also the presence of a deficiency of cations.

Table 2. Chemical analysis of hydrohetaerolite from Maruyama mine, Hokkaido

<table>
<thead>
<tr>
<th>Element</th>
<th>Determined</th>
<th>Recalculated</th>
<th>Numbers of ions on the basis of 8(O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>51.32</td>
<td>63.66</td>
<td>Mn³⁺</td>
</tr>
<tr>
<td>ZnO</td>
<td>22.09</td>
<td>27.40</td>
<td>Zn</td>
</tr>
<tr>
<td>MgO</td>
<td>3.75</td>
<td>4.70</td>
<td>Mg</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
<td></td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.18</td>
<td></td>
<td>Fe³⁺</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.93</td>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.75</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.11</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Thermal Studies

DTA and TG of hydrohetaerolite were carried out simultaneously in air by means of a Thermoflex unit made by Rigaku-Denki Co., using about 100 mg of purified sample with small amounts of goethite, cerussite, and quartz as impurities. Heating rate was 10°C per minute.

The DTA and TG curves of hydrohetaerolite are shown in Fig. 3. The DTA curve shows four weak endothermal breaks at 170, 280, 510 and 590°C. The TG curve shows two steps of the weight loss, namely between room temperature and 315°C, and between 315°C and 750°C. The first step of weight loss is probably due to the dehydration of the admixed goethite and partial dehydration of hydrohetaerolite. The second step is closely related to the expulsion of remaining water of hydro-
The X-ray diffraction pattern of the product of heating at 1,000°C was compared with those of Sterling Hill hetaerolite (Frondel and Klein, 1965) and synthetic ZnMn$_2$O$_4$ (JCPDS Card No. 24-1133) in Table 3. This pattern is indexed for a tetragonal cell with $a_0 = 5.73$, $c_0 = 9.29\AA$, in comparison with the parameters $a_0 = 5.721$, $c_0 = 9.229\AA$ obtained for Sterling Hill hetaerolite by Frondel and Klein (1965) and $a_0 = 5.7204$, $c_0 = 9.245\AA$ measured for pure synthetic ZnMn$_2$O$_4$ (JCPDS Card No. 24-1133).

The subsolidus in the system Fe$_3$O$_4$-Mn$_3$O$_4$-ZnMn$_2$O$_4$-ZnFe$_2$O$_4$ has been described by Mason (1947). A complete solid solution exists in the spinel structure type above a temperature between 900°C and 1,000°C. At lower temperatures the two phase region between isometric spinel type and tetragonal hausmannite type solid solutions widens out (Fig. 4).

The purified sample of Maruyama hydrohetaerolite using thermal studies contains some amounts of goethite as impurity (Table 2). However, Fe$_2$O$_3$ (hematite) phase was not detected after this heat-treatment. This indicates that Fe$^{3+}$ substitutes for Mn$^{3+}$ of ZnMn$_2$O$_4$ (hetaerolite) phase. It is considered, therefore, that the composition of heated product at 1,000°C is close to $(Zn_{0.7}Mg_{0.2})_{0.9}(Mn_{1.7}Fe_{0.4})_{2.1}O_4$ (Fig. 4).

Acknowledgement: A part of expense for

![Fig. 3. DTA and TG curves of hydrohetaerolite from Maruyama mine.](image-url)
this study was supported by a Grant in Aid of Scientific Research provided by Ministry of Education for which the writers gratefully acknowledge.

References


Mason, B. (1947), Mineralogical aspects of the system Fe₂O₄-Mn₃O₄-ZnMn₂O₄-ZnFe₂O₄. *Amer. Mineral.*, **32**, 426–441.


北海道円山鉱山産ハイドロヘテロライト

谷田 勝俊・北村 強・南部 松夫・加藤 栄一

北海道檜山郡上ノ国町にある円山鉱山は、主として松前層群中に産する銅、鉛、亜鉛、マンガンの深熱水性鉱脈鉱床であるが、露頭部は強く酸化され、多数の2次鉱物を産する。ハイドロヘテロライトもその一つであり、クリプトメレーン鉱、針鉱鉱、白鉱鉱および石英と共生する塊状鉱として得られた。ハイドロヘテロライトは静岡県河津鉱山から産出が報告されていて、円山鉱山は本邦第2の産地である。しかし、河津鉱山産鉱料の鉱物学的データはまだ報告されていない。ハイドロヘテロライトは帯褐色を呈し、反射光下で帯黄灰色、強い異方性を示す。精選試料（若干の針鉱鉱、白鉱鉱、石英を混入）の湿式分析から、実試式は（Zn_{1.62}Mg_{0.56})_{2.18}Mn_{3.88}O_{8.00}·1.13H_{2}O となり、理想式
Zn_{2}Mn_{4}O_{8}·H_{2}O と一致する。粉末回折線から計算した格子定数は a=5.72, c=9.09 Â（正方晶系）であって、これを使用して指数配当を合理的に行えない。本鉱の1,000℃加熱物はヘテロライトであるが、混入している針鉱鉱から生じた Fe_{2}O_{3} に相当する粉末回折線が認められなかったため、Fe はヘテロライト中に固溶したものと考えられる。

Maruyama 円山, Hiyama 檜山, Kaminokuni 上ノ国, Kawazu 河津

付記: 本報文投稿後、河津鉱山産ハイドロヘテロライトの記載が下記の論文に報告されているのを知った。