

## HISINGERITE FROM JAPAN

TOSHIO SUDÔ AND TAKESHI NAKAMURA, *Geological Institute,  
Faculty of Science, Tôkyô University.*

### ABSTRACT

The mineralogical properties of hisingerite from the Kawayama Mine, Yamaguchi Prefecture, Japan, are described and discussed. The specimen is dark brown in color, massive, and intimately associated with the ore body—a bedded deposit in graphite-sericite-quartz schist. Under the microscope, it is apparently isotropic but shows tension polarization. The chemical analysis shows it to be a more highly hydrated variety than specimens previously reported in the literature. The differential thermal analysis curve resembles allophane, that is, a very strong endothermic peak between 100° and 200° C. and a weak exothermic peak between 900° and 1000° C. The *x*-ray powder pattern shows three broad bands which agree with some of the strong lines of nontronite, however, a line of 12~15 Å was not detected. The occurrence indicates that hisingerite is an alteration product derived from pyrrhotite and other iron minerals that were attacked by hot spring water of hypogene origin.

Hisingerite is found associated with certain metallic ore deposits of Japan, for example, with tin, copper and pyrrhotite deposits. One of the typical examples is at the Kawayama Mine, Yamaguchi Prefecture. The mineralogical properties of the hisingerite are recorded here and discussed.

The ore deposit of the Kawayama Mine is a bedded deposit formed along the thrust zones in graphite-sericite-quartz schist and is partly a replacement deposit in limestone. The ore is largely composed of pyrrhotite, chalcopyrite, sphalerite, pyrite, and marcasite with small amounts of cubanite, arsenopyrite, and galena. The gangue minerals are hedenbergite, actinolite, garnet, calcite, and quartz. The mineralization took place in four stages: (1) pyrrhotite, sphalerite (marmatite), cubanite, and chalcopyrite, (2) pyrrhotite, (3) chalcopyrite, (4) pyrite. A fault movement was recognized between stages (3) and (4). The deposits are pyrometasomatic.

Hisingerite is found in the ore body and in the surrounding country rock. In the ore body, it is intimately associated with pyrrhotite, chalcopyrite, and pyrite and is found as small patches included in the ore, or as a filling in small fissures or fault zones in the ore body, and also in the country rock near the ore body. There is no relationship between the amount of hisingerite and the depth from the present earth surface, that is there are no indications that most of the hisingerite is the result of a weathering process.

Hisingerite is commonly dark brown in color when massive with a somewhat vitreous luster. Also dark green masses were observed which may turn brown in daylight.

Under the microscope hisingerite is commonly brown or golden-yellow in color and isotropic. Some portions of the hisingerite show polarization tints, the isotropic areas show a mottled appearance and a gradation can be seen between an isotropic and an anisotropic area. However, as shown in the differential thermal analysis curves mentioned below, no differences were recognized between the curves of the isotropic and the anisotropic grains. From this it is inferred that the birefringence is due to "tension polarization" commonly recognized in gel materials.

The chemical analysis of the hisingerite which was concentrated and carefully selected for purity is shown in Table 1. It contained very small amounts (less than 1%) of pyrite and calcite. It is noteworthy that this analysis shows more adsorptive water than has been reported in other analyses (1) (2) (3).

TABLE 1. CHEMICAL ANALYSIS OF HISINGERITE

	(1)	(2)	(3)	(4)
SiO <sub>2</sub>	27.99%	35.57%	38.14%	32.85%
Al <sub>2</sub> O <sub>3</sub>	none	0.38	—	2.64
Fe <sub>2</sub> O <sub>3</sub>	34.25	39.20	36.66	40.70
FeO	0.54	4.80	0.84	—
CaO	2.33	0.85	none	1.50
MgO	none	1.60	2.45	2.05
H <sub>2</sub> O(—)	27.89(<110° C.)	6.00(<110° C.)	13.20	11.40(<110° C.)
Ig. Loss	7.11*	11.60(>110° C.)	8.53	7.90(>110° C.)
Total	100.11	100.12	99.82	100.04
SiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	2.16	2.40	2.80	2.14

(1) Hisingerite from the Kawayama Mine.

(2) After G. M. Schwartz (3). TiO<sub>2</sub>, 0.12%.

(3) After D. F. Hewett and W. T. Schaller. MnO tr.; P<sub>2</sub>O<sub>5</sub>, SO<sub>4</sub>, and CO<sub>2</sub> absent.

(4) After A. C. Hawkins and E. V. Shannon (1): (canbyite) MnO 0.74%, TiO<sub>2</sub>, 0.26%.

\* Ignition loss above 110° C.

The *x*-ray powder pattern of the specimen analyzed chemically shows three broad bands between 1 Å and 15 Å, as shown in Table 2. The powder lines of pyrite and calcite are not present because of their small amounts. The diffuseness of each band is symmetrical with no indications of two dimensional imperfection. Although it is very difficult to evaluate the powder pattern because of the presence of only three broad bands, reference to the summarized data of the *x*-ray powder patterns of clay minerals prepared in the writer's laboratory shows that the three bands are in approximate correspondence to a few strong lines of nontronite.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR HISINGERITE

<i>I</i>	<i>d</i>
ss	4.4 <sub>4</sub> Å
ss	2.6 <sub>1</sub>
ss	1.5 <sub>0</sub>

Three broad bands of the hisingerite from the Kawayama Mine.

The spacing (*d*) is calculated from the measurement of the middle part of each broad band. The radius of the camera used is 56.8 mm. Filtered Cr radiation.

However, it is noteworthy that the strong line of nontronite occurring at 12~15 Å is not present. This is one of the important lines of nontronite.

The differential thermal analysis curve of the specimen analyzed chemically is shown in Fig. 1. The curve shows a strong sharp endothermic reaction at 134° C. and a weak exothermic peak at 907° C., with a trace of an exothermic peak at 463° C.~483° C. caused by pyrite. The endothermic reaction of calcite was not observed because it is eliminated by the exothermic reaction of hisingerite. The type of the curve is quite similar to that of allophane, heated at the same rate, although the exothermic peak is shifted slightly downward from that of allophane (commonly at 957° C.). The differential thermal curves are the same for both the isotropic grains and the anisotropic flakes.

Thus the mineralogical properties of hisingerite show that it is largely a gel mineral like allophane and contains submicroscopic nuclei of a

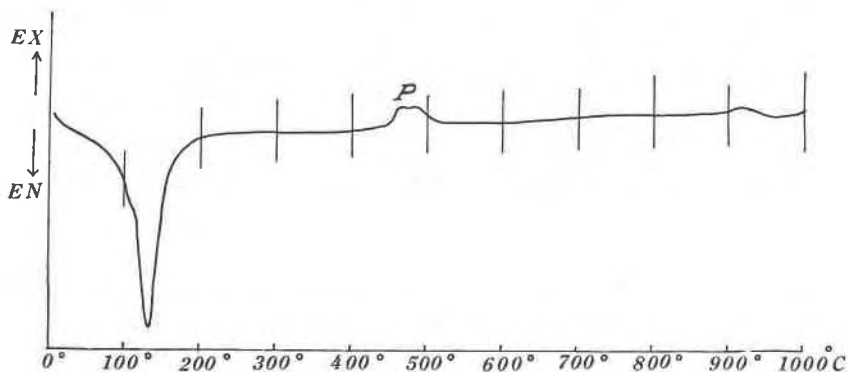


FIG. 1. Differential thermal analysis curve of hisingerite from the Kawayama Mine, Yamaguchi Prefecture, Japan. A mixture of 25 per cent hisingerite and 75 per cent of alumina was used. Pure hisingerite produced such a violent reaction during its dissociation that the cover of the sample holder was blown off. The specimen is composed chiefly of apparently isotropic grains. The rate of heating is 10° C. per minute. P=pyrite.

crystalline phase which shows three broad  $x$ -ray bands. It is difficult to identify the crystalline phase, however, the ratio of silica to ferric oxide near 2, as shown in the chemical analysis, strongly suggests that hisingerite may crystallize to a phase with the ideal chemical formula of  $2\text{SiO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This has already been reported as canbyite by A. C. Hawkins and E. V. Shannon (1).

The occurrence of hisingerite shows that it is not the result of weathering but is clearly an alteration product from pyrrhotite and other iron minerals which were attacked by hot spring waters of hypogene origin.

In Japan, hisingerite is also found in other metallic ore deposits, for example, the epithermal copper-quartz vein of the Sano Mine, Wakayama Prefecture and the tin deposit of the Suzuyama Mine, Kagoshima Prefecture. The mineralogical properties of the hisingerite from the Sano Mine agree well with the Kawayama material.

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