

Mikasaite, $(\text{Fe}^{3+}, \text{Al})_2(\text{SO}_4)_3$, a new ferric sulphate mineral from Mikasa city, Hokkaido, Japan

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Abstract

The new ferric sulphate mineral, mikasaite, the Fe analogue of millosevichite was found in Ikushunbetsu, Mikasa city, Hokkaido, Japan. Mikasaite occurs as a sublimate around fractures from which coal gas escapes. The white–light brown coloured mineral shows aggregates of fine porous crystals. The SEM micrographs indicate that the aggregates are hollow spherical crystals of 100 μm average diameter and 1–5 μm thickness. Microprobe analysis, SO_3 by wet analysis and H_2O by moisture evolution analyser gives Fe_2O_3 24.3, Al_2O_3 4.3, Mn_2O_3 0.5, SO_3 46.8, $\text{H}_2\text{O}^{(-)}$ 23.0, total = 98.9 wt.%. The specimen adsorbed a large amount of H_2O on its surface because of its strong deliquescence. As H_2O is not essential to the mikasaite structure, the empirical formula on the basis of 3SO_4 is $(\text{Fe}_{1.56}\text{Al}_{0.44}\text{Mn}_{0.03})_{\Sigma 2.03}(\text{SO}_4)_{3.00}$, ideally $\text{Fe}_2(\text{SO}_4)_3$. The strongest 10 lines in the X-ray powder diffraction patterns, indexed on a hexagonal unit cell are ($d, I/I_0, hkl$): 3.56, 100, 113; 5.99, 28, 012; 4.35, 23, 104; 2.97, 20, 024; 2.72, 20, 116; 2.64, 11, 211; 2.35, 7, 300; 2.24, 6, 303; 1.78, 6, 226; 3.68, 5, 006. It has space group $R\bar{3}$ with hexagonal lattice parameters of $a = 8.14(1)$ and $c = 21.99(8)$ Å.

KEYWORDS: mikasaite, new mineral, ferric sulphate, Japan.

Introduction

A new ferric sulphate mineral, $\text{Fe}_2(\text{SO}_4)_3$, the Fe analogue of millosevichite, was discovered in Ikushunbetsu, Mikasa city, an important coal mining area in Japan. The new species is named mikasaite after the locality. The new species and the name were approved by the Commission on New Minerals and Mineral Names of the I.M.A. (International Mineralogical Association). The type specimen is preserved in the Department of Geology and Mineralogy, Faculty of Science, Hokkaido University, Sapporo, Japan.

Occurrence and genesis

Mikasaite was discovered in Ikushunbetsu, Mikasa city, Hokkaido, Japan ($141^\circ 58' \text{E}$,

$43^\circ 16' \text{N}$). Mikasa city is located on the eastern side of the Ishikari plain which has many large coal mines. The left bank of Ponbetu river in the Ikushunbetsu area is covered by the Ikushunbetsu coal-bearing formation of the Palaeogene period. The coal-bearing formation consists of altered sandstone, siltstone and mudstone containing two or three coal seams. Coal-gas escape fractures have been discovered in this area. There is a difference in the gas volume and temperature between the fractures. The gas temperature for the most active fracture was 307°C and mikasaite occurs as a sublimation mineral around it. Ferric sulphate minerals usually occur as hydrated minerals such as quenstedtite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 10 \text{H}_2\text{O}$], coquimbite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$], paracoquimbite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$] and kornelite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 7 \text{H}_2\text{O}$]. Mikasaite was formed mainly

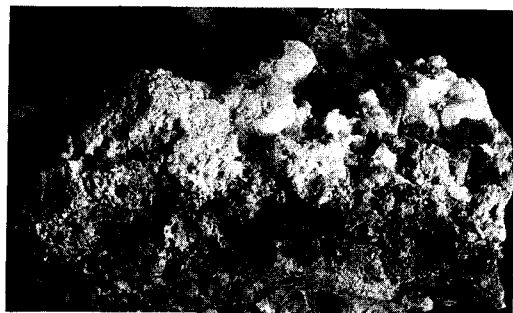


FIG. 1. Mikasaite deposited on the wall rock. Mikasaite is white-light-brown in colour and shows aggregates of fine porous crystals. The field is 8 cm wide.

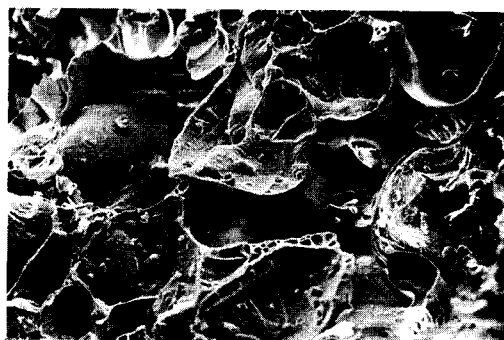


FIG. 2. Scanning electron micrograph shows the aggregates of the hollow spherical crystals. The field is 640 μm wide.

TABLE 1. X-ray powder diffraction data for mikasaite

<i>I</i>	$d_{\text{meas.}}^*$	$d_{\text{calc.}}^{**}$	<i>h k l</i>
28	5.99	5.934	0 1 2
23	4.35	4.335	1 0 4
4	4.10	4.070	1 1 0
5	3.68	3.665	0 0 6
100	3.56	3.558	1 1 3
20	2.97	2.967	0 2 4
20	2.72	2.724	1 1 6
11	2.64	2.645	2 1 1
3	2.40	2.398	2 1 4
7	2.35	2.350	3 0 0
6	2.24	2.238	3 0 3
4	2.08	2.095	1 1 9
2	2.03	2.032	2 1 7
2	1.98	1.978	3 0 6
3	1.92	1.925	3 1 2
2	1.90	1.913	1 2 8
2	1.87	1.865	0 2 10
2	1.84	1.842	1 3 4
6	1.78	1.779	2 2 6
2	1.74	1.740	0 4 2
3	1.69	1.696	2 1 10
2	1.66	1.660	1 3 7
2	1.59	1.593	3 1 8
4	1.546	1.552	3 2 4
4	1.536	1.538	4 1 0
2	1.514	1.517	2 3 5
2	1.505	1.505	4 1 3

* Data obtained with diffractometer with graphite monochromated $\text{CuK}\alpha$ radiation.

** Calculated using cell dimensions $a = 8.14$, $c = 21.99 \text{ \AA}$

because the temperature around gas escape fractures is high enough to form an anhydrous ferric sulphate.

Physical and optical properties

The mineral consists of aggregates of fine porous crystals which may have been formed by the sublimation and the loss of volatile materials (Fig. 1). Scanning electron micrographs show that the aggregate is made up of hollow spherical crystals of 100 μm average diameter and 1–5 μm thickness (Fig. 2). Mikasaite is white–light-brown in colour and the streak is white–light-brown. The refractive indices were measured by the liquid immersion method. Mikasaite is uniaxial(+) and the refractive indices are $\omega = 1.504(2)$, $\epsilon = 1.518(3)$. The crushed fine grained sample is amorphous because it adsorbs H_2O in air and/or the reaction between the immersion liquid and samples. The amorphous grains are easily distinguished because they are isotropic. However, as most of the grains are surrounded by the amorphous part, measurement of refractive index is very difficult.

X-ray crystallography

The X-ray powder diffraction pattern was recorded on a diffractometer with $\text{Cu-K}\alpha$ radiation (35 kV, 20 mA). The X-ray intensity was counted after monochromatization by pyrolytic graphite. The powder pattern (Table 1), indexed on a hexagonal cell, shows good agreement with that of synthetic $\text{Fe}_2(\text{SO}_4)_3$ (Masse *et al.*, 1973). Least-squares refinement was undertaken using seven strong reflections. The parameters obtained were $a = 8.14(1)$ and $c = 21.99(8) \text{ \AA}$ respectively.

TABLE 2. Chemical composition of mikasaite

Oxide	wt. %
Fe ₂ O ₃	24.3
Mn ₂ O ₃	0.5
Al ₂ O ₃	4.3
SO ₃	46.8
H ₂ O ⁽⁻⁾	23.0
Total	98.9

Chemical composition

Mikasaite was analysed using a JEOL electron microprobe operating at 15 kV with a specimen current of 2×10^{-8} A. The standards used were hematite (Fe₂O₃) and synthetic MnO and Al₂O₃. Levels of SO₃ and H₂O were measured by the wet analysis method and by using a DuPont 902-H moisture evolution analyser respectively. No other elements were detected by the energy dispersive EPMA. On the basis of the X-ray powder diffraction data, Fe and Mn are assumed to be Fe₂O₃ and Mn₂O₃ respectively. The average of seven analyses is given in Table 2. As H₂O is not essential to the mikasaite structure (details are discussed later), the empirical formula, calculated on the basis of 3SO₄ is (Fe_{1.56}Al_{0.44}Mn_{0.03})_{Σ2.03}(SO₄)_{3.00}.

TG-DTA analysis

The DTA and TG curves in air with the heating rate of 10°C/min, are shown in Fig. 3. Weight loss, which occurs between 100 and 300°C, is due to the release of adsorbed H₂O. Weight loss at 780°C is due to the decomposition of Fe₂(SO₄)₃ to Fe₂O₃ and SO₃.

Discussion

On the problem of the H₂O content. Samples which were kept in air for a month, have 23.0 wt.% of H₂O because of the strong deliquescence. Mass spectrometry proved that H₂O is released between 100 and 300°C. The present authors consider that the H₂O is not essential to the mikasaite structure, because: (1) Mikasaite has strong deliquescence and a very large surface area which is due to the fine porous texture. Hence it easily adsorbs moisture in air. (2) Mikasaite had not adsorbed H₂O when it was formed because the temperature was more than 300°C around the gas escape fractures. After it cooled to room temperature, it adsorbed moisture in the air. (3) The absolute intensity of X-ray powder diffraction (XRD) peaks of mikasaite decrease gradually as it adsorbs H₂O, however the *d*-value of each diffraction peak and their relative intensity do not change. The XRD data agree completely with

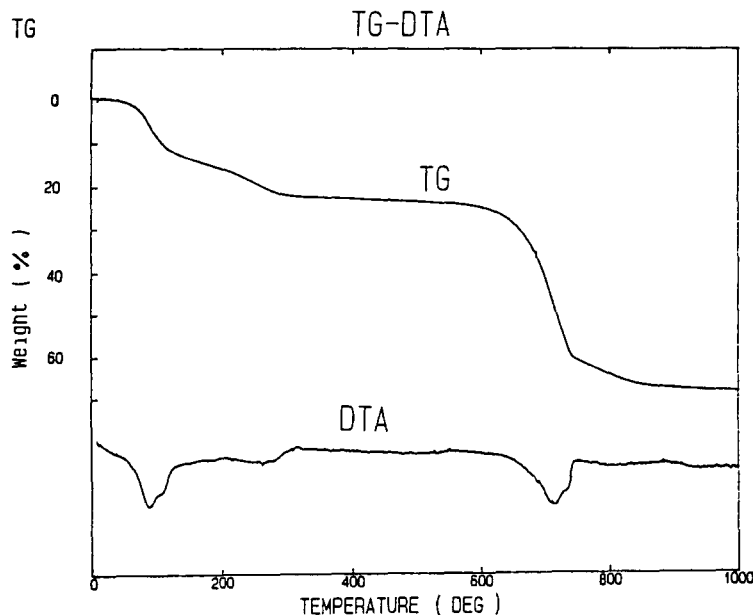


FIG. 3. TG-DTA curves for mikasaite.

that of synthetic $\text{Fe}_2(\text{SO}_4)_3$, JCPDS 33-679, before and after release of adsorbed H_2O . (4) Synthetic $\text{Fe}_2(\text{SO}_4)_3$ shows similar behaviour. We can obtain the synthetic phase by heating the reagent $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ at 400°C , for 1 hr at atmospheric pressure. The product consists of rhombohedral $\text{Fe}_2(\text{SO}_4)_3$ and a small amount of the monoclinic phase of $\text{Fe}_2(\text{SO}_4)_3$ (Kokkoros, 1964). The XRD data of the synthetic phase show good agreement with JCPDS 33-679. When we keep the synthetic phase in air for 14 hr, the absolute intensity of XRD data decreases. However the d -value and the relative intensity do not change. The TG-DTA curves for the sample show the weight loss of 15.4% between 100 and 250°C . The present authors recognized that the weight loss was caused by the release of adsorbed H_2O which had turned part of rhombohedral $\text{Fe}_2(\text{SO}_4)_3$ crystal into an amorphous phase. As the amorphous phase does not contribute to the XRD data, absolute X-ray intensity decreased. These facts indicate that the H_2O present is not structural water. It is adsorbed on the surface of the specimen and dissolves the crystal. Therefore we consider that the H_2O is not essential to the crystal structure of mikasaite.

Relation with millosevichite. Anhydrous trivalent sulphate minerals are not common in nature and millosevichite was a solitary instance. Srebrodol'skii (1974*a,b*) reported millosevichite, occurring in fractures in the rocks from which H_2S and SO_3 were escaping in the coal basin in Russia. It is interesting to note that the occurrence of millosevichite is very similar to mikasaite. The empirical formula of millosevichite reported by Srebrodol'skii (1974*a,b*) is $(\text{Al}_{1.82}\text{Fe}_{0.19})(\text{SO}_4)_{3.00}$. X-ray powder diffraction data of mikasaite show good agreement with that of millosevichite except for peak positions. All of the diffraction peaks of mikasaite shift towards lower angles because of the large cell constants. The X-ray data and chemical analysis data indicate that both millosevichite and mikasaite are isostructural. The Space group $R\bar{3}$ is proposed for mikasaite by analogy of millosevichite and synthetic $\text{Fe}_2(\text{SO}_4)_3$.

Solid solutions in the system $\text{Al}_2(\text{SO}_4)_3$ – $\text{Fe}_2(\text{SO}_4)_3$ were synthesized at 1 kbar, 600°C and unit cell parameters and refractive indices are reported by Miura *et al.* (1994). The data for the synthetic phase as well as for millosevichite and mikasaite are shown in Fig. 4. The c -axes of mikasaite and millosevichite agree well with experimental data; however, the a -axes of both minerals are smaller than that of the synthetic phase. As the length of the a -axis is the same for the synthetic sample at 600°C , 1 kbar and 400°C in air, substitution of metallic elements for Al or Fe

in natural samples is one reason for the deviation from experimental data.

The Gladstone-Dale relationship gives the empirical refractive index from cell volume and chemical compositions (Gladstone and Dale, 1864; Larsen, 1921; Larsen and Berman, 1934). The calculated data with the precise refractive energies of each component (Mandarino, 1976, 1978) are shown by the dashed line in Fig. 4. The averaged refractive indices of millosevichite and the synthetic phase show good agreement with the calculated data; however, the refractive index of mikasaite is lower than that of the synthetic phase and calculated data. The adsorbed moisture and the reaction between sample and immersion liquid is the reason for the discordance of the refractive index of mikasaite.

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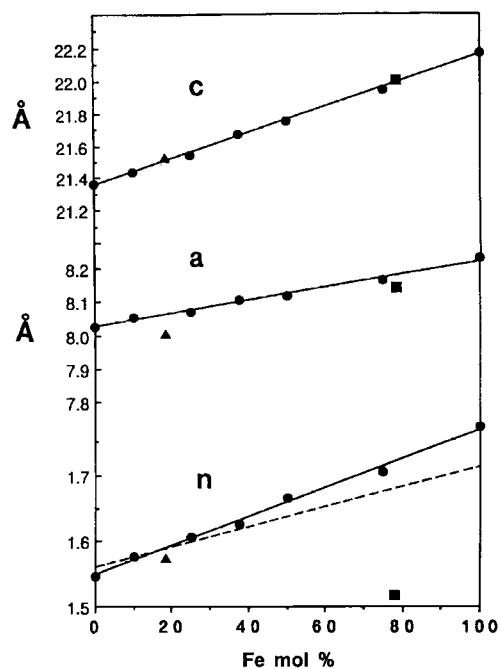


FIG. 4. Correlation between refractive indices, cell constants and atomic percent of $\text{Fe}/(\text{Al} + \text{Fe})$ for the system $\text{Al}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$. circle: synthetic data, triangle: millosevichite, square: mikasaite. Solid lines are fitted by least-squares method. Dashed line shows the calculated refractive index on the basis of Gladstone and Dale relationship (after Miura *et al.*, 1994).

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