Ktenasite from the Hirao mine at Minoo, Osaka, Japan

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Ktenasite was found as a vein forming mineral in the altered shale of Tamba zone of Jurassic age, at the Hirao mine, Minoo, Osaka, Japan. The mineral was also found in a marginal part of sphalerite in the host rock. This is the first occurrence of ktenasite in Japan. Ktenasite occurred as aggregates of flattened prismatic crystals up to 0.5 mm long and 0.1 mm wide, in association with minerals such as chalcopryite, serpierite, smithsonite, hydrozincite, and limonite. An EPMA and CHNS/O analyzer gave the empirical formula $(\text{Cu}_{3.446}\text{Zn}_{1.451}\text{Co}_{0.080}\text{Pb}_{0.018}\text{Ni}_{0.007})_{25.002}(\text{SO}_4)_{2.003}(\text{OH})_{5.998} \cdot 5.99\text{H}_2\text{O}$ on the basis of O = 20. The unit cell parameters were $a = 5.590(1)$, $b = 6.161(1)$, $c = 23.741(3)$ Å, and $\beta = 95.628(3)^\circ$. The Vickers microhardness was 113 kg/mm² and Moh's hardness was 2.5. The density was 2.93 g/cm³. It is likely that ktenasite at Minoo was formed by a reaction of the Cu-bearing fluids with sphalerite.

Introduction

Ktenasite was originally found as a new mineral at the Kamaresa mine in Lavrion, Greece by Kokkoros (1950). It occurred sparingly as blue-green platy crystals up to 1 mm in association with smithsonite, glaucocerinite and serpierite. The mineral was also reported by Rankin (1969) from the Ecton mine, Montgomery County, Pennsylvania, but no data were given, and there must be doubt as to the identification. A green platy mineral from the Glomsrudkollen zinc mine, Modum, Norway was identified as ktenasite by Raade et al. (1977), who proposed the ideal chemical formula $(\text{Cu,Zn})_5(\text{SO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$. Subsequently, the mineral was described from Contrada Trentini, Italy and the Drakewall mine, Cornwall by Mellini et al. (1981) and from the Tui mine, Te Aroha, New Zealand by Courtney and Rodgers (1990). Mellini and Merlino (1978) determined the structure of ktenasite from Miniera Trentin, Italy. Olsen and Lewis (1979) reported that ktenasite from Creede, Colorado was richer in zinc than copper. The zinc analogue of ktenasite was also found from the Smallcleugh and Brownley Hill mines, Cumbria by Livingstone (1991). Moreover, cobaltoan nickeloan-ktenasite was found at Cap Garonne, France by Sarp et al. (1990).

During a mineralogical survey of the Hirao mine at Minoo, Osaka, ktenasite was found. This is the first

occurrence of ktenasite to be reported in Japan. The present paper deals with its mode of occurrence and mineralogical properties.

Occurrence

The Hirao ore deposit is located in shale belonging to Tamba zone of the Jurassic age in Minoo, in the northern part of Osaka. The deposit had been worked for zinc and copper. The host rock has been greatly altered by a hydrothermal solution. The ore and gangue minerals found in the gallery include sphalerite, chalcopryite, pyrite, galena, calcite, quartz, limonite, gypsum, smithsonite, hydrozincite, aragonite, schulenbergitte, brianyoungite, hemimorphite, serpierite, ramsbeckite, brochantite, and aurichalcite. These minerals have been summarized in Ohnishi et al. (2001).

Ktenasite occurs as aggregates of flattened prismatic crystals up to 0.5 mm in length. The mineral was divided into two types according to the mode of occurrence. The first type occurs as a vein forming mineral in association with serpierite, smithsonite, hydrozincite, limonite, sphalerite and chalcopryite in an altered Jurassic formation. The veins cut through the host rock and nodules up to 1 m in size in the host rock, which were composed mainly of sphalerite and a small amount of chalcopryite. The width of the veins is up to 1 mm. The second type occurs in a marginal part of sphalerite in the host rock. A photomicrograph of ktenasite of the second type associated with sphalerite is shown in Figure 1.

Figure 1. Photomicrograph of ktenasite from Minoo. Abbreviations: K, ktenasite; Sp, sphalerite; Ch, chlorite. Scale bar indicates 0.2 mm.

Physical and optical properties

Ktenasite is emerald green to pale green with a vitreous luster in hand specimen, and colorless in thin section. The density measured by heavy liquid is 2.93 g/cm³.

The Vickers microhardness and Moh's hardness are 113 kg/mm² (10g load) and 2.5, respectively. These properties are in agreement with those reported by Kokkoros (1950) and Raade et al. (1977). The mineral exhibits a perfect {001} cleavage in the same manner as that reported by Mellini and Merlino (1978) and Adiwidjaja et al. (1996).

The infrared (IR) absorption spectrum of ktenasite was measured by the KBr method for the region 4000 to 250 cm⁻¹, as shown in Figure 2. The absorption band at 3580 cm⁻¹ is attributed to OH stretching vibration. Broad bands at 3420 and 1630 cm⁻¹ are due to stretching and bending vibrations of H₂O, respectively. Several absorption bands in the region 1000 to 1200 cm⁻¹ and numerous low frequency bands are attributed to the vibrations of [SO₄] tetrahedra and [(Cu,Zn)O₆] octahedra, respectively. The IR spectrum is in agreement with those showed by Raade et al. (1977), Courtney and Rodgers (1990) and Livingstone (1991).

Figure 2. Infrared absorption spectrum of ktenasite from Minoo.

Table 1. X-ray powder diffraction data for ktenasite

1						2		1						2	
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> calc	<i>d</i> meas	<i>I</i>	<i>d</i>	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> calc	<i>d</i> meas	<i>I</i>	<i>d</i>	<i>I</i>
0	0	2	11.82	11.79	100	11.82	100	2	2	0	2.06				
0	1	1	5.96	5.92	52	5.93	85	2	2	2	2.06	2.06	3	2.061	10
0	0	4	5.91			5.44	5	1	2	7	2.06				
0	1	2	5.46			4.85	90	2	1	6	2.05				
1	0	2	4.85	4.86	40	4.85	90	0	3	1	2.05	2.04	2	2.037	5
0	1	3	4.85			4.26	15	2	2	1	2.04				
1	0	4	4.26			4.12	30	1	2	8	2.04				
0	1	4	4.26	4.12	16	4.12	30	2	2	3	2.03	2.01	5	2.008	5
1	1	0	4.13			4.02	10	0	1	11	2.03				
1	1	1	4.12			3.947	20	2	1	8	2.01				
1	1	1	4.02	3.94	18	3.881	10	2	2	2	2.01	1.967	3	1.962	5
0	0	6	3.94			3.754	20	0	2	9	2.00				
1	0	4	3.86			3.377	15	0	0	12	1.969				
0	1	5	3.75	3.75	17	3.227	5	1	1	11	1.965	1.926	10	1.920	5
1	0	6	3.37			3.083	10	2	2	3	1.962				
1	1	5	3.23			3.067	10	2	2	5	1.944				
0	2	0	3.08	3.07	4	2.955	50	1	0	12	1.916	1.887	2	1.879	5
1	0	6	3.07			2.955	50	2	2	4	1.906				
0	1	7	2.96			2.785	60	1	3	3	1.886				
1	1	6	2.96	2.96	23	2.785	60	2	2	6	1.886	1.838	1	1.838	5
0	0	8	2.95			2.688	60	0	1	12	1.875				
2	0	0	2.78			2.665	50	1	2	9	1.837				
1	1	7	2.71	2.70	18	2.620	5	1	3	5	1.806	1.805	1	1.804	5
1	2	0	2.69			2.620	5	3	0	2	1.805				
1	2	1	2.69			2.620	5	1	0	12	1.801				
1	2	1	2.66	2.66	11	2.620	5	3	0	3	1.768	1.766	2	1.768	5
0	1	8	2.66			2.620	5	3	1	4	1.746				
1	2	2	2.65			2.620	5	3	0	6	1.745				
2	0	2	2.65	2.59	23	2.620	5	1	2	11	1.720	1.720	5	1.720	10
2	0	4	2.62			2.584	70	2	0	10	1.719				
1	2	2	2.60			2.584	70	0	0	14	1.688	1.687	3	1.687	5
1	2	3	2.59	2.53	7	2.535	10	2	0	12	1.687				
0	2	5	2.58			2.535	10	3	0	8	1.645				
2	1	1	2.54			2.530	5	3	2	1	1.594	1.592	5	1.593	30
2	1	0	2.54	2.50	6	2.530	5	3	2	2	1.592				
2	1	2	2.53			2.496	10	3	2	3	1.583	1.581	4	1.582	10
1	1	7	2.52			2.496	10	1	0	14	1.573				
1	0	8	2.51	2.50	6	2.496	10	1	2	13	1.541	1.540	7	1.540	7
2	1	1	2.50			2.433	20	0	4	0	1.540				
1	2	4	2.50			2.433	20	3	1	9	1.539	1.532	6	1.532	6
1	1	8	2.49	2.43	8	2.433	20	2	3	5	1.532				
2	1	2	2.43			2.409	5	0	4	3	1.512	1.511	2	1.511	2
2	0	4	2.43			2.409	5	1	4	0	1.484				
0	2	6	2.43	2.41	8	2.409	5	0	3	11	1.484	1.484	3	1.484	3
0	1	9	2.42			2.385	40	1	4	1	1.484				
2	1	4	2.41			2.385	40	1	4	2	1.478	1.477	3	1.477	3
1	2	4	2.41	2.39	15	2.385	40	0	0	16	1.477				
2	0	6	2.38			2.320	5	2	2	11	1.437	1.436	2	1.436	2
1	1	8	2.32			2.320	5	2	3	9	1.437				
2	1	5	2.32	2.29	5	2.296	20	3	1	11	1.436				
1	2	5	2.29			2.269	5	0	1	16	1.436	1.411	1	1.411	1
1	1	9	2.29			2.269	5	3	1	9	1.411				
0	2	7	2.28	2.16	15	2.269	5	1	3	11	1.411				
1	2	6	2.27			2.200	10	3	2	7	1.393	1.392	2	1.392	2
2	1	4	2.26			2.200	10	2	3	10	1.393				
0	1	10	2.21	2.13	7	2.200	10	4	0	0	1.391				
1	2	7	2.16			2.154	40	2	0	14	1.384	1.383	2	1.383	2
2	1	5	2.15			2.154	40								
1	1	9	2.15	2.13	7	2.130	10								
2	0	8	2.13			2.130	10	<i>a</i> (Å)			5.590 (1)			5.598	
0	2	8	2.13			2.130	10	<i>b</i> (Å)			6.161 (2)			6.121	
2	1	7	2.12			2.130	10	<i>c</i> (Å)			23.741 (3)			23.762	
								β (°)			95.628 (3)			95.55	

1. Hirao mine, Minoo, Osaka, Japan (The present work).

2. Glomsrudkollen zinc mine, Modum, Norway (Raade et al., 1977).

X-ray study

Because of remarkable preferred orientation, the X-ray powder diffraction pattern for the ktenasite was obtained using a Gandolfi camera, 114.6 mm in diameter at the National Science Museum, Tokyo. The data were recorded on an Imaging Plate with Ni-filtered CuK α radiation, and processed with a Fuji BAS-2500 bio-imaging analyzer and with a computer program by Nakamuta (1999). The refractions of ktenasite from Minoo were indexed on the monoclinic cell reported by Raade et al. (1977). The unit cell parameters calculated from the data with internal Si standard (NBS, #640b) are $a = 5.590(1)$, $b = 6.161(2)$, $c = 23.741(3)$ Å, and $\beta = 95.628(3)^\circ$. The data are given in Table 1, and compared with those of ktenasite from Norway (Raade et al., 1977).

Chemical composition

The chemical composition of ktenasite from Minoo was obtained using an electron microprobe analyzer (JEOL

JSM-5410LV+JED-2140) with the exception of H₂O. The accelerating voltage was 15kV and the beam current was 0.15nA, and areas of approximately 5 x 5 μ m were scanned for 100 seconds. The concentration of H₂O was determined by a Perkin-Elmer CHNS/O analyzer (2400II) using a 2 mg sample of handpicked crystals under a binocular microscope. The empirical formula of ktenasite from Minoo is $(\text{Cu}_{3.446}\text{Zn}_{1.451}\text{Co}_{0.080}\text{Pb}_{0.018}\text{Ni}_{0.007})_{\Sigma 5.002}(\text{SO}_4)_{2.003}(\text{OH})_{5.998} \cdot 5.99\text{H}_2\text{O}$ on the basis of O = 20. The results are given in Table 2, and compared with those reported by Kokkoros (1950), Raade et al. (1977), Olsen and Lewis (1979), Courtney and Rodgers (1990) and Livingstone (1991). Although a small part of Cu and/or Zn seems to be replaced by Co, Pb, Ni, and Fe, the chemical composition of ktenasite from Minoo is very close to those reported by Raade et al., (1977) and Courtney and Rodgers (1990). The chemical composition, for example the values of H₂O and SO₃, however, did not agree with analytical data reported by Kokkoros (1950) and Olsen and Lewis (1979). The mineral was also easily soluble in dilute hydrochloric acid, but insoluble in ammonia water.

Table 2. Chemical composition of ktenasite

	1	2	3	4	5	6
Weight percentages						
CuO	37.87	32.44	37.9	37.55	12.4	2.84
ZnO	16.31	28.14*	16.6	16.29	48.0	52.96
CoO	0.83	----	----	----	----	----
PbO	0.54	----	----	----	----	----
NiO	0.07	----	----	----	----	----
FeO	tr.	----	----	----	----	----
SO ₃	22.15	19.92	24.0	22.7	22.0	21.97
H ₂ O	22.38	19.50	22.0	23.49*	17.6*	22.23
Total	100.15	100.00	100.50	100.00	100.00	100.00
Mole ratios (basis : O=20)						
Cu	3.446	3.158	3.402	3.341	1.224	0.262
Zn	1.451	2.678	1.457	1.417	4.632	4.746
Co	0.080	----	----	----	----	----
Pb	0.018	----	----	----	----	----
Ni	0.007	----	----	----	----	----
Fe	----	----	----	----	----	----
S	2.003	1.926	2.14	2.004	2.158	2.0
H	17.982	16.766	17.44	18.458	15.342	18.0

1. Hirao mine, Minoo, Osaka, Japan (The present work).

2. Kamaresa mine, Lavrion, Greece (Kokkoros, 1950).

Zinc was not determined ; H₂O as loss on ignition.

3. Glomsrudkollen zinc mine, Modum, Norway (Raade et al., 1977).

4. Tui mine, Te Aroha, New Zealand (Courtney and Rodgers, 1990).

5. Commodore mine, Creede, Colorado, USA (Olsen and Lewis, 1979).

H₂O was not determined.

6. Smallcleugh mine, Nenthead, Cumbria, UK (Livingstone, 1991).

Analyses from raw data calculated using the same Zn:Cu ratio and stoichiometric SO₃ and H₂O values.

* by difference.

Discussion

Kokkoros (1950) proposed the chemical formula of ktenasite from the type locality to be $(\text{Cu,Zn})_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. Subsequently, Olsen and Lewis (1979) confirmed the chemical formula. Raade et al. (1977), and Mellini and Merlino (1978), however, suggested that the chemical formula proposed by Kokkoros gave a value for calculated density as 3.26 g/cm^3 , which was in poor agreement with the measured density 2.97 g/cm^3 . Raade et al. (1977) and Courtney and Rodgers (1990) proposed the ideal chemical formula of $(\text{Cu,Zn})_5(\text{SO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$. The calculated density of ktenasite from Minoo was 2.96 g/cm^3 , and is in agreement with the measured density of 2.93 g/cm^3 . The chemical formula of ktenasite from Minoo supports the formula proposed by Raade et al. (1977) and Courtney and Rodgers (1990). On the other hand, Mellini and Merlino (1978) determined the crystal structure of ktenasite from Italy as having a chemical formula of $\text{Cu}_{5.2}\text{Zn}_{4.8}(\text{SO}_4)_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$. The ktenasite structure was shown to contain two copper sites of Cu(1) and Cu(2) into which zinc enters, and a pure zinc site also; $\text{Zn}_2(\text{Cu}(1),\text{Zn})_4(\text{Cu}(2),\text{Zn})_4(\text{SO}_4)_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$. They also showed that copper atoms in the Cu(1) site are probably replaced by zinc atoms at higher degree than in Cu(2) site. Therefore, assuming that zinc atoms except the pure zinc site occupy in Cu(1) site, the empirical formula of ktenasite from Minoo can be rewritten $\text{Zn}_{2.000}(\text{Cu}(1)_{2.892}\text{Zn}_{0.902}\text{Co}_{0.160}\text{Pb}_{0.036}\text{Ni}_{0.014})_{\Sigma 4.004}\text{Cu}(2)_{4.000}(\text{SO}_4)_{4.006}(\text{OH})_{11.996} \cdot 11.98\text{H}_2\text{O}$ on the basis of $\text{O} = 40$. $\text{Cu} / (\text{Cu} + \text{Zn})$ ratio of ktenasite from Minoo shows 0.704 which is nearly equal to those reported by Raade et al. (1977) and Courtney and Rodgers (1990).

Ktenasite from Minoo occurs as a vein and in a marginal part of sphalerite in the altered shale, and it is closely associated with sphalerite, and H_2O bearing secondary minerals, such as serpierite, ramsbeckite, hydrozincite, and schulenbergite. The occurrence at Minoo shows that Cu-bearing fluids intruded into the altered shale after mineralization of the ore such as sphalerite, chalcopyrite and so on. It is likely that ktenasite was formed by a reaction of the fluids with sphalerite.

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