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CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR KTENASITE

RIASSUNTO. — La ktenasite è un solfato basico idrato di rame e zinco, con formula

$$Zn_2(Cu_xZn_{8-x})(SO_4)_4(OH)_{12} \cdot H_2O\ ,$$

monoclino, $P2_1/c$, $a \simeq 5{,}6$, $b \simeq 6{,}2$, $c \simeq 23{,}7$ Å, $\beta \simeq 95{,}5°$.

Nuovi ritrovamenti del minerale, a Contrada Trentini (Vicenza) e Drakewall Mine (Cornovaglia), unitamente alla caratterizzazione della ktenasite della 79 Mine (Arizona) e ai dati di letteratura, permettono di definirne i limiti di composizione. Il contenuto di zinco varia da un minimo di tre ad un massimo di otto atomi per cella, su un totale di dieci cationi presenti. La composizione più frequente si riscontra attorno al rapporto rame/zinco uguale a uno. Variazioni di composizione si registrano anche tra due diversi cristalli della stessa località.

Mentre la ktenasite tipo proveniente dal Laurium ha, secondo KOKKOROS (1950), un parametro *a* di 11,16 Å, tutte le tre ktenasiti da noi studiate, come pure il campione di Modum descritto da RAADE et al. (1977), hanno un parametro *a* di 5,6 Å. Dal momento che non sembra esistere ktenasite del Laurium nelle principali istituzioni scientifiche, resta aperto il problema della definizione della specie, se cioè sistano due ktenasiti cristallograficamente differenti (e quali siano allora le modificazioni strutturali o i fenomeni di ordinamento in gioco) o se la descrizione originale necessiti di revisione.

ABSTRACT. — Ktenasite is a hydrate basic copper and zinc sulphate, with unit cell content:

$$Zn_2(Cu_xZn_{8-x})(SO_4)_4(OH)_{12} \cdot H_2O\ ,$$

monoclinic, $P2_1/c$, $a \simeq 5.6$, $b \simeq 6.2$, $c \simeq 23.7$ Å, $\beta \simeq 95.5°$.

Two new findings of the mineral, from Contrada Trentini, Vicenza, Italy and from Drakewall Mine, Cornwall, together with relevant data for ktenasite from 79 Mine, Arizona, are reported. The comparison with previous data leads to specify the extent of copper-zinc substitution, which ranges from three to eight zinc cations per unit cell. The most common composition occurs at copper/zinc ratios nearly equal one.

While all the three studied specimens, as also ktenasite from Modum, are characterized by the unit cell parameter $a \simeq 5.6$ Å, a doubled parameter $a \simeq 11.16$ Å was reported for the holotype ktenasite from Laurium.

Introduction

Ktenasite, first described by KOKKOROS (1950) from the Kamareza Mine, Laurium (Greece), is a hydrate basic copper and zinc sulphate. The mineral was

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reported to be monoclinic, crystallizing in the $P2_1/c$ space group, with $a = 11.16$, $b = 6.11$, $c = 23.74$ Å, $\beta = 95°24'$. The formula was given as:

$$(Cu, Zn)_3 SO_4 (OH)_4 \cdot 2 H_2O .$$

The mineral has been subsequently reported from the Ecton Mine, Montgomery County, Pennsylvania (RANKIN, 1969) and from 79 Mine, Gila Co., Arizona. Unfortunately, no data were published about these two occurrences of the mineral. More recently, RAADE et al. (1977) described ktenasite from Modum (Norway). They proposed:

$$Cu_{3.5} Zn_{1.5} (SO_4)_2 (OH)_6 \cdot 6 H_2O$$

as the chemical formula of ktenasite from Modum and reported the unit cell parameters $a = 5.598$, $b = 6.121$, $c = 23.762$ Å, $\beta = 95.55°$. RAADE et al. (1977) also hypothesized that the doubled value of the a parameter in ktenasite from Laurium might be explained by ordering of Cu^{2+} and Zn^{2+} cations. The crystal structure analysis of ktenasite, led by MELLINI and MERLINO (1978) on crystals from Contrada Trentini, Vicenza (Italy) confirmed the crystal chemical formula proposed by RAADE et al. (1977), as well as the halved value for the unit cell parameter a. Subsequently, OLSEN and LEWIS (1979) described a third documented finding of ktenasite, from Creede, Colorado; unfortunately, unit cell data were not given, probably due to the small size of the crystals.

By the present paper, we report further data on ktenasite. Namely, the specimen previously used by MELLINI and MERLINO (1978) for crystal structure analysis is described; a new finding of ktenasite from Cornwall is reported; further, crystallographic and chemical data for ktenasite from 79 Mine are given.

Description of the specimens

Ktenasite from Contrada Trentini: the mineral was found inside a prospecting pit, located on the northern slope of Monte Naro, not far from Contrada Trentini, Vicenza, Italy. The pit crosses a grey limestone located at the bottom of the anisic series and mineralized by pyrite and sphalerite (GIACOMELLI and OMENETTO, 1969). Several sulphide minerals have been occasionally recorded: chalcopyrite, galena, pyrrothine, marcasite, tennantite and enargite (BURTET et al., 1969; BOSCARDIN et al., 1975; ZORDAN, 1977). The alteration of these primary minerals leads to the formation of secundary minerals like gypsum, goethite, azzurrite, malachite, hydrozincite, baryte, hemimorphite, aurichalcite and serpierite (BOSCARDIN, 1979).

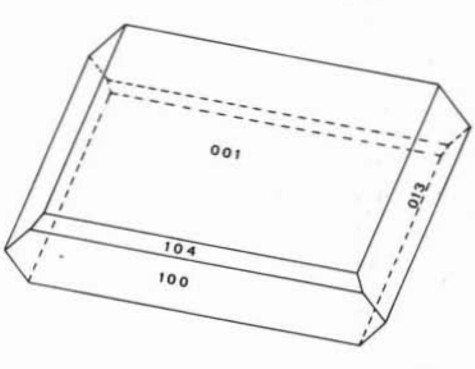

Fig. 1. — Typical habit of ktenasite from Contrada Trentini.

Ktenasite occurs as thin platelets associated with gypsum. It is found as well crystallized specimens, emerald green in colour, with vitreous lustre. The crystal size approaches 1 mm; the habit is tabular, owing to the development of the {001} form. Also the forms {100}, {013}, {104} are present. The most common cleavage is (001). The typical habit of the crystal is sketched in fig. 1. The density, measured by heavy liquid methods, is 2.97 g cm^{-3}.

Ktenasite from Cornwall: the Drakewalls Mine, Gunnislake, Cornwall, is known for previous reports of other hydrate basic copper sulphates (Knight and Barstow, 1970), namely posnjakite and langite. A sample from the Drakewall Mine, constituted by very small crystals, revealed the presence of ktenasite, together with more abundant langite.

Ktenasite occurs as small (up to 50 µm), well crystallized blue green platelets; langite as larger, badly crystallized, blue platelets. {001} is the most developed form.

Ktenasite from 79 Mine: the specimen we studied is constituted by a fragment of quartz, partially covered by crystals of pyrite and galena. A thick crystalline crust coats the quartz matrix. The crust is constituted by several alteration minerals. We identified anglesite, subordinate brochantite, olivenite and ktenasite itself. The crystals of ktenasite are small (up to 50 µm), poorly crystallized, with no definite habit.

X-ray crystallography

The X-ray powder diffraction patterns were recorded by the Gandolfi method, using a 114.6 mm diameter camera and nickel filtered copper radiation. All our patterns closely fit the data published by Raade et al. (1977) and support their interpretation of the pattern given by Kokkoros (1950). No line at $d = 7.19$ Å was recorded. Such a line, reported also by Olsen and Lewis (1979), has been explained as due to contamination of langite.

A systematic investigation of the unit cell parameters was performed, on several crystals from the three localities. The results are summarized in Table 1, together with the previous data. All the analyzed crystals are characterized by halved value for the *a* parameter, with respect to the holotype specimen. Several efforts to reinvestigate ktenasite from Laurium were unsuccessful. Indeed, as we know, no recorded specimen seems to exist in the most important museums, or also in the Tessaloniki University.

In our opinion, this results in an ambiguous characterization of the mineral. On one hand, we can postulate the existence of two different phases, both named ktenasite, closely related amongst them. The most common and diffuse would be the 5.6 Å ktenasite, while the 11.2 Å parameter would be characteristic of the Laurium ktenasite. On the other hand, we should be obliged to admit the presence of some shortcoming, occurred during the first study of the mineral.

TABLE 1
Unit cell parameters

	Contrada Trentini 1)	Cornwall 2)	79 Mine 2)	Modum 3)	Laurium 4)	
a	5.589(1)	5.63(2)	5.60(1)	5.598(3)	11.16	Å
b	6.166(1)	6.20(2)	6.22(2)	6.121(4)	5.10	
c	23.751(7)	23.84(4)	23.79(4)	23.762(15)	23.74	
β	95.55(1)	95.8(2)	95.7(3)	95.55(1)	95.2	°
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	

1) Present work, single crystal four circles diffractometer. 2) Present work, Weissenberg photographs. 3) RAADE et al. (1977), Guinier camera. 4) KOKKOROS (1950), Weissenberg photographs.

Chemical analyses

Ktenasite from Contrada Trentini, as also ktenasite from 79 Mine, were analyzed by electron microprobe. No chemical analysis was made on the specimen from Cornwall; indeed, the extremely low quantity at our disposal prevented even an electron microprobe analysis. The specimen from Contrada Trentini was analyzed also by atomic absorption spectrometry (for copper, zinc and sulphur) and by the Carlo Erba 1104 analyzer for hydrogen. The results of the chemical analysis are summarized in Table 2, together with the literature data.

TABLE 2
Chemical analyses of ktenasite

	Laurium (Kokkoros, 1950)		Modum (Raade et al., 1977)		Creede (Olsen and Lewis, 1979)			Contrada Trentini 6)	
	1)	2)	1)	2)	1)	3)	4)	1)	2)
CuO	32.44	5.41	37.9	7.00	12.4	11.6	2.09	27.5	5.15
ZnO	28.14 5)	4.59	16.6	3.00	48.0	45.0	7.91	26.5	4.85
SO_3	19.92	3.30	24.0	4.41	22.0	20.6	3.68	23.4	4.35
H_2O	19.50	14.36	22.0	17.94	17.6 5)	22.7	18.02	20.5	16.95

	Contrada Trentini 7)			Contrada Trentini 8)			79 Mine 9)		
	1)	3)	4)	1)	3)	4)	1)	3)	4)
CuO	32.7	27.0	4.85	44.9	33.4	5.95	29.1	25.9	4.87
ZnO	35.5	29.3	5.15	31.4	23.3	4.05	31.3	27.9	5.13
SO_3	25.4	21.0	3.75	27.8	20.6	3.64	26.3	23.4	4.37
H_2O	-	22.7	18.01	-	22.7	17.84	-	22.7	18.80

1) Weight percent. 2) Atomic ratios based on ten (Cu + Zn) atoms per unit cell. 3) Weight percent, recalculated assuming an ideal content of 22.7 wt.% H_2O and normalizing to 100 %. 4) Atomic ratios, based on ten (Cu + Zn) atoms per unit cell, calculated using the 3) data. 5) Calculated by difference to 100 %. 6) Atomic absorption and elemental analyzer. 7) Electron microprobe, first grain, average of ten homogeneous areas. 8) Electron microprobe, secon grain, average of three homogeneous analyses. 9) Electron microprobe.

The electron microprobe analysis of ktenasite resulted to be far from straightforward, owing to the softness and the low thermal stability of the mineral (Olsen and Lewis, 1979). Indeed, the mineral dramatically dehydrates under the electron beam, leading to oxyde contents higher than expected. Moreover, also the obtainement of well polished surfaces in the microprobe specimens is far from easy.

Owing to the too high oxyde contents, we recalculated all the electron microprobe analyses assuming a constrained, ideal water content (22.7 wt. %) and normalizing the oxyde contents by difference to 100 %. This procedure results in a total of CuO and ZnO contents ranging from 53.8 to 56.6 wt. %. Such values are in agreement with the wet analysis of Raade et al. (1977) (53.5 wt. %) and the present atomic absorption analysis (54.0 wt. %). The highest value is recorded for the Laurium specimen (60.6 wt. %), where ZnO was not analyzed, but calculated by difference to 100 %. Apart from the absolute values, the copper/zinc ratios are not biased, as due to the contiguous atomic numbers, which result in very similar X-ray production efficiencies, absorption and fluorescence effects.

Fig. 2. — Copper and zinc distribution in ktenasite: *a*) Creede; *b*) Contrada Trentini, first grain; *c*) 79 Mine; *d*) Contrada Trentini, atomic absorption; *e*) Laurium; *f*) Contrada Trentini, second grain; *g*) Modum.

Fig. 2 evidentiates the wide variation of copper and zinc contents in ktenasite. It shows also that the most frequent composition is recorded at copper/zinc ratios nearby one. As regards ktenasite from Laurium, it seems interesting to observe that its anomalous *a* parameter cannot be explained on the basis of an anomalous chemical composition.

The analysis of two different grains of ktenasite from Contrada Trentini reveals also the existence of chemical heterogeneity in crystals from the same locality, with copper/zinc ratios which are 0.94 and 1.47 respectively. The individual grains resulted to be homogeneous, when analyzed by an electron beam nearly 10 μm in diameter.

Conclusions

Ktenasite is characterized by wide range of copper-zinc substitution. The known limits are three and eight zinc atoms per unit cell, on a total of ten copper and zinc cations. The results of the crystal structure analysis (Mellini and Merlino, 1978) indicate the presence of three different sites, Cu(1), Cu(2) and Zn, with different crystalchemical behaviour. While Cu(1) and Cu(2) sites are characterized by the usual [4 + 2] coordination of copper (distortion of the octahedron by Jahn-Teller effect), Zn site is a very regular octahedron. In our opinion, substitution of copper for zinc in the Zn site would modify the hydrogen bond network around the $Zn(H_2O)_6$ octahedron, thus preventing copper content higher than eight atoms per unit cell. On the other hand, zinc content can be hypothesized to range from zero to ten cations per unit cell. These observations lead to the proposal of the following crystalchemical formula:

$$Zn_2\,(Cu_xZn_{8-x})\,(SO_4)_4\,(OH)_{12}\cdot 12\,H_2O\,.$$

As final remark, the usefulness of a new study of the holotype ktenasite from Laurium cannot be overemphasized.

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During this study, the electron microprobe facilities present at the Istituto di Mineralogia dell'Università di Modena were used.

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