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New data on ktenasite

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SUMMARY. Ktenasite from Glomsrudkollen zinc mine, Modum, Norway, is monoclinic, space group $P2_1/c$. The cell dimensions are a 5·598, b 6·121, c 23·762Å, β 95·55°. The chemical formula is $(Cu_{3.5}Zn_{1.5})(SO_4)_2(OH)_6.6H_2O$ with $Z = 2$; ρ_{calc} 2·96 g/cm³, ρ_{obs} 2·94 g/cm³. The mineral is biaxial negative with α (colourless) 1·574, β (bluish green) 1·615, γ (light green) 1·628, $2V_\alpha$ 59°.

KTENASITE was originally described by Kokkoros (1950) from the Kamariza mine, Laurium, Greece, where it occurs sparingly as blue-green, platy crystals up to 1 mm, in association with smithsonite, glaucocerinite, and serpierite. The symmetry of ktenasite, determined by Weissenberg studies, is monoclinic, space group $P2_1/c$. Kokkoros concluded from a partial microchemical analysis on 2·5 mg (Table II) that the mineral is a sulphate of copper and zinc with the formula $(Cu,Zn)_3SO_4(OH)_4.2H_2O$; there was, however, poor agreement between the observed and calculated densities.

No other well-established occurrence of ktenasite seems to be reported in the literature. Ktenasite is mentioned by Rankin (1969) from the Ecton mine, Montgomery County, Pennsylvania, but no data are given and there must be doubt as to the identification.

In 1972 a green, platy mineral was detected by amateur collectors on material from the Glomsrudkollen zinc mine, Modum, Norway. It was subsequently identified as ktenasite by Raade, who also noted that Kokkoros's X-ray powder data were obtained on impure material. Some of the Norwegian ktenasite was later sent to Dr. A. Livingstone, Edinburgh, who, because of poor agreement with the published X-ray powder data, asked the British Museum (N.H.) for assistance. A description of this mineral is the subject of the present paper. Specimens are deposited in the British Museum (N.H.), London, the Mineralogical-Geological Museum, University of Oslo, and in the Royal Scottish Museum, Edinburgh.

Occurrence. Glomsrudkollen mine is a contact deposit between quartz porphyry and limestone, situated within the Oslo Region (Goldschmidt, 1911). The dump at the entrance of the lowest adit, now partly removed, was locally rich in sulphides, mainly sphalerite, pyrite, and chalcopyrite. Rock and mineral fragments of the dump were commonly cemented to a sort of breccia by secondary sulphates, mainly gypsum. In some places ktenasite occurred rather abundantly as aggregates of thin platy crystals or laths up to 1 mm, often growing on, and thus younger than, clear gypsum crystals. A thin coating of a pale blue mineral, shown by microchemical tests to be a Cu–Zn–Al sulphate, has so far not been identified. Its X-ray powder pattern has broad and diffuse lines; scanning electron micrographs reveal an aggregate of platy crystals.

The ktenasite-bearing material appeared when the dumps were taken out for road filling. Temporarily, large amounts of bianchite were seen to have precipitated as a white powder

TABLE I. *X-ray powder diffraction data for ktenasite*

	Modum, Norway*			Laurium†	
hkl	d_{calc}‡	d_{obs}	I	d_{obs}	I
002	11·83 Å	11·82 Å	100	11·9 Å	100b
	—	—	—	7·19	30
	—	—	—	6·45B	40
011	5·93	5·93	85	5·86	90
004	5·91				
100	5·57	—	—	—	—
012	5·44	5·44	5	5·36b	40
$\bar{1}$02	5·24	—	—	—	—
102	4·86	4·85	90	4·84	90
013	4·83				
$\bar{1}$04	4·27	4·26	15	4·26	20
014	4·25				
110	4·12	4·12	30	4·09	30
$\bar{1}$11	4·11				
111	4·01	4·02	10	—	—
$\bar{1}$12	3·980	—	—	—	—
006	3·942	3·947	20	3·97	70
104	3·872	3·881	10	—	—
112	3·807	—	—	—	—
$\bar{1}$13	3·764	3·754	20b	3·73	60
015	3·743	—	—	—	—
113	3·549	—	—	—	—
	—	—	—	3·53S	90
$\bar{1}$14	3·500	—	—	—	—
$\bar{1}$06	3·376	3·377	15	3·38	30
016	3·314	—	—	—	—
114	3·272	—	—	—	—
$\bar{1}$15	3·223	3·227	5	3·20B	30
106	3·081	3·083	10	—	—
020	3·061	3·067	10	3·04	60
021	3·035	—	—	—	—
115	3·002	—	—	—	—
022	2·963	—	—	—	—
017	2·958	—	—	—	—
008	2·956	2·955	50	2·95	60
$\bar{1}$16	2·956				
023	2·853	—	—	—	—
200	2·786	2·785	60	2·74S	100
$\bar{2}$02	2·772	—	—	—	—
116	2·752	—	—	—	—
$\bar{1}$08	2·723	—	—	—	—
024	2·718	—	—	—	—
$\bar{1}$17	2·709	—	—	—	—
120	2·682	2·688	60	2·69B	40
$\bar{1}$21	2·679	—	—	—	—
018	2·662	—	—	—	—
202	2·655	2·655	50	—	—

	Modum, Norway			Laurium	
hkl	d_{calc}	d_{obs}	I	d_{obs}	I
121	2·652	—	—	—	—
$\bar{1}$22	2·643	—	—	—	—
$\bar{2}$04	2·620	2·620	5	—	—
122	2·590	2·584	70	2·57	60
$\bar{1}$23	2·576	—	—	—	—
025	2·570	—	—	—	—
$\bar{2}$11	2·545	—	—	—	—
210	2·536	2·535	10	2·53B	60
117	2·526 Å	2·530	5	—	—
$\bar{2}$12	2·525				
108	2·513	—	—	—	—
123	2·504	—	—	—	—
211	2·498	2·496	10b	—	—
$\bar{1}$18	2·488	—	—	—	—
$\bar{1}$24	2·487	—	—	—	—
$\bar{2}$13	2·478	—	—	—	—
212	2·436	2·433	20b	2·42	60
204	2·431				
026	2·417	—	—	—	—
019	2·415	—	—	—	—
$\bar{2}$14	2·408	2·409	5	—	—
124	2·401	—	—	—	—
$\bar{2}$06	2·386	2·385	40	2·38	60
$\bar{1}$25	2·381	—	—	—	—
0.0.10	2·365	—	—	—	—
213	2·354	—	—	—	—
118	2·325	—	—	—	—
$\bar{2}$15	2·321	2·320	5	2·32S	60
$\bar{1}$19	2·291	2·296	20	2·28	30
125	2·288	—	—	—	—
027	2·268	2·269	5	—	—
$\bar{1}$26	2·267				
214	2·259	—	—	—	—
$\bar{1}$.0.10	2·257	—	—	—	—
$\bar{2}$16	2·223	—	—	—	—
0.1.10	2·206	2·200	10b	2·20	20
206	2·178	—	—	—	—
126	2·171	—	—	—	—
215	2·157	2·154	40	2·15	60
$\bar{1}$27	2·150	—	—	—	—
119	2·147	—	—	—	—
$\bar{2}$08	2·133	2·130	10	2·11S	60
028	2·126	—	—	—	—
$\bar{2}$17	2·120	—	—	—	—
$\bar{1}$.1.10	2·118	—	—	—	—
1.0.10	2·105	—	—	—	—
$\bar{2}$21	2·065	—	—	—	—

* Guinier quadruple focusing camera, 22·9 cm diameter, quartz monochromator, Fe–$K\alpha$ radiation (λ 1·93728Å), Pb $(NO_3)_2$ internal standard, visual intensities.

† θ values from Kokkoros (1950), d-spacings and intensities from JCPDS card 13-309 (11·9 on the card is an error for 12·9). Unfiltered Cu-K radiation.

‡ Calculated for a monoclinic cell with a 5·598, b 6·121, c 23·762 Å, β 95·55°. All possible spacings for space-group $P2_1/c$ are listed.

S, B, strongest lines of smithsonite and brochantite respectively.

b, broad line.

TABLE I (*cont.*)

	Modum, Norway*			Laurium†	
hkl	d_{calc}‡	d_{obs}	I	d_{obs}	I
220	2·060	2·061	10	2·04	30
127	2·055	—	—	—	—
$\bar{2}$22	2·055	—	—	—	—
216	2·052	—	—	—	—
221	2·040	2·037	5	—	—
$\bar{1}$28	2·034	—	—	—	—
031	2·033	—	—	—	—
$\bar{2}$23	2·029	—	—	—	—
0.1.11	2·029	—	—	—	—
$\bar{2}$18	2·014	—	—	—	—
032	2·011	—	—	—	—
222	2·005	2·008	5	—	—
029	1·994	—	—	—	—
1.1.10	1·991	—	—	—	—
$\bar{2}$24	1·990	—	—	—	—
033	1·975	—	—	—	—
0.0.12	1·971	—	—	—	—
$\bar{1}$.1.11	1·965	—	—	—	—
223	1·959	1·962	5	—	—
217	1·947	—	—	—	—
128	1·942	1·941	5b	1·938S	70
$\bar{2}$25	1·940				
208	1·936	—	—	—	—
034	1·929	1·926	10	—	—
$\bar{1}$29	1·922	—	—	—	—
$\bar{1}$.0.12	1·917	1·920	5	—	—
130	1·916	—	—	—	—
$\bar{1}$31	1·915	—	—	—	—
$\bar{2}$19	1·911	—	—	—	—
131	1·905	1·907	5	—	—
224	1·904				
$\bar{1}$32	1·901	—	—	—	—
$\bar{2}$.0.10	1·896	—	—	—	—
$\bar{2}$26	1·882	1·879	5b	1·885	30
132	1·881				
$\bar{1}$33	1·876				
0.1.12	1·876				
035	1·873	—	—	—	—
0.2.10	1·871	—	—	—	—
$\bar{3}$02	1·863	—	—	—	—
300	1·857	—	—	—	—
1.1.11	1·853	—	—	—	—
133	1·848	—	—	—	—
218	1·846	—	—	—	—
225	1·841	1·838	5	1·828	30
$\bar{1}$34	1·841				
129	1·835				
$\bar{1}$.1.12	1·830	—	—	—	—
$\bar{3}$04	1·823	—	—	—	—
$\bar{2}$27	1·818	—	—	—	—
$\bar{1}$.2.10	1·816	—	—	—	—
036	1·812	—	—	—	—
$\bar{2}$.1.10	1·811	—	—	—	—
302	1·808	—	—	—	—
134	1·805	1·804	5b	—	—
1.0.12	1·804				
$\bar{1}$35	1·797	—	—	—	—
$\bar{3}$11	1·785	—	—	—	—
$\bar{3}$12	1·782	—	—	—	—
310	1·777	—	—	—	—
226	1·774	—	—	—	—
$\bar{3}$13	1·769	1·768	5	—	—
311	1·760	—	—	—	—
0.2.11	1·759	—	—	—	—
135	1·756	—	—	—	—
$\bar{2}$28	1·750	—	—	—	—
219	1·749	—	—	—	—
$\bar{3}$14	1·747	1·745	10	1·740	20
037	1·747				
$\bar{3}$06	1·746				
$\bar{1}$36	1·746	—	—	—	—
1.2.10	1·734				
312	1·734	—	—	—	—
1.1.12	1·730	—	—	—	—
304	1·725	—	—	—	—
2.0.10	1·723	1·720	10	—	—
$\bar{1}$.2.11	1·717				
$\bar{3}$15	1·717				
$\bar{2}$.1.11	1·716	—	—	—	—
227	1·706	—	—	—	—
136	1·701	—	—	—	—
	—	—	—	1·701S	90
313	1·700	—	—	—	—
$\bar{1}$37	1·691	—	—	—	—
$\bar{2}$.0.12	1·688	1·687	5	—	—
$\bar{2}$29	1·681	—	—	—	—
$\bar{3}$16	1·679	—	—	—	—
038	1·679	—	—	—	—
314	1·660	—	—	—	—
2.1.10	1·658	—	—	—	—
0.2.12	1·657	—	—	—	—
$\bar{2}$31	1·649	—	—	—	—
230	1·646	1·644	5	1·637	30b
$\bar{3}$08	1·646				
137	1·643				
$\bar{2}$32	1·643				
1.2.11	1·641	—	—	—	—
$\bar{3}$17	1·637	—	—	—	—
228	1·636	—	—	—	—
231	1·636	—	—	—	—
$\bar{1}$38	1·633	—	—	—	—
$\bar{2}$33	1·630	—	—	—	—
$\bar{2}$.1.12	1·627	—	—	—	—
$\bar{1}$.2.12	1·625	—	—	—	—
306	1·621	—	—	—	—
232	1·618	—	—	—	—
315	1·615	—	—	—	—
039	1·612	—	—	—	—

TABLE I (*cont.*)

	Modum, Norway*			Laurium†			Modum, Norway			Laurium	
hkl	d_{calc}‡	d_{obs}	I	d_{obs}	I	*hkl*	d_{calc}	d_{obs}	I	d_{obs}	I
$\bar{2}$.2.10	1·612	—	—	—	—	138	1·584				
$\bar{2}$34	1·610	—	—	—	—	$\bar{2}$35	1·583	1·582	10	—	—
233	1·593					$\bar{3}$23	1·582				
$\bar{3}$21	1·593	1·593	30	—	—	321	1·576				
$\bar{3}$22	1·591					$\bar{1}$39	1·573				
$\bar{3}$18	1·590	—	—	—	—	2.1.11	1·573	1·575	10	1·573	30b
320	1·588	—	—	—	—		—	—	—	1·527S	60
							—	—	—	1·492S	60

between barren rock fragments that were overlain by a sulphide-rich layer, *c.* 1 m thick, but this mineral was soon dissolved by the rain. It was identified by the X-ray powder method, and is rather pure $ZnSO_4.6H_2O$; no iron was detected microchemically.

Physical properties. Ktenasite is transparent, emerald green to bluish green, and has a vitreous lustre. It is non-fluorescent in short- and long-wave ultraviolet radiation. The density is 2·94±0·01 g/cm³, determined by suspension in a mixture of di-iodomethane and acetone. It is biaxial negative, α 1·574, β 1·615, γ 1·628 (all for Na light and ±0·002), $2V_\alpha$ (obs.) 59°, $2V_\alpha$ (calc.) 58°. The pleochroism is α colourless, β bluish green, γ light green, and the optical orientation α near c, $\gamma \parallel b$. The agreement with Kokkoros's data is good except for the calculated density (see below).

X-ray crystallography. Rotation and zero, first, and second layer Weissenberg photographs around the a and b axes confirmed the space group $P2_1/c$, but with the a dimension halved as compared with Kokkoros's data. A strong first layer Weissenberg photograph around b showed slight streaks halfway between the 01*l* central line and the first loop 11*l* on one side only, indicating some degree of disorder in the structure.

TABLE II. *Chemical composition of ktenasite*

	Laurium Greece*	Modum, Norway†				Theor. comp.‡	
	Wt %	Wt %	Number of atoms based on O = 40				Wt %
CuO	32·44	37·9	Cu 6·80	9·71	10	CuO	38·52
ZnO	[28·14]	16·6	Zn 2·91			ZnO	16·89
SO_3	19·92	24·0	S 4·28		4	SO_3	22·16
H_2O	19·50	22·0	H 34·89		36	H_2O	22·43
Total	[100·00]	100·5					100·00

* Kokkoros (1950). Zinc was not determined; H_2O as loss on ignition.

† Analysis by C. J. Elliott. Copper was determined by electrolysis; zinc and sulphate gravimetrically as $ZnHg(CSN)_4$ and $BaSO_4$ respectively; H_2O in duplicate (22·2 and 21·8%) using a Perkin Elmer Elemental Analyser.

‡ $(Cu,Zn)_5(SO_4)_2(OH)_6.6H_2O$ with Cu:Zn = 7:3.

An indexed X-ray powder pattern (51 lines) is given in Table I. The refined unit cell dimensions based on 34 uniquely indexed spacings are: a 5·598±0·003 Å, b 6·121±0·004 Å, c 23·762 ±0·015 Å, β 95·55±0·06°, v 810·4 Å³. The powder pattern published by Kokkoros in 1950 was evidently obtained from impure material; admixed smithsonite and brochantite account for most of the extra lines; the rather strong line at 7·19 Å could be explained by langite or spangolite leaving only one or two still unexplained lines and intensities (*cf.* Table I).

Chemical composition. An electron-probe scan showed no other elements than Cu, Zn, S, and O present above the 0·1–0·2 % level. A chemical analysis of a 4 mg sample of handpicked crystals is given in Table II. The unit cell is calculated to contain 40 oxygens and from this, and consistent with the space group positions, the formula $(Cu, Zn)_5(SO_4)_2(OH)_6.6H_2O$ is proposed. The Cu:Zn ratio is very nearly 7:3. With a Z value of 2 the calculated density is 2·96 g/cm³, in excellent agreement with the measured density of 2·94±0·01 g/cm³. The density calculated from the Gladstone and Dale rule is 2·82 g/cm³, using the theoretical composition in Table II and specific refractive energies from Larsen and Berman (1934). Kokkoros's formula $(Cu,Zn)_2SO_4(OH)_4.2H_2O$, gives ρ_{calc} 3·18 g/cm³, in much poorer agreement with observation.

Infrared spectrum. The presence of OH groups is shown by the sharp O–H stretching vibration at 3600 cm⁻¹ (fig. 1). A broad band in the region 3100–3500 cm⁻¹ and the rather sharp peak at 1630 cm⁻¹ are due to water of crystallization (stretching and bending vibrations respectively). The ν_3 vibration of the SO_4^{2-} group absorbs strongly in the region 1000–1200 cm⁻¹ with a rather sharp peak at 1090 cm⁻¹.

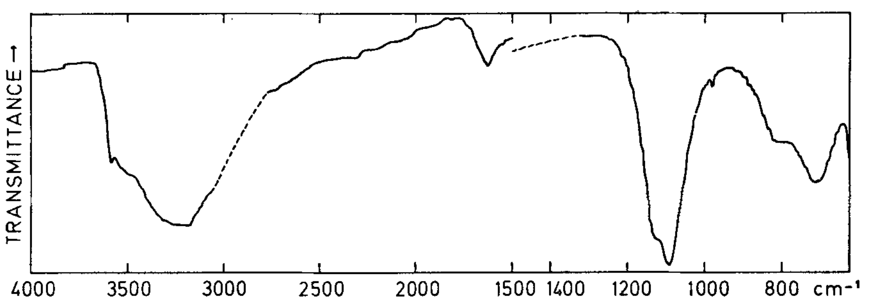

FIG. 1. Infrared spectrum of ktenasite, 0·07% Nujol mull on NaCl disc. Regions of Nujol absorbance are stippled. Note change in scale at 1500 cm⁻¹.

Discussion. Minerals chemically related to ktenasite are langite $Cu_4SO_4(OH)_6.H_2O$, posnjakite $Cu_4SO_4(OH)_6.H_2O$, and wroewolfeite $Cu_4SO_4(OH)_6.2H_2O$. The number of water molecules in these three minerals is uncertain and they may conceivably be polymorphous phases (Dunn and Rouse, 1975); however, ktenasite is the most hydrated of these minerals, indicating a lower temperature of formation. The restricted occurrence of ktenasite may be due to the conditions under which it is stable. Its recent formation in a mine dump must have taken place around atmospheric pressure and in the temperature interval 0 to 30 °C.

The structural chemistry of copper and zinc minerals is rather complex. In spite of stereochemical differences between Cu^{2+} and Zn^{2+}, however, these ions are known to replace each other in several minerals (Ghose *et al.*, 1974). The doubled cell of the Laurium ktenasite could be explained by an ordered arrangement of Cu^{2+} and Zn^{2+} in the structure, compared with disordering in the Norwegian mineral.

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