THE ZINC ANALOGUE OF KTENASITE FROM SMALLCLEUGH AND BROWNLEY HILL MINES, NENTHEAD, CUMBRIA

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Within the Northern Pennine Orefield, at Nenthead [Nat. grid ref. NY 788 430], in the Parish of Alston, Cumbria, are the Smallcleugh and Brownley Hill Mines, which previously worked lead-zinc ores. The specimens on which this investigation has been based are derived mainly from the Middlecleugh First Sun Vein, Smallcleugh Mine. They may be generally described as 'collapsed-rubbly' material with secondary deposition in fissures and cavities. A sample from Brownley Hill Mine is very similar in origin.

A small suite of specimens collected underground at the Smallcleugh and Brownley Hill Mines contain blue-green and blue grains which have been identified as the rare species ktenasite, $(Cu,Zn)_5(SO_4)_2(OH)_6.6H_2O$, using X-ray powder photography. Energy dispersive X-ray fluorescence and electron microprobe analyses, however, reveal that the ktenasite is zinc-dominant. Raade *et al.* (1977) demonstrated that ktenasite from Modum, Norway, possessed the empirical composition $(Cu_{6.80},Zn_{2.91})_{9.71}(SO_4)_4(OH)_{12}.12H_2O$ [SO_4, OH and H_2O are idealised throughout], containing 37.9% CuO and 16.6% ZnO. The Modum mineral occurs as blue-green, platey crystals up to 1 mm and is associated with gypsum and bianchite, $(Zn,Fe)(SO_4).6H_2O$, on a breccia of rock and mineral fragments; primary sulfides are sphalerite, pyrite and chalcopyrite. Mellini and Merlino (1978) determined the structure of a ktenasite from Miniera Trentin, Italy, which is richer in zinc than that from Modum and gave the unit cell contents as $(Cu_{5.2},Zn_{4.8})_{10}(SO_4)_4(OH)_{12}.12H_2O$ (28.5% CuO and 27.0% ZnO). Olsen and Lewis (1979) demonstrated that a ktenasite from Creede, Colorado, was zinc-dominant and contained 48.0% ZnO and 12.4% CuO, which yields an empirical formula of $(Zn_{8.22},Cu_{2.16})_{10.38}(SO_4)_4(OH)_{12}.12H_2O$. The above formulae show that zinc can replace copper in the

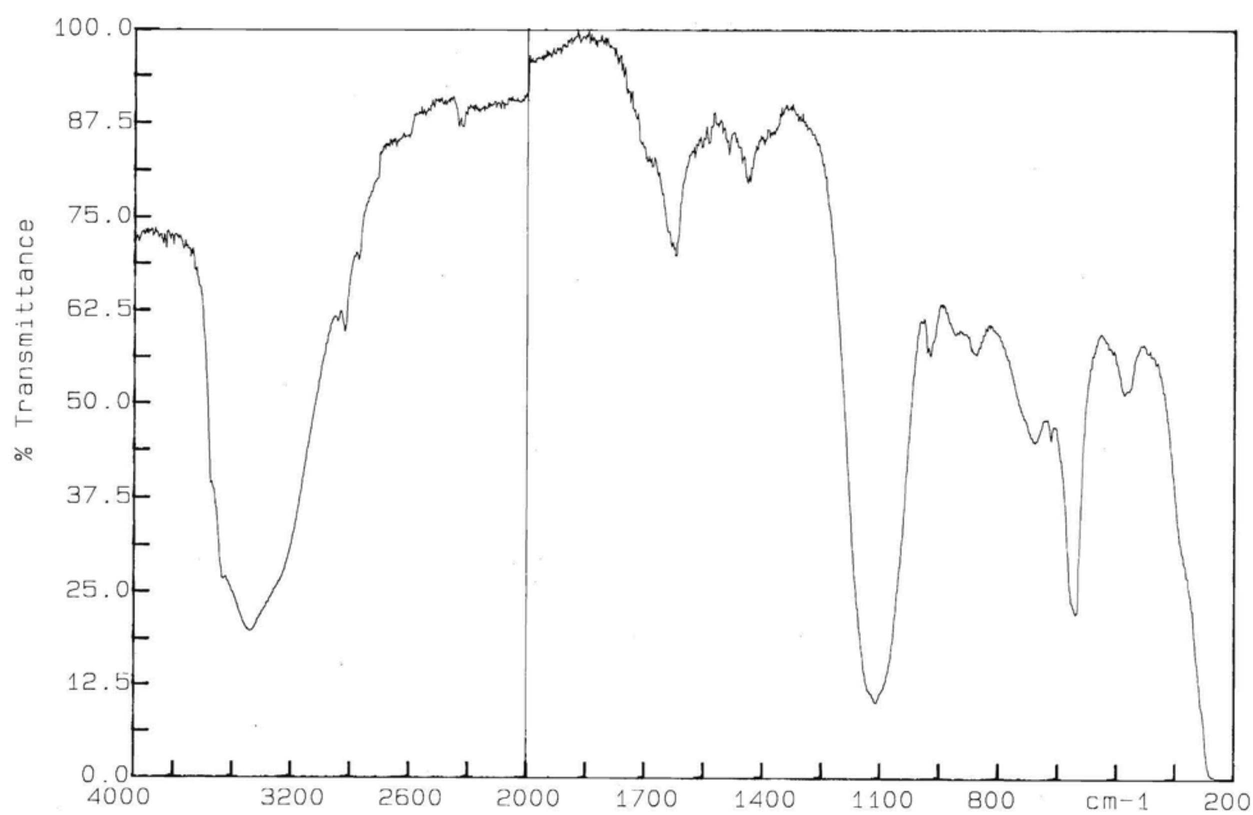

FIGURE 1. Infrared scan of bright-blue ktenasite from Nenthead.

TABLE I

Electron-microprobe analyses of a zinc analogue of Ktenasite.

Analysis	1	2	3	4	5	6	7	8
ZnO	73.19	62.01	61.67	59.09	60.67	60.65	31.52	24.77
CuO	2.79	2.61	4.49	2.74	4.10	3.41	27.19	26.25
SO_3	19.67	17.74	17.20	16.77	17.54	17.20	23.59	22.11
Total	95.65	82.36	83.36	78.60	82.31	81.26	82.30	73.13
Analysis	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
ZnO	27.11	30.21	30.78	29.72	28.89	29.19	35.07	34.99
CuO	28.36	21.90	22.27	21.59	22.31	20.00	21.06	29.07
SO_3	22.79	22.91	23.46	23.50	22.29	23.76	21.82	26.65
Total	78.26	75.02	76.51	74.81	73.49	72.95	77.95	90.71
Analysis	**17**	**18**	**19**	**20**	**21**	**22**	**23**	
ZnO	29.17	30.82	45.57	28.22	26.45	25.56	28.54	
CuO	23.05	20.24	16.38	21.47	21.80	22.84	21.30	
SO_3	22.74	21.85	17.10	23.04	22.43	22.66	22.85	
Total	74.96	72.91	79.05	72.73	70.68	71.06	72.69	

	Average analyses			
	1–6	7–12	13–19	20–23
ZnO	62.88	29.02	33.38	27.19
CuO	3.36	24.59	21.73	21.85
SO_3	17.68	23.06	22.31	22.74
Total	83.92	76.67	77.42	71.78

Analyses 1–6: small polycrystalline area 1.5 mm across, 10–12 μm rasters across a single, bright blue grain; Smallcleugh Mine. Analyses 7-12: bright blue grains on edge of oval-shaped area of blue-green phase; 7-9 on single grain, 10-12 on separate grains; Smallcleugh Mine. Analyses 13-19: separate, bright blue grains, each rastered; Brownley Hill Mine. Analyses 20-23: Grains from the blue-green phase area; Smallcleugh Mine.

species, although the full extent of the replacement has not yet been defined for natural material.

The Nenthead samples contain two colour variants of ktenasite: (1) blue-green and (2) bright blue (the latter is exceedingly rare). Gypsum covers most samples and tiny crystals pervade the ktenasite areas and are included in both types. Smithsonite is finely disseminated throughout some gypsum-bearing regions of the specimens. Additional minerals identified using X-ray powder diffraction methods include dolomite, ankerite, chalcopyrite, malachite, serpierite, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6.3H_2O$, beaverite, $Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6$, namuwite, $(Zn,Cu)_4(SO_4)(OH)_6.4H_2O$ and schulenbergite, $(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10}.3H_2O$. Both the blue-green and bright blue varieties of ktenasite form irregular grains, though generally platey and approximately 0.2-0.3 mm across. The grains are soft and do not fluoresce under long or short wave ultraviolet light. Devoid of cleavage, they are optically biaxial with a negative sign, the blue-green variety having $\alpha = 1.588$, $\beta = 1.604$ and $\gamma = 1.619$ (all ± 0.003 NaD). X-ray powder diffraction data for both types show virtually no differences from those published by Raade *et al.* (1977) or Olsen and Lewis (1979). Cell parameters for the blue-green type, as refined from the powder data, are a = 5.652Å, b = 6.101Å, c = 23.645Å, β = 95.6°, which yields a unit cell volume of 811Å^3. Again there is very little difference in these cell data from those determined for the Modum ktenasite.

An infrared spectrum (Fig. 1) of the blue-green type reveals marked similarities with that of Modum ktenasite. Major differences in copper-zinc ratios are apparent, however, between Modum and Nenthead ktenasites. Although grains of the latter are small, soft and difficult to hand-pick free from impurities (mainly gypsum), electron microprobe and X-ray fluorescence analysis reveals zinc is dominant over copper with variable ratios from sample to sample. Due to the high water content, the mineral is difficult to analyse when using electron microprobe methods; consequently, analyses in Table I are presented as raw data (analyses 1-23), which have been recalculated in Table II utilising the same Zn:Cu ratios and stoichiometric SO_3 and H_2O (analyses 1S-23S). Wide variations in the Zn:Cu ratios

TABLE II
Analyses from Table I calculated using the same Zn:Cu ratio and stoichiometric SO_3 and H_2O values (totals equal 100%).

Analysis	1S	2S	3S	4S	5S	6S	7S	8S
ZnO	53.74	53.53	51.99	53.34	52.25	52.85	29.83	26.96
CuO	2.05	2.26	3.78	2.47	3.53	2.97	25.73	28.57
SO_3	21.97	21.98	21.98	21.97	21.98	21.96	22.09	22.11
H_2O	22.24	22.23	22.25	22.22	22.24	22.22	22.35	22.36
Analysis	9S	10S	11S	12S	13S	14S	15S	16S
ZnO	27.15	32.22	32.25	32.19	31.36	32.98	34.74	30.35
CuO	28.40	23.36	23.33	23.29	24.21	22.60	20.86	25.21
SO_3	22.09	22.08	22.08	22.08	22.08	22.08	22.07	22.09
H_2O	22.36	22.34	22.34	22.34	22.35	22.34	22.33	22.35
Analysis	17S	18S	19S	20S	21S	22S	23S	
ZnO	31.04	33.56	40.95	31.56	30.46	29.33	31.82	
CuO	24.52	22.04	14.72	24.01	25.10	26.21	23.75	
SO_3	22.09	22.07	22.04	22.09	22.09	22.10	22.09	
H_2O	22.35	22.33	22.29	22.34	22.35	22.36	22.34	

	Average analyses			
	1–6S	7–12S	13–19S	20–23S
ZnO	52.96	30.10	33.57	30.79
CuO	2.84	25.46	22.02	24.77
SO_3	21.97	22.09	22.08	22.09
H_2O	22.23	22.35	22.33	22.35
Zn/Cu	18.2	1.15	1.50	1.21

clearly exist from almost 50:50 Zn:Cu through to compositions very close to the pure zinc end-member. On a 1 mg sample the blue-green variety, using a carbon, hydrogen, nitrogen analyser, yielded 20.5% H_2O.

The ktenasite structure was shown to contain two copper sites (CuI and CuII) (Mellini and Merlino, 1978) into which zinc enters, and a pure zinc site also, *viz* $Zn_2(CuI, Zn)_4(CuII,Zn)_4(SO_4)_4(OH)_{12}.12H_2O$. Empirical formulae derived from average analyses 1S-6S and 13S-19S, on the basis of 40 oxygen atoms are as follows, A: $(Zn_{9.48}Cu_{0.52})_{10}(SO_4)_4(OH)_{12}.12H_2O$ and B: $(Zn_{6.0}Cu_{4.0})_{10}(SO_4)_4(OH)_{12}.12H_2O$. By use of the crystal chemical formula, A can be rewritten (for the metal part) as $Zn_2(Zn_4)_4(Zn_{3.48},Cu_{0.52})_4$ and for B, if a 1:1 Zn:Cu site occupancy is assumed, we then have $Zn_2(Zn_2,Cu_2)_4(Zn_2,Cu_2)_4$. However, zinc tends to preferentially enter the CuI site so the occupancy may be greater than 50%. Although formula A clearly demonstrates that Zn can dominate in all sites, the zinc analogue of ktenasite has not been named and must await further investigation.

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