

McBriar, 1958) have been found as fire products at Broken Hill, that the lead oxycarbonates, $2\text{PbCO}_3 \cdot \text{PbO}$ and $\text{PbCO}_3 \cdot 2\text{PbO}$, may also occur.

The status of the lead oxycarbonate from Broken Hill has been clarified by a vote of the IMA Commission for New Minerals and Mineral Names. It is not a mineral since it formed as the result of an artificial process (the mine fire).

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Copper–aluminium analogues of hydrohonnessite and honessite, and woodwardite relationships

AN old nickel mine at Craignure (NM 995011) about 12km southwest of Inveraray, Argyll and Bute District, Scotland, was worked before 1845 (Wilson, 1921). It lies on Forestry Commission ground, very close to one of the numerous, small tributaries of Abhainn Dubhan; and a forest road separates the mine adit to the north from small dumps just to the south. Primary ore collected from the dump close to the mine consists of rapidly oxidizing pyrrhotine and pentlandite, with chalcopyrite. Slightly downstream a small rock dump contains blue–green, copper–aluminium analogues of hydrohonnessite and honessite which partially coat rocks at the surface of the dump. The general lithology of dump material is a chlor-

ite schist with narrow quartz veins and calcite-rich bands. The hydrohonnessite and honessite Cu–Al analogues form incoherent, multi-layer coatings, stringers, and pocket linings. On one specimen botanical debris is coated thus indicating a very recent origin.

Close on 40 X-ray powder photographs from tiny grains (unground) reveal coatings, in the main, to be mixtures of hydrohonnessite and honessite/takovite-like phases. Reevesite is present also as fluffy, citron yellow coatings. The quality of X-ray powder photographs is rather poor (apart from reevesite) with broad reflections and high backgrounds. Nevertheless, when combined with infrared and chemical data it is possible

TABLE 1 X-ray powder data for an 11Å Cu-Al hydrohonnessite-type mineral

Craignure				"Caernarvonshire Woodwardite"		
d meas	I est	hkl	d calc	d	I	JCPDS 17-132
11.3	100	003	11.34	10.9	100	
5.67	10	006	5.67	5.46	60	
3.80	10	009	3.78	3.66	50	
2.61	15	101)	(2.59	2.613	40	
		012)	(2.57			
2.45	10	015	2.43	2.454	20b	
1.50	5	110	1.50	1.535	5b	

a 3.00Å, c 34.02Å

Camera diam. 114.6mm, Fe Kα Mn filter, b = broad line.

TABLE 2. Microprobe analyses of X-rayed grains

	1	2	3	4	5	6	7	8
CuO	16.32	3.31	10.59	16.01	16.90	27.45	3.03	23.48
NiO	5.62	1.31	5.09	28.02	18.63	13.43	2.81	11.58
Al ₂ O ₃	36.72	42.78	40.85	16.39	13.68	28.27	48.43	33.77
Fe ₂ O ₃	0.21	4.54	0.40	4.06	1.42	0.34	0.19	0.32
SO ₃	8.64	8.46	7.93	8.72	8.89	9.35	4.70	8.63
SiO ₂	<u>14.67</u>	<u>9.59</u>	<u>15.93</u>	<u>4.96</u>	<u>2.54</u>	<u>8.16</u>	<u>16.91</u>	<u>10.15</u>
	82.18	69.99	80.79	78.16	62.06	87.00	76.07	87.93
	9	10	11	12	13	14	15	16
CuO	25.52	13.34	27.11	17.20	7.62	22.68	16.32	38.32
NiO	14.47	19.50	13.92	0.53	4.72	1.24	1.82	3.60
Al ₂ O ₃	24.46	32.43	27.16	31.44	12.16	28.63	25.31	17.05
Fe ₂ O ₃	0.09	0.09	0.10	0.44	10.47	0.76	0.26	2.01
SO ₃	8.04	8.02	8.19	4.04	2.36	3.92	3.34	7.33
SiO ₂	<u>9.50</u>	<u>9.95</u>	<u>9.92</u>	<u>13.21</u>	<u>19.10</u>	<u>14.38</u>	<u>15.83</u>	<u>4.03</u>
	82.08	83.33	86.40	66.86	56.43	71.61	62.88	72.34
	17	18	19	20	21	22	23	24
CuO	29.48	29.23	31.83	9.16	20.36	14.87	25.01	29.47
NiO	6.74	7.18	5.84	1.13	1.59	1.17	11.76	8.72
Al ₂ O ₃	25.33	23.81	21.45	33.72	32.53	34.68	20.38	15.23
Fe ₂ O ₃	0.88	0.68	1.47	0.62	0.48	0.45	0.99	0.57
SO ₃	7.67	8.29	7.35	1.50	2.41	2.01	4.34	3.33
SiO ₂	<u>2.69</u>	<u>1.67</u>	<u>4.29</u>	<u>9.71</u>	<u>13.59</u>	<u>11.15</u>	<u>7.57</u>	<u>14.99</u>
	72.79	70.86	72.23	55.84	70.96	64.33	70.05	72.31

Each grouping below indicates a single grain, or fragments thereof.

Analyses 1-5 hydrohonnessite pattern; 1 and 2 from green crust, 3-5 from a yellow layer within the grain.

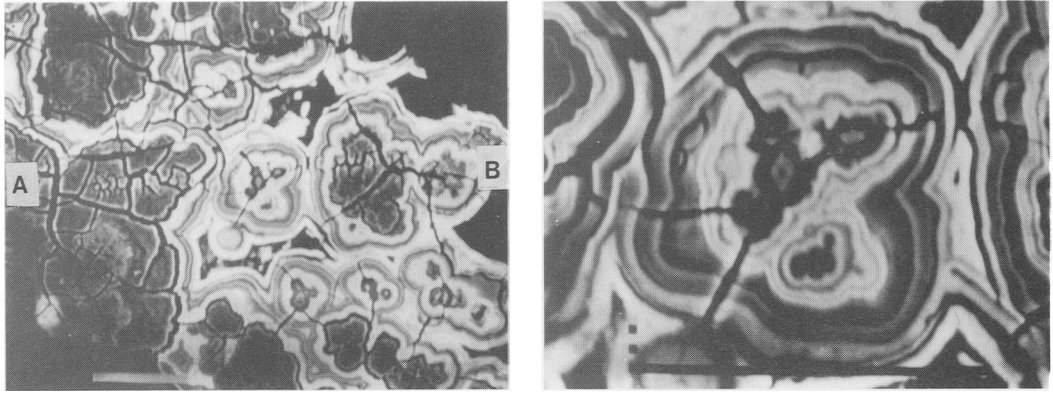
Analyses 6-8 hydrohonnessite pattern; 6 and 8 from green areas, 7 colourless area.

Analyses 9-11 hydrohonnessite pattern; all from green areas. (This grain used for XRD data, Table 1).

Analyses 12-15 hydrohonnessite pattern.

Analyses 16-19 honnessite material.

Analyses 20-24 honnessite/takovite material.



FIGS. 1 and 2. FIG. 1 (left). Back scattered electron image of hydrohonnessite grain showing complex formational features (A–B line scan, see Fig. 3). FIG. 2 (right). Enlargement of central area showing fine banding.

to identify the blue–green material either as a Cu–Al analogue of hydrohonnessite or honnessite (or mixtures of these phases). X-ray powder data produced from a Cu, Al-rich grain, are presented in Table 1 and these data are similar to those published by Bish and Livingstone (1981) for hydrohonnessite from Unst, Shetland. Hydrohonnessite was first established as a new species by Nickel and Wildman (1981) who indexed their powder data with a 3.09 and c 10.80 Å. The Cu–Al analogue a parameter, 3.00 Å, is virtually identical with that of hydrohonnessite whereas c $\approx 3 \times 10.8$ Å. Nickel and Wildman (1981) suggest that the actual

unit cell of hydrohonnessite may well be a multiple of their parameters and Raade *et al.* (1985) also indexed glaucocerinite powder data with a c value $\approx 3 \times 10.8$ Å.

Chemistry Chemical characterization of the Cu–Ni secondary phases was achieved by mounting the unground grains utilized for X-ray validation in resin followed by polishing, and analysis using a Camibax Cameca instrument. The instrument was operated at 20 kV and 10 nA, using either spot or line scans and Cu, Ni and Fe metals, celestine, corundum and wollastonite standards. Infrared spectra reveal water, sulphate and carbo-

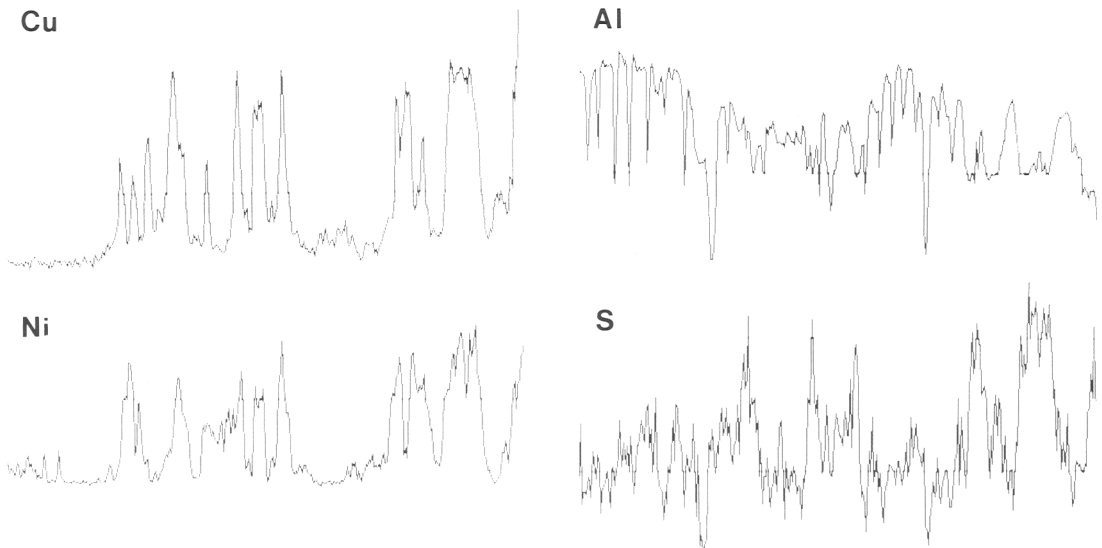


FIG. 3. Line scan for Cu, Ni, Al and S. (A–B).



FIG. 4. Infrared spectra of hydrohonnellite phase (1) and X-ray amorphous, aluminium-rich coating (2) allophane.

nate absorptions with sulphate always dominant over carbonate, except in reevesite.

Twenty-four analyses, from six grains of single phases identified by X-ray diffraction, are presented in Table 2. Apart from Cu dominance over Ni (except in anal. 4, 5 and 10) the analyses reveal high alumina and appreciable silica values. Only three analyses (nos. 2, 4 and 13) show total iron in excess of 2 wt.%; thus the trivalent site in the Craignure hydrohonnellite and honessite structure is fully occupied by Al. Excess Al, over that required for Cu + Ni, is probably present in allophane which would also account for the majority of the silica. After slow dissolution in dilute HCl a skeletal silica residue is formed. Whether this is from the allophane, and/or excess silica is unknown (a non-crystalline, aluminium-rich, white coating is present on one sample and this produced an allophane infrared spectrum).

Back-scattered electron imaging of a hydrohonnellite grain reveals a complex depositional pattern with some bands less than 1 μm in width (Figs. 1 and 2). A line scan (Fig. 3) demonstrates wide variation in composition with Cu dominant over nickel except in a few short regions. The line scans, combined with the high water content of the grains, demonstrate the inherent analytical

difficulties associated with this material. Qualitative XRF analysis of the grain utilized for powder photography, from which data in Table 1 were derived, showed Cu \gg Ni whereas spot EPMA of this grain revealed wide variation in Cu:Ni ratios (Table 2, anal. 9–11).

Bish (1980) demonstrated the relative ease with which SO_4 replaced CO_3 in takovite and related synthetic phases. Furthermore, Bish and Livingstone (1981) published X-ray powder data for sulphate-exchanged takovite and noted a very close similarity between that of honessite and 8.9 \AA SO_4 takovite, and between hydrohonnellite and 10.9 \AA SO_4 takovite. The Craignure material, structurally similar to hydrohonnellite or honessite/takovite and with Cu $>$ Ni, and Al \gg Fe $^{3+}$, demonstrates that six compositions are possible, as follows: (a) honessite and hydrohonnellite with Ni Al, or Cu Al, in both structures; and (b) takovite and a higher hydrate of takovite with Cu fully substituting for nickel.

In exchange experiments (Bish, 1980) showed that related minerals had a pronounced preference for carbonate over sulphate. On this basis it is tentatively suggested that reevesite formed initially and as CO_3 ions became depleted the Cu–Al analogues of hydrohonnellite and honessite

then precipitated. Textural evidence lends some credence to this view, for yellow reevesite coatings underlie blue-green coatings on several samples, although reevesite tends to be associated with calcite-rich bands. Thornber (1975) reported pH values in excess of 7 for solutions in weathering Ni-sulphides; thus the Cu–Al analogues probably precipitated in a SO_4 -rich, alkali environment.

Woodwardite-related mineral The powder data in Table 2 for the analysed Craignure Cu–Al analogue of hydrohonesite are almost identical with those of the Caernarvonshire, N. Wales, “woodwardite” reported on JCPDS set 17–132. From four spot microprobe analyses of the Caernarvonshire “woodwardite” Nickel (1976) reported Cu:Al ratios ranged from 0.62 to 0.82 and that the material contained appreciable silica. A partial “woodwardite” analysis by Din (Raade *et al.*, 1985) revealed CuO and Al_2O_3 values of 34.48 and 16.5 wt.% respectively. If allophane is admixed with the “woodwardite” then the Cu:Al ratio in the latter will change dramatically and approach that of the Cu–Al analogue of hydrohonesite, viz. $\text{Cu}_6\text{Al}_2(\text{SO}_4)(\text{OH})_{16}\cdot 7\text{H}_2\text{O}$ (theoretically this compound contains 52.3% CuO, 11.2% Al_2O_3 , 7.0% SO_3 and 29.5% H_2O). Additionally, the infrared spectrum published by Nickel (1976) of Caernarvonshire “woodwardite” is identical with that of the Craignure Cu–Al analogue of hydrohonesite in which the spectrum of the non-crys-

talline aluminium and silica-rich phase is completely masked (Fig. 4). The Caernarvonshire “woodwardite” may well be a Cu–Al analogue of hydrohonesite.

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