

The crystal chemistry and paragenesis of honessite and hydrohonessite: the sulphate analogues of reevesite

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ABSTRACT. Honessite and hydrohonessite from Unst, Shetland, and Linden, Wisconsin, are sulphate-containing members of the pyroaurite group and are analogous to reevesite. The structural formula can be written $(\text{Ni}_{5.55}\text{Mg}_{0.10}\text{Fe}_{2.35}^{3+})(\text{OH})_{16}(\text{SO}_4)_{1.18} \cdot x\text{H}_2\text{O}$ for the Unst material, with sulphate groups replacing the interlayer carbonate groups in reevesite. Microprobe analyses of the Unst material show amounts of SO_3 in excess of that required to balance all trivalent cations and this may be due to the presence of an amorphous nickel sulphate material. We find no evidence for the presence of trivalent nickel in honessite.

The Unst material occurs in both 8.8 (honessite) and 11.1 Å (hydrohonessite) forms, depending on composition, humidity, and temperature, similar to carboydite, motukoreaite, and SO_4 -exchanged takovite. The Wisconsin material occurs only with an 8.8 Å basal spacing. The increase from the 7.7 Å basal spacing of reevesite is due to the difference in molecular geometry of carbonate and sulphate groups. The presence of the sulphate molecule is unambiguously shown by the infra-red spectra, and the observed bands are consistent with the sulphate groups lying in the interlayer with their trigonal axes parallel to *c*. The Unst material is found intimately mixed in variable proportions with reevesite, distributed in patches on chromite, and the mixed nature is revealed by X-ray powder diffraction, by variations in total SO_3 content, and by the presence of absorptions due to both SO_4^{2-} and CO_3^{2-} in the infra-red spectra.

In 1959 Heyl *et al.* described a basic nickel, iron sulphate mineral which occurred as an alteration product of millerite, violarite, and bravoite (?), all of which form abundant accessory minerals in lead-zinc deposits near Linden, Wisconsin. On the basis of three micro-chemical analyses and limited X-ray powder data (4 lines) the mineral was believed

to be a new species and named honessite. From 1959 to the present, honessite has remained in the literature as an inadequately described species. Applying the results of anion-exchange experiments on pyroaurite-type minerals and using the data of Heyl *et al.* (1959) and Finkelman (personal communication), Bish (1980) concluded that honessite was a sulphate form of reevesite, $\text{Ni}_6\text{Fe}_2^{3+}(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (White *et al.*, 1967).

Macpherson and Livingstone (1974) described several unnamed nickel hydroxides (one blue-green and the second yellow) from the chromite deposits at Hagdale, Unst, Shetland, and further work on the yellow material has shown it to be a mixture of reevesite and honessite in variable proportions. It is from this material that a fuller understanding of the structure, chemistry, and paragenesis of honessite has become possible.

Occurrence and physical properties. The reevesite-honessite-hydrohonessite mixture occurs as very thin, scaly, citron-yellow encrusting films, distributed in patches on chromite. It may be associated with blue-green nickel hydroxide and zaratite but commonly occurs independently and is very soft, easily breaking into tiny flakes. The only sulphides positively identified (by X-rays) in the chromitite are pentlandite and heazlewoodite, and green nickel hydroxide is seen around the latter.

Under high magnification and plane-polarized light, the mixture is obscurely platy to fibrous with a mean refractive index of 1.635. The material is slowly soluble in weak, cold HCl, H_2SO_4 , and HNO_3 but rapidly soluble in hot, very dilute HCl.

X-ray powder data. X-ray powder diffraction data for the yellow crusts were given by Macpherson and Livingstone and a salient feature of the patterns

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is the set of intense 11.1 and 7.7 Å lines of approximately equal intensity. After taking many more powder photographs of very minute single flakes using a 114.6 mm-diameter Debye-Scherrer camera, it became apparent that the 11.1:7.7 Å intensity ratio was not constant and a mixture of two phases was obvious. Electron-probe microanalysis of previously X-rayed flakes which possessed different 11.1 to 7.7 Å intensity ratios enabled the 7.7 Å line to be attributed to reevesite whereas the 11.1 Å line was attributed to the sulphur-bearing phase. The problem was made more interesting by the discovery of two minute flakes which gave an 8.8 Å basal spacing. Subsequent treatment of this material with glycerol for 24 hours resulted in an expansion to 11.1 Å, although the 8.8 Å line did not completely disappear.

X-ray data indexed on a three-layer rhombohedral cell and refined cell parameters for the 11.1, 8.8, and 7.7 Å material are presented in Table I, together with X-ray data for sulphate-exchanged

takovite, $[\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{SO}_4 \cdot 4\text{H}_2\text{O}]$ from Var, France (Bish, 1980). From Table I it should be noted that there is a very close similarity between honessite and 8.9 Å SO_4 -takovite and between hydrohonessite and 10.9 Å SO_4 -takovite. The hydrohonessite pattern is very similar to that of the sulphate-takovite, although the hydrohonessite a parameter is larger. The hydrohonessite pattern shows several lines not indexable on a three-layer rhombohedral cell; the 7.65 Å is due to admixed reevesite and the remaining very weak extra lines are probably due to an unknown impurity. The reevesite is indexed on a three-layer cell with an a parameter of about 3 Å; this indexing scheme is different than that used by White *et al.* (1967) and de Waal and Viljoen (1971) but is consistent with the pyroaurite-type structure determined by Ingram and Taylor (1967) and Allmann (1968).

Infra-red spectra. In order to more fully understand the nature of the anions in these materials, infra-red spectra of the yellow hydroxide and

TABLE I. X-ray powder data for honessite, hydrohonessite, and reevesite from Unst and sulphate-takovite exchanged from natural Var, France takovite

Var, takovite* 30% RH			Honessite		Var, takovite* 100% RH			Hydrohonessite		Reevesite		
<i>hkl</i>	$d_{\text{meas.}}$	<i>I</i>	$d_{\text{meas.}}$	<i>I</i>	<i>hkl</i>	$d_{\text{meas.}}$	<i>I</i>	$d_{\text{meas.}}$	<i>I</i>	<i>hkl</i>	$d_{\text{meas.}}$	<i>I</i>
003	8.95 Å	100	8.84	100	003	10.89	100	11.12	s†	003	7.68	100
006	4.46	52	4.43	40				7.65	vbr	006	3.84	50
009	3.00	8	—	—	006	5.41	40	5.58	s	101	2.64	10
101	2.62	6	2.65	10				(?) 4.31	vw	012	2.59	60
012	2.58	2	2.62	20	009	3.62	20	3.74	ms	104	2.42	5
104	2.50	8	—	—				(?) 3.07	vw	015	2.32	40
015	—	—	2.39	10				(?) 2.89	vw	107	2.07	5
0.0.12	2.24	5	—	—	101	—	—	2.67	ms	018	1.957	20
018	2.06	2	2.09	8	012	2.59	10	—	—	1.0.10	1.741	5
1.0.10	1.86	8	1.90	2	104	2.49	3	—	—	0.1.11	1.640	5
0.0.15	1.77	4	1.79	2	015	2.43	8	2.50	m	110	1.545	30
0.1.11					107	—	—	2.33	mw	113	1.508	30
0.1.14	1.55	2	—	—	018	2.21	5	2.25	mw	116	1.433	10
110	1.513	5	1.54	15	0.0.15	2.16	3	—	—	202	1.330	10
113	1.490	5	1.52	15	1.0.10	2.05	3	2.09	mw	0.0.18	1.285	5
116	1.436	4	1.46	2	0.1.11	1.97	5	2.01	mw	208	1.211	5
					1.0.13	1.81	3	—	—			
					1.0.16(?)	—	—	1.624	m			
					110	1.51	10	1.536	m, sh			
					113	1.482	5	—	—			
					116	1.452	7	1.497	mw			
					1.0.19	1.437	5	—	—			
					119	1.385	5	1.437	w			
					0.1.20							
					1.1.12	—	—	1.339	w			
$a = 3.024(1)$ Å			$a = 3.083(4)$		$a = 3.024(2)$			$a = 3.087(8)$		$a = 3.081(3)$		
$c = 26.74(4)$			$c = 26.71(9)$		$c = 32.47(4)$			$c = 33.4(3)$		$c = 23.05(4)$		

* Bish (1980). † s = strong, m = medium, w = weak, mw = medium weak, vw = very weak, ms = medium strong, vbr = very broad, sh = sharp.

TABLE II. Microprobe analyses of Hagdale honessite, hydrohonessite, and reevesite

	1	2	3	4	5	6	7	8	9	10	11
NiO	43.4	40.0	42.2	40.7	36.7	28.7	33.3	37.5	35.2	48.5	46.9
Fe ₂ O ₃	18.3	18.0	17.6	17.4	15.9	12.6	19.7	15.3	16.1	20.4	22.4
Al ₂ O ₃	—	3.7	—	0.4	—	0.2	0.2	—	—	—	—
MgO	0.5	0.9	0.4	0.5	0.7	0.4	0.6	—	—	—	—
Na ₂ O	—	1.6	0.7	1.6	0.8	0.8	—	—	—	—	—
SO ₃	10.1	12.2	11.3	13.8	10.4	9.3	10.6	3.4	2.5	0.9	0.7
Total	72.3	76.4	72.2	74.4	64.5	52.0	64.4	56.2	53.8	71.0*	70.9*

Formulae on basis of eight cations, i.e. (OH) ₁₆											
Ni	5.65	5.01	5.75	5.56	5.56	5.50	5.16	5.78	5.60	5.64	5.46
Fe	2.23	2.11	2.25	2.24	2.24	2.28	2.84	2.22	2.40	2.22	2.44
Al	—	0.68	—	0.08	—	0.07	—	—	—	—	—
Mg	0.12	0.20	—	0.12	0.20	0.15	—	—	—	—	—
S	1.22	1.43	1.44	1.77	1.47	1.67	1.53	0.50	0.38	0.1	0.08
+2/+3	2.59	1.87	2.55	2.44	2.57	2.40	1.81	2.60	2.33	2.39	2.15

Analyses 1–7 are of 11.1 Å (hydrohonessite) sulphur-rich areas in reevesite and 8 and 9 are of 8.8 Å (honessite) flakes only. Analyses 3 and 4 are two single-spot analyses on the same grain and 8 and 9 are single-spot analyses on two separate grains. On an eight cation basis, the +2: +3 cation ratio is 6:2 for a 3:1 ratio and 5.33:2.67 for a 2:1 ratio. Analyses 10 and 11 are of reevesite.

* The total for number 10 contains 1.2% Cr₂O₃ (0.14 Cr ions/8 cations) and the total for number 11 contains 0.9% Cr₂O₃ (0.1 Cr ions/8 cations).

personal communication) that the mineral contains an amorphous Ni-sulphate. This may well be the case for the Unst hydrohonessite-reevesite mixture. Analyses 8 and 9 have amounts of SO₃ which are too small to balance all trivalent cations if we assume that all iron is present as Fe³⁺. This is very likely due to a mixture with CO₃²⁻-containing material, i.e. reevesite. It may also be due to material containing CO₃²⁻ and SO₄²⁻ mixed on a unit-cell scale but the available infra-red evidence (Bish, 1977) does not support such a conclusion.

The structural, chemical, and paragenetic data presented here support the conclusions of Bish (1980) that honessite is a sulphate form of reevesite. The infra-red spectra clearly show the presence of SO₄²⁻ and are very similar to those given by Bish (1980) for related minerals. X-ray data for the Unst honessite and hydrohonessite are in excellent agreement with the data for other SO₄²⁻-containing pyroaurite-type minerals; sulphate-exchanged takovite (Bish, 1980), carrboydite (Nickel and Clarke, 1976), and motukoreaite (Brindley, 1979) all have approximately 8.8 and 11 Å basal spacings depending on temperature and humidity. Bish (1980) showed that sulphate-exchanged takovite expanded to about 11.5 Å with ethylene glycol, similar to the expansion of the Unst honessite in glycerol. While the type honessite described by

Heyl *et al.* occurred only in an 8.7 Å form, the Unst material occurs in both 8.8 and 11.1 Å forms. Bish (1980) has shown that the sulphate forms of pyroaurite-type minerals exist in both 8.8 and 11 Å forms, depending both on composition and on temperature and humidity. Nickel and Clarke (1976) also observed the same behaviour for carrboydite. It is probable that the type honessite will expand in a hydrous or ethylene glycol atmosphere just as the 8.8 Å Unst material did.

It is noteworthy that we find only Ni(OH)₂ around heazlewoodite, Ni₃S₂, and it is obvious that trivalent cations, Fe³⁺ in this case, are necessary for the formation of pyroaurite-type minerals. To our knowledge, there are no substantiated occurrences of Ni³⁺ in minerals so that we expect honessite and hydrohonessite to form only in proximity to pentlandite, (Fe, Ni)₉S₈. Without thermodynamic data for hydrohonessite, it is difficult to predict its stability range in solution. However, from the law of mass action it follows that less Ni²⁺ will be required for the precipitation of hydrohonessite with high sulphate concentrations than with low concentrations of sulphate. It appears, with even small trivalent ion concentrations, that hydrohonessite will form before pure Ni(OH)₂ as we seldom find Ni(OH)₂ intimately associated with the hydrohonessite. Without further data,

however, it is impossible to determine whether hydrohonestite precipitation is a significant factor in controlling sulphate, Fe, and Ni mobility.

Based on the anion-exchange results of Bish (1980), it is tempting to draw conclusions as to whether the hydrohonestite represents a primary phase or a sulphate-exchanged reevesite. Precipitation of hydrohonestite or reevesite at the low pH's commonly associated with weathering sulphides will require high concentrations of Ni and Fe. However, Thornber (1975) has shown that the pH's of solutions in weathering Ni-sulphide ore bodies and, in particular, of pentlandite, may exceed 7. In general, the pH of solutions from weathering pentlandite and heazlewoodite will tend to be more alkaline than those from pyrite and pyrrhotite. Thus, although our knowledge of the pH and the concentrations of Ni, Fe, SO_4^{2-} , and CO_3^{2-} on a microscopic scale is very limited, Thornber's results plus our chemical data, showing the presence only of Ni and Fe in substantial amounts in hydrohonestite, suggest that honestite may precipitate directly from weathering solutions if SO_4^{2-} concentrations are high enough. Synthesis experiments of carbonate and sulphate forms of pyroaurite-type minerals (Bish, 1977) show that these materials have a marked preference for CO_3^{2-} over SO_4^{2-} ; therefore, precipitation of SO_4^{2-} -containing pyroaurite-type minerals must require either unusually low CO_3^{2-} concentrations or very high SO_4^{2-} concentrations. The predominant occurrence of hydrohonestite intimately mixed with reevesite shows that SO_4^{2-} concentrations were not high enough to preclude the formation of CO_3^{2-} -bearing material. Further work on the solubility of various pyroaurite-type minerals and on the preference of these structures for CO_3^{2-} over SO_4^{2-} must be done before more quantitative

statements can be made regarding the conditions of formation of the various forms of these interesting minerals.

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