

Hydrohonessite—a new hydrated Ni-Fe hydroxy-sulphate mineral; its relationship to honessite, carrboydite, and minerals of the pyroaurite group

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ABSTRACT. Hydrohonessite has a composition that can be expressed by the formula $[\text{Ni}_x^{2+}\text{Fe}_{7-x}^{3+}(\text{OH})_{16}][\frac{2}{3}\text{SO}_4^{2-} \cdot y\text{H}_2\text{O} \cdot z\text{NiSO}_4]$, where x is approximately 2.6, y is 7, and z is 1. The X-ray powder diffraction pattern has strongest lines at 11.0 (10), 5.56 (5), 3.68 (4), and 2.709 Å (3), and can be indexed on a hexagonal unit cell with $a = 3.09$ Å and $c = 10.80$ Å. It is optically uniaxial negative with $\epsilon = 1.59$ and $\omega = 1.63$; bright yellow in hand specimen and transmitted light. Hydrohonessite is the hydrated equivalent of honessite, and is related to carrboydite, motukoreaite, and mountkeithite. These minerals are related to brucite and pyroaurite-type minerals in that they have a layered structure consisting of brucite-like layers separated by about 7 Å of interlayer material consisting predominantly of water, but also containing anions that balance the charge of the brucite-like layer. Hydrohonessite is a secondary mineral resulting from the weathering of Ni-Fe sulphides, and appears to be stable between pH 6 and 7.

HYDROHONESSITE was first found in samples collected in 1971 from underground workings in the Otter Shoot, one of the nickel mines at Kambalda, Western Australia. Although the mineral was regarded as a probable new species at the time, it was not possible to isolate sufficient amounts of the pure mineral to undertake a definitive characterization. The mineral was subsequently found in a sample collected at the Otter Shoot ore dump by L. B. Collins of the Western Australian Institute of Technology, and in a sample taken from a rock dump at the Carr Boyd nickel mine, Western Australia, by J. Just of Seltrust Mining Corporation. In 1974 Macpherson and Livingstone described a yellow mineral from Unst, Shetland, which gave an X-ray diffraction pattern, some lines of which correspond closely to hydrohonessite, and which was subsequently found to be a mixture of hydrohonessite and reevesite (Bish and Livingstone, 1981).

The X-ray powder diffraction pattern of hydrohonessite is characterized by a very strong basal reflection at about 11 Å, and it was not until other minerals of a similar nature, i.e. carrboydite (Nickel and Clarke, 1976), motukoreaite (Rodgers *et al.*, 1977), and mountkeithite (Hudson and Bussell, 1981) were described, and anion-exchange experiments were carried out on pyroaurite-type minerals (Bish, 1980), that the true nature of hydrohonessite became apparent.

The mineral was approved as a new species in 1980 by the IMA Commission on New Minerals and Mineral Names, and the name was approved in 1981. The name was chosen to indicate its relationship to honessite.

Honessite, until recently an inadequately characterized species, has been redefined by Bish and Livingstone (1981) as the sulphate analogue of reevesite, i.e. with SO_4^{2-} taking the place of CO_3^{2-} , and a basal spacing of 8.8 Å. The empirical formula given for honessite by Bish and Livingstone is $(\text{Ni}_{5.55}\text{Mg}_{0.10}\text{Fe}_{2.35}^{3+})(\text{OH})_{16}(\text{SO}_4)_{1.18} \cdot x\text{H}_2\text{O}$, where x is approximately 4. This paper will demonstrate that honessite and hydrohonessite have similar compositions except for additional water in hydrohonessite, to which this mineral's greater basal spacing of 11 Å is attributed.

Occurrence. The hydrohonessite sample collected from the Otter Shoot workings (sample no. 4632) was taken from a wall of stope 103, about 42 m below the land surface. The mineral occurs as a thin surface encrustation of tiny hexagonal crystals on botryoidal quartz and magnesite in a fracture in supergene Ni-Fe sulphides, mainly violarite and pyrite. This hydrohonessite is intimately associated with amorphous silica, making it unsuitable for analysis. Other secondary minerals occurring with the hydrohonessite are magnesite, gaspéite, goethite, and pecoraite.



FIG. 1. Scanning-electron micrograph of hydrohonesite crystals in sample no. 7504.

The sample from the Otter Shoot ore dump (sample no. 7504) consists of a mass of secondary minerals, mainly gaspéite and pecoraite, with some coarse gypsum crystals and minor goethite. The hydrohonesite in this sample occurs as small pockets of tiny hexagonal flakes with a maximum diameter of about 10 μm (fig. 1).

The sample from the Carr Boyd occurrence (sample no. 5764) consists largely of coarse gabbroic rock, with secondary minerals along one fracture surface. The hydrohonesite here occurs in very minor amounts as a fine surface dusting on gypsum, reevesite, pecoraite, and goethite.

Physical and optical properties. The hydrohonesite in all three samples is bright yellow in colour, both in hand specimen and in transmitted light. The hexagonal flakes remain completely extinguished between crossed Nicols when lying flat on the microscope stage, but they are too small to give an optical interference figure. In this position, the flakes have a refractive index of 1.63. On-edge flakes exhibit high birefringence, refractive indices of 1.59, and 1.63 normal and parallel, respectively, to the flake edges, have parallel extinction, and are length-slow. From this it can be deduced that the mineral is uniaxial negative, with $\epsilon = 1.59$, and $\omega = 1.63$. A Gladstone-Dale calculation, using Mandarino's constants (Mandarino, 1976), gives $\bar{n} = 1.633$.

The mineral is too fine-grained to permit measurements of hardness and density to be made. However, the calculated specific gravity, assuming $z = 1/8$, is 2.636.

Composition. It has not been possible to concentrate a sufficient amount of pure hydrohonesite for chemical analysis, and it was therefore necessary to resort to electron-microprobe analysis. Results of the analysis of hydrohonesite from sample 7504 are given in Table I. No additional elements with atomic number above 10 were detected, and CO_2 is assumed to be absent because of lack of visible CO_2 evolution in HCl.

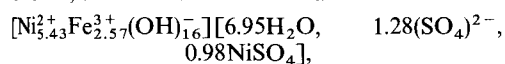
TABLE I. Results of electron-microprobe analysis of hydrohonesite from Kambalda, sample no. 7504

	Analysis, wt % (av. of 3)	Recalculated wt %*	Atomic proportions
<i>Brucite layer</i>			
Ni	25.7	33.2	Ni^{2+} 5.43
Fe	10.3	12.6	Fe^{3+} 2.57
SO_4	15.6	19.2	OH^- 16.00
OH	—	24.0 (calc.)	<i>Interlayer</i>
H_2O	—	11.0 (calc.)	SO_4^{2-} 1.28
			NiSO_4 0.98
		100.0	H_2O 6.95

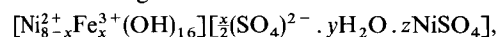
* See text for details.

Unfortunately, it was not possible to obtain a water analysis on the sample, and it is not safe to assume that the shortfall from 100% is due entirely to water, since the electron-microprobe correction procedures are probably inaccurate in the case of very small particles such as these (the flakes are estimated to average about 0.3 μm in thickness). In recalculating the analysis, therefore, a number of assumptions have been made, based on our knowledge of related minerals: (a) the iron is all trivalent, as in honessite, reevesite, and pyroaurite; (b) the number of moles of charge-balancing SO_4^{2-} equals 1/2 the moles of Fe^{3+} ; (c) the remaining SO_4^{2-} is combined with an equal number of moles of Ni^{2+} in the interlayer part of the formula, as in mountkeithite; (d) the number of OH^- ions equals twice the number of Fe^{3+} and Ni^{2+} ions in the brucite part of the structure, as in honessite, reevesite, and pyroaurite; and (e) the number of water molecules in the interlayer part of the formula is such that, added to the oxygen atoms in SO_4 , the total number of interlayer oxygen atoms is 16, i.e. approximate structural close-packing. The formula has been calculated on the basis of 8(Ni + Fe) atoms to facilitate comparison with honessite and minerals of the pyroaurite group. Further justification for some of the assumptions used in the calculations are given in the discussion which follows.

The results of the recalculations are shown in Table I, and lead to the formula:



which can be generalized to



where x, y, and z are approximately 2.6, 7.0, and 1.0, respectively. The content of the first square brackets represents the brucite-like layer; that of the second square bracket, the interlayer material.

X-ray crystallography. The hydrohonessite crystallites are far too small for single-crystal X-ray diffraction analysis. However, good Debye-Scherrer patterns were obtained, and measurements of one of them are given in Table II, together with published data for motukoreaite. The powder pattern can be indexed on a hexagonal unit cell similar to those proposed for carrboydite and motukoreaite, and least-squares refinement of the data gives $a = 3.09 \text{ \AA}$ and $c = 10.80 \text{ \AA}$. The actual unit cell may well be a multiple of these parameters, as has been suggested for the related minerals (Table III), but there is no X-ray evidence for it. The main problem with the small unit cell is that one is forced to accept a fractional Z value, in this case 1/8, as Allmann (1968) did for pyroaurite, or to reduce the formula to the basis of 1(Ni + Fe), which makes direct comparison with the generally

accepted formulae of related minerals more difficult.

The similarity between the X-ray diffraction patterns of hydrohonessite and motukoreaite (Table II) is very evident. The minerals carrboydite (Nickel and Clarke, 1976), mountkeithite (Hudson and Bussell, 1981), and the unnamed Ni-Al sulphate from Caernarvonshire (Nickel, 1976) have similar diffraction patterns, as does the synthetic product 'Green Rust II' (Bernal *et al.*, 1959).

Synthesis and stability of hydrohonessite. A precipitate corresponding to hydrohonessite was obtained by slowly adding an aqueous 0.1 M ferrous sulphate solution to a 0.1 M nickel sulphate solution. The pH of the solution was maintained between 6.0 and 6.5 by the addition of 0.01 M sodium carbonate. Above pH 7.5, Ni(OH)₂ is precipitated, and below pH 6, FeOOH. The oxidation of the iron and precipitation of the hydrohonessite is slow, so care must be taken that the pH does not drop too low during the approximately 24 hours that the precipitation requires. After drying at 25 °C, the precipitate gives a diffuse X-ray powder pattern similar to that of hydrohonessite. Chemical analysis of the precipitate confirmed that the composition is close to that of hydrohonessite. The infra-red spectrum of the synthetic hydrohonessite (fig. 2) is similar to that of honessite (Bish and Livingstone, 1981), and is characterized by strong absorptions due to H₂O and SO₄.

The synthetic hydrohonessite dehydrates slowly at 25 °C, and after ten days it gives a diffuse X-ray diffraction pattern of four lines which correspond to the strongest lines of the honessite diffraction pattern (Bish and Livingstone, 1981), i.e. with a

TABLE II. X-ray powder diffraction patterns of hydrohonessite and motukoreaite

Hydrohonessite*				Motukoreaite (Brindley, 1979)		
$d_{\text{obs.}}$	$d_{\text{calc.}}$	hkl	$I_{\text{obs.}}$	$d_{\text{obs.}}$	hkl	$I_{\text{obs.}}$
11.0	10.8	001	10	11.26	003	10
5.56	5.40	002	5	5.59	006	4
3.68	3.60	003	4	3.720	009	7
†3.53	—	—	1			
2.709	{ 2.700 2.676 }	{ 004 100 }	3	2.646	101	0.5
2.595	2.597	101	2	2.576	103	4
2.394	2.398	102	2	2.392	106	3
2.152	{ 2.160 2.147 }	{ 005 103 }	1	2.160	109	2
†2.085	—	—	1			
1.914	1.907	104	1	1.924	1, 0, 12	2.5
1.675	1.681	105	1	1.710	1, 10, 15	3
1.541	1.545	110	1	1.529	{ 110 1, 10, 18 }	1
1.527	1.529	111	1	1.516	113	1
1.479	{ 1.485 1.494 }	{ 112 016 }	1	1.476	116	0.5

* Sample 7504; Ni-filtered Cu radiation; 57.8 mm Debye-Scherrer camera.

† Gaspéite lines.

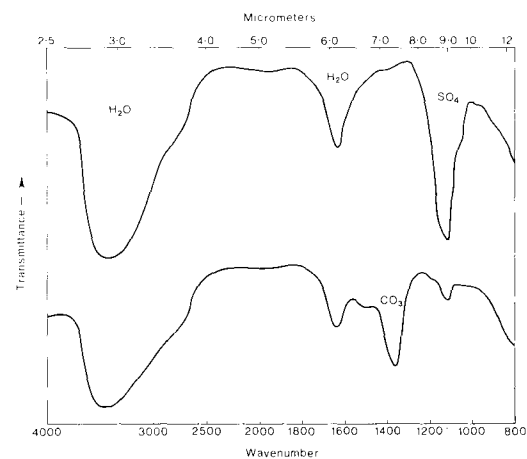


FIG. 2. Infra-red absorption spectra of synthetic hydrohonessite (top) and synthetic hydrohonessite in which the SO₄ has been largely replaced by CO₃.

basal spacing in the neighbourhood of 9 Å; the conversion can also be achieved more rapidly by heating the synthetic hydrohonessite at 110°C. The natural hydrohonessite is more stable than its synthetic equivalent, since it retains its integrity at 110°C, and dehydration requires a temperature between 150 and 170°C. The dehydration experiments indicate that hydrohonessite is the hydrated equivalent of honessite.

Exchange experiments of the type reported by Bish (1980) cause the conversion of hydrohonessite to a reevesite-type product with a basal spacing of about 8 Å. This was achieved for the natural mineral by immersion in 1 M NaOH at 60°C. Similar results were obtained on the synthetic product by immersion in a 0.1 M sodium carbonate solution at room temperature. The IR spectrum of the latter product is characterized by a pronounced absorption peak due to CO₃ and the almost complete disappearance of the SO₄ absorption peak (fig. 2). Apparently when the SO₄ is exchanged for CO₃ or OH, the interlayer H₂O is also expelled.

Some exchange experiments were also done in an attempt to determine if interlayer NiSO₄, the presence of which is indicated by the recalculation of the microprobe analysis, can be readily exchanged in a similar manner to the MgSO₄ in mountkeithite (Hudson and Bussell, 1981), but the results were negative.

Discussion. Hydrohonessite belongs to a group of minerals with basal spacings of 10–11 Å, and which appear to have structures related to that of brucite by the addition of interlayer material. Pyroaurite-type minerals are similarly related to brucite, except that the amount of interlayer material is less, giving a basal spacing of about 8 Å. Bish (1980) has shown that these two types of minerals can readily be converted from one to the other by anion exchange, resulting in mineral pairs with the same cations, but with different interlayer anions and different amounts of water. The reported minerals in these categories are summarized in Table III.

All the minerals in both categories have divalent and trivalent cations, and sufficient divalent anions in their interlayers to maintain charge neutrality. If the strict analogy with the pyroaurite structure (Allmann, 1968) is maintained, as seems likely, then the structures consist of (a) a brucite-type layer consisting of 8–x divalent cations and x trivalent cations in the octahedral interstices of a double layer of 16 hexagonal close-packed OH ions, and (b) an interlayer containing enough divalent anions (x/2) to maintain charge balance, plus water molecules sufficient to fill up the interlayer space.

All combinations of divalent Ni and Mg and trivalent Al and Fe are represented among the 8 Å

hydrous carbonates, as shown in Table III. So far, honessite is the only known representative among the 9 Å hydrous sulphates. Among the 10–11 Å minerals, the dominant divalent anion is SO₄²⁻, with one exception—motukoreaite—in which CO₃ predominates (Rodgers *et al.*, 1977). The uncharged molecules making up the remainder of the interlayer material in the 10–11 Å minerals are predominantly water, but in one of them—mountkeithite—there are substantial amounts of MgSO₄ (Hudson and Bussell, 1981). The existence of MgSO₄ in mountkeithite suggests the possibility of some NiSO₄ in hydrohonessite, and the calculated formula incorporates this assumption.

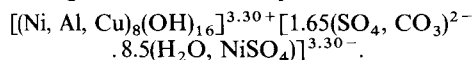
TABLE III. Minerals related to the brucite structure by the incorporation of interlayer material

Principal cations	Hydrous 8 Å carbonates	Hydrous 9 Å sulphates	10–11 Å sulphates and carbonates with additional H ₂ O
Ni, Al	Takovite $a = 3.02 \text{ \AA}$ $c = 3 \times 7.53 \text{ \AA}$	—	Carrboydite $a = 3 \times 3.05 \text{ \AA}$ $c = 10.34 \text{ \AA}$
Mg, Al	Hydrotalcite $a = 2 \times 3.07 \text{ \AA}$ $c = 6 \times 7.71 \text{ \AA}$	—	Motukoreaite $a = 3 \times 3.11 \text{ \AA}$ $c = 3 \times 11.17 \text{ \AA}$
Ni, Fe	Reevesite $a = 2 \times 3.08 \text{ \AA}$ $c = 6 \times 7.59 \text{ \AA}$	Honessite $a = 3.083 \text{ \AA}$ $c = 3 \times 8.90 \text{ \AA}$	Hydrohonessite $a = 3.09 \text{ \AA}$ $c = 10.80 \text{ \AA}$
Mg, Fe	Pyroaurite $a = 3.11 \text{ \AA}$ $c = 3 \times 7.80 \text{ \AA}$	—	Mountkeithite $a = 2\sqrt{3} \times 3.09 \text{ \AA}$ $c = 2 \times 11.27 \text{ \AA}$

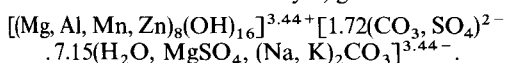
The unit-cell parameters of all the minerals shown in Table III can be related to those of brucite which has $a = 3.13 \text{ \AA}$ and $c = 4.74 \text{ \AA}$. The a dimensions of these minerals are all close to 3.1 Å or simple multiples thereof. The c dimensions of the 8–9 Å minerals correspond to the basal spacing of brucite with the addition of 3–4 Å of interlayer material; the 10–11 Å minerals have about 7 Å of interlayer material. Superstructures are evidently caused by various types of cation or anion ordering, although proof of this must await detailed structure analyses.

The original formula for carrboydite (Nickel and Clarke, 1976), was calculated on the basis of 36 oxygen atoms in the unit cell; Brindley (1979) suggested a calculation based on 3 cations per unit cell. It now appears that a more useful calculation is one that demonstrates the relationship to hydrohonessite and minerals of the pyroaurite group,

namely 8 cations per brucite layer. This gives the following formula for carrboydite:



A similar calculation for motukoreaite, assuming Mn to have a valency of +4, and assuming that the alkalies are in the interlayer, gives:



The hydrated Cu-Al sulphate mineral from Caernarvonshire (Nickel, 1976) has a basal spacing of 10.9 Å, and therefore can probably be considered as a member of this mineral group. Woodwardite, with a basal spacing of 9.1 (Nickel, 1976) would appear to be the Cu-Al analogue of honessite.

The conditions for the formation of hydrohonessite in nature can be deduced from the conditions under which its synthetic equivalent was formed. It would appear that the mineral is precipitated from groundwater carrying Ni^{2+} , Fe^{2+} , and sulphur species from the dissolution of Ni-Fe sulphides during weathering. Precipitation occurs when the pH is between 6 and 7, and the oxidation potential is sufficiently high to oxidize the Fe^{2+} to Fe^{3+} . Rapid drying of the newly formed precipitate probably results in the formation of honessite, whereas if the precipitate is immersed sufficiently long for crystal growth to occur, hydrohonessite is stabilized. Analogous conditions can be anticipated for other minerals of this group.

Acknowledgements. The authors are grateful to J. Just and L. B. Collins for providing samples containing hydrohonessite. We also appreciate the kindness of D. L. Bish and A. Livingstone for making their information on honessite and hydrohonessite available before publication, as well as that of D. R. Hudson and M. Bussell for their information on mountkeithite. Dr C. Milton of The George Washington University has also contributed to the characterization of honessite, and we are indebted to him for unpublished information on the subject. Our colleague, D. R. Hudson, read the manuscript in preparation, and made some helpful suggestions.

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[Manuscript received 5 May 1981]