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Nickelblödite, $Na_2Ni(SO_4)_2 . 4H_2O$, a new mineral from Western Australia

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SUMMARY. Nickelblödite, the nickel analogue of blödite, has been discovered in nickel mines at Kambalda and Carr Boyd Rocks in Western Australia. The Kambalda sample, found in an underground opening, has a composition corresponding to $Na_{2\cdot02}(Ni_{0\cdot79}Mg_{0\cdot14}Fe_{0\cdot05})(SO_4)_{2\cdot00}\cdot 3\cdot17H_2O$. The sample from Carr Boyd Rocks, collected from an open pit, is a more magnesian variety, with a composition corresponding to $Na_{1\cdot93}(Ni_{0\cdot55}Mg_{0\cdot46}Cu_{0\cdot03}Co_{0\cdot02})(SO_4)_{2\cdot01}\cdot 4\cdot39H_2O$. The mineral occurs as a surface efflorescence on nickel-rich sulphide ore in both cases. Nickelblödite is light green and transparent, and occurs as tabular crystallites up to 150 μm in diameter. The Kambalda material is biaxially negative with $2V = 60–70°$, $\alpha = 1\cdot513$, β(calc) $= 1\cdot518$ and $\gamma = 1\cdot520$. *D* 2·43, indentation hardness VHN 139. The Carr Boyd material has lower refractive indices and hardness. Strongest lines of the indexed powder pattern (Kambalda sample) are 4·466(9), 4·193(7), 3·720(6), 3·223(10), 3·190(8), 2·589(6). These measurements conform to a monoclinic unit cell with $a = 10\cdot87$, $b = 8\cdot07$, $c = 5\cdot46$Å, and $\beta = 100\cdot72°$. The possibility of H_3O^+ substitution is discussed.

NICKELBLÖDITE has been found at two localities in Western Australia. At Kambalda, the mineral was found among samples collected by M. R. Thornber, CSIRO, in 1971, on the wall of an underground opening at the Durkin nickel mine (31° 10′ S, 121° 40′ E), operated by Western Mining Corporation Limited. Unfortunately only one sample was collected, since at the time the mineral was not recognized as being unusual; that portion of the mine has now been worked out and is no longer accessible. The sample consists largely of violarite, pyrite, and siderite, representing an intermediate stage in the oxidation of an original pentlandite–pyrrhotine assemblage (Nickel *et al.*, 1974). The nickelblödite occurs as an efflorescence on several surfaces, together with some cryptocrystalline halite.

At Carr Boyd Rocks (30° 04′ S, 121° 37′ E), the mineral was first recognized by one of the authors (P. J. B.) in 1975 in samples collected from the open pit at the Carr Boyd Rocks nickel mine, which, though now dormant, was previously operated by Great Boulder Mines Limited. The nickelblödite in these samples occurs as a surface coating intergrown with morenosite on broken ore fragments. Only a small sample was collected as it was thought to be morenosite and, before further collections could be arranged, the pit bottom was collapsed into a stope. The Carr Boyd Rocks mine is becoming noted for its assemblage of unusual secondary minerals. The rare minerals glaukosphaerite, takovite, chalconatronite, and paratacamite have been found there, as well as the new minerals carrboydite, nickelblödite, and possibly another one that is currently undergoing investigation.

The name nickelblödite is given in recognition of the fact that the mineral is the nickel analogue of blödite ($Na_2Mg(SO_4)_2.4H_2O$). It is intended that the name apply to compositions in which nickel comprises at least 50 % of the cations in the Mg structural site. Both mineral and name were approved before publication by the I.M.A. Commission on New Minerals and Mineral Names.

Physical properties. Nickelblödite is translucent, and exhibits colour variations from pale yellowish green to pale green. The Kambalda sample has a colour approximating to the Munsell colour coding 5GY 8/2; the Carr Boyd Rocks material varies from 5GY 8·5/2 to 2·5G 8/2.

Scanning electron micrographs show that individual crystallites from the Kambalda occurrence have a tabular morphology, with a thickness of about 10 μm and a maximum diameter of about 150 μm. Since nickelblödite is monoclinic, the large flat faces probably represent {001} planes, and the smaller faces, {*hk*0}. The morphology is thus different from that of blödite, which is reported to occur as short prismatic crystals || [001] (Palache *et al.*, 1951, p. 448). The Carr Boyd material does not exhibit good crystal forms, and scanning-electron micrographs show smooth, rounded forms, suggesting that the original crystallite surfaces have been rounded, probably by solution effects, as might be expected from samples collected from an open pit exposed to the weather.

Indentation hardness measurements, using a 5 gram load, gave VHN 139 (standard deviation on 5 determinations = 19·7) for the Kambalda sample, and VHN 104 (standard deviation on 5 determinations = 15·0) for the sample from Carr Boyd Rocks. Specific gravity of the Kambalda sample, determined by suspension in a mixture of methylene iodide and acetone, is 2·43; the calculated value is 2·455. The specific gravity of the magnesian nickelblödite from Carr Boyd Rocks could not be reliably measured because of its intergrowth with morenosite; its calculated specific gravity is 2·431.

Optical properties. In transmitted light, nickelblödite is colourless to very pale green, depending on the thickness of the sample. It is biaxially negative with 2V estimated to be 60–70°. Refractive indices were determined on grains showing the maximum birefringence, hence in an orientation approximating α and γ in the plane of the section. The minimum and maximum values in monochromatic light were taken as α and γ, respectively. The Kambalda sample has $\alpha = 1{\cdot}513$, β(calc.) $= 1{\cdot}518$, $\gamma = 1{\cdot}520$, $B = 0{\cdot}007$. The Carr Boyd Rocks sample has $\alpha = 1{\cdot}504$, β(calc.) $= 1{\cdot}507$, $\gamma = 1{\cdot}509$, $B = 0{\cdot}005$. Direct measurements of the birefringence confirmed the values obtained from γ–α.

X-ray data. It was not possible to isolate single crystals of sufficiently large size for single-crystal X-ray diffraction analysis. However, the powder diffraction patterns (Table I) can readily be indexed using published data for synthetic $Na_2Ni(SO_4)_2.4H_2O$. (Swanson *et al.*, 1968, p. 68). Cell parameters calculated from the powder data by a least-squares computer programme are given in Table II. Comparison with the cell parameters of blödite (Swanson *et al.*, 1968, p. 63) shows that both nickelblödites have smaller cell parameters than blödite. A rather surprising feature is that the nickelblödite from Kambalda has a substantially smaller unit cell than the one reported for synthetic $Na_2Ni(SO_4)_2.4H_2O$. A possible explanation for this, based on the partial substitution of H_2O by H_3O^+, is given in the Discussion.

Chemical composition. Nickelblödite from both occurrences was analysed by electron-probe microanalyser. The instrument, of M.A.C. manufacture, was operated at a low specimen current (5×10^{-9} A) and the beam was defocused in order to reduce heating effects. Nevertheless, the samples were seen to decompose slowly under even those conditions. Synthetic $Na_2Ni(SO_4)_2.\ 4H_2O$, produced according to the method outlined by Giglio (1958), was used as a standard for Na, Ni, and SO_4, synthetic MgO was used for Mg, and pure metals for Fe, Co, and Cu. Water was assumed to make up the difference, and the probe data were corrected using the MAGIC IV computer programme (Colby, 1971). The results are shown in Table II.

The probe results when recalculated into atomic proportions reveal a charge imbalance, with the SO_4^{2-} charge exceeding the total positive charge of the cations. As will be shown in the discussion, there is a possibility of H_3O^+ substituting for some of the H_2O, thereby giving electrostatic balance and also accounting for the anomalously small unit-cell parameters. However, lacking direct evidence for such substitution, and taking account of the fact that analytical errors could be quite large due to decomposition of the samples under the electron beam, it was decided to recalculate the analysis according to more generally recognized usage, by increasing the cation proportions and decreasing the SO_4^{2-} proportions equally to arrive at electrostatic neutrality, then re-computing the proportions to bring the total number of cations and anions to five. The results are shown in Table II.

TABLE I. *X-ray powder diffraction data for nickelblödite, magnesian nickelblödite, and synthetic* $Na_2Ni(SO_4)_2.4H_2O$

Nickelblödite			Magnesian Nickelblödite			Synthetic $Na_2Ni(SO_4)_2.4H_2O$		
Kambalda			Carr Boyd Rocks			(Swanson *et al.*, 1968)		
d (calc.)	*d* (obs.)	*I*	*d* (calc.)	*d* (obs.)	*I*	*d* (obs.)	*I*	*hkl*
6·439	6·45	3	6·561	6·53	1	6·53	0	110
5·365 5·340	5·37	3	5·442 5·450	5·44	2	5·430	9	001 200
4·468 4·453	4·466	9	4·537 4·541	4·534	9	4·523	62	011 210
4·370	4·370	3	4·438	4·438	2	4·433	13	$\bar{1}11$
4·195	4·193	7	4·265	4·265	7	4·249	25	$\bar{2}01$
4·035	—	—	4·108	—	—	4·009	2	020
3·912	3·920	5	3·977	3·977	4	3·976	14	111
3·775	—	—	3·844	3·850	1	3·834	3	120
3·722	3·720	6	3·785	3·786	7	3·773	13	$\bar{2}11$
3·475	—	—	3·537	—	—	3·538	3	201
3·257	3·256	4	3·323	3·322	4	3·309	27	310
3·225 3·219	3·223	10	3·279 3·280	3·279	10	3·270	100	021 220
3·192 3·187	3·190	8	3·249 3·241	3·250	8	3·243 3·236	55	211 $\bar{1}21$
3·022	3·016	2	3·076	3·078	2	3·066	7	$\bar{3}11$
2·996	—	—	3·047	—	—	3·043	2	121
2·908	2·902	5	2·959	2·960	7	2·951	13	$\bar{2}21$
2·670 2·670 2·682	2·671	4	2·725 2·721 2·721	2·721	7	2·713	17	400 320 002
2·633	2·637	3	2·681	2·681	6	2·677	20	221
2·608	—	—	2·656	2·654	2	2·647	13	130
2·590	2·589	6	2·639	2·635	7	2·628	31	$\bar{4}01$
2·581	—	—	2·618	2·616	1	—	—	$\bar{1}12$
Nickelblödite (continued)			Magnesian Nickelblödite (continued)			Synthetic $Na_2Ni(SO_4)_2.4H_2O$ (continued)		
d (calc.)	*d* (obs.)	*I*	*d* (calc.)	*d* (obs.)	*I*	*d* (obs.)	*I*	*hkl*
2·545	2·557	4	2·583	2·582	6	2·582	17	012
			?	2·545	1			
2·474	—	—	2·511	2·511	1	2·506	2	$\bar{2}12$
2·402 2·405	— —	— —	2·447 2·446	2·447	1	2·441	3	230 031
2·389 2·383	2·387	1	2·430 2·420	2·420	2	2·420	7	$\bar{1}31$ 112
2·305	2·289	1	2·346	2·344	2	2·342	3	131
2·267 2·264	— —	— —	2·309 2·304	2·307	2	2·306 2·298	7 1	321 $\bar{2}31$
2·258	2·254	3	2·290	2·292	3	2·290	13	$\bar{1}22$
2·227 2·231 2·234 2·236	2·235	5	2·271 2·274 2·268 2·272	2·271	5	2·271 2·266	21	420 401 022 202
2·185	—	—	2·219	—	—	2·214	1	$\bar{2}22$
2·155	—	—	2·190	—	—	2·190	2	212
2·146	—	—	2·187	—	—	2·180	4	330
2·127 2·122	2·126	3	2·166 2·155	2·165 2·156	4 2	2·161 2·155	13	231 122
2·097	2·094	2	2·132	2·132	3	2·124	9	$\bar{4}02$
2·065	2·069	2	2·107	2·107	3	2·099	10	510
2·055	—	—	2·095	2·092	1	2·087	4	$\bar{5}11$
2·040	—	—	2·073	—	—	2·068	2	$\bar{3}22$
2·017	—	—	2·054	2·055	1	2·049	4	040
1·982	1·983	4	2·018	2·020	5	2·012	17	140
1·952 1·956	— —	— —	1·989 1·988	1·990	2	1·987	6	421 222

All measurements on nickelblödite and magnesian nickelblödite were made on patterns obtained by a Guinier-Hägg focusing camera, Cu-*K*α radiation, ThO_2 internal standard.

It can be seen that the Kambalda nickelblödite is closer to the nickel end-member of a hypothetical Na_2 (Ni, Mg) $(SO_4)_2$. $4H_2O$ solid solution; the sample from Carr Boyd Rocks is close to the mid-point, although still on the nickel side. There are also appreciable differences in the amounts of the minor elements (Fe, Co, and Cu) present in the two samples.

Discussion. The unit-cell parameters of nickelblödite are appreciably smaller than those of blödite. This is not unexpected, since isomorphous substitution of magnesium by nickel in sulphates generally causes a contraction of the unit cell. What is surprising, however, is that the cell parameters of the nickelblödite from Kambalda are substantially smaller than those of synthetic $Na_2Ni(SO_4)_2.4H_2O$. The low sodium value, as determined by microprobe analysis, suggests the possibility of some component substituting for this element, but lithium, the only element that can reasonably be expected to substitute for sodium and at the same time reduce the cell parameters, was shown by flame photometry to be absent.

Other possible substituting components such as H_3O^+ or NH_4^+ would be expected to increase, rather than decrease, the cell parameters if they substituted for Na^+ directly. However, if H_3O^+ were to be accommodated in the H_2O structural sites, with charge balance maintained by the creation of an equal number of Na^+ vacancies (somewhat analogous to the analcime-pollucite relationship), then a reduction in unit-cell size would seem to be more plausible.

TABLE II. *Composition and optical and physical properties of nickelblödite and magnesian nickelblödite*

	Nickelblödite Kambalda			Magnesian Nickelblödite Carr Boyd Rocks			$Na_2Ni(SO_4)_2.4H_2O$ (Swanson *et al.*, 1968)	
	Weight percent		Atomic props.	Weight percent		Atomic props.	Weight percent	Atomic props.
	Determined	Recalc.		Determined	Recalc.			
Composition								
Na	11·96	13·32	2·016	11·90	12·20	1·927	12·47	2
Ni	11·94	13·27	0·787	8·62	8·84	0·547	15·92	1
Mg	0·91	1·01	0·145	3·04	3·11	0·465	—	—
Cu	0·03	0·03	0·001	0·54	0·56	0·032	—	—
Co	—	—	—	0·30	0·31	0·019	—	—
Fe	0·79	0·88	0·055	—	—	—	—	—
SO_4	57·97	55·09	1·996	53·81	53·19	2·010	52·08	2
H_2O	16·40†	16·40	3·168	21·79†	21·79	4·391	19·53	4
	100·00	100·00	8·168	100·00	100·00	9·391	100·00	9
Refractive indices								
α	1·513			1·504			1·518	
β	1·518 (calc.)			1·507 (calc.)			1·520	
γ	1·520			1·509			1·522	
Specific gravity	2·43 (meas.) 2·455 (calc.)			2·431 (calc.)			2·487 (calc.)	
Unit-cell parameters								
a (Å)	10·87			11·09			11·045	
b (Å)	8·07			8·216			8·193	
c (Å)	5·46			5·537			5·535	
β	100° 43′			100° 39′			100° 30′	

Compositions determined by electron-probe microanalysis; see text for description of procedure and recalculation details.

† H_2O determined by difference.

The specific gravity calculated on this assumption, using the uncorrected analysis and taking $(SO_4+Ni+Mg+Cu+Fe)$ as 3·00 atoms, comes to 2·472, which is not greatly different from the value obtained from the analysis recalculated in the more conventional way. However, because of uncertainties in the microprobe analyses, the authors feel that it would be premature to advance the suggestion of a coupled Na^+ vacancy – H_3O^+ substitution as a firm proposal at this stage.

Regarding the formation of nickelblödite, the synthetic compound crystallizes readily from an aqueous solution of the hydrated sulphates of sodium and nickel (Giglio, 1958; Kuznetsov and Imanakunov, 1962), and it can therefore be assumed that the naturally occurring mineral is formed under similar conditions. An analysis of ground water from a drill hole in the Durkin orebody gave Na and SO_4 values of 1·5 % and 0·5 %, respectively (Nickel *et al.*, 1974); even higher values than these can be expected locally, particularly where evaporation is taking place. The halite occurring with the nickelblödite at Kambalda suggests that the solutions were saline, as well. At Carr Boyd Rocks, on the other hand, the presence of trona and chalconatronite, as well as other unusual carbonate minerals, suggest that the solutions there were high in sodium bicarbonate; high bicarbonate content would also be consistent with the higher $Mg/(Ni+Fe)$ ratio in the nickelblödite from this deposit.

The type specimens of nickelblödite are preserved in the CSIRO mineral collection under the number 4397, and in the mineral collection of the Government Chemical Laboratories under the number MDC 5657. Small fragments of the Carr Boyd Rocks material have been placed in the collections of the British Museum (Natural History) and the Smithsonian Institution. No further samples exist for distribution.

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