

Dwornikite, $(\text{Ni,Fe})\text{SO}_4 \cdot \text{H}_2\text{O}$, a member of the kieserite group from Minasragra, Peru

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ABSTRACT. Dwornikite, $(\text{Ni}_{1-x}\text{Fe}_x)\text{SO}_4 \cdot \text{H}_2\text{O}$ is a member of the kieserite group, monoclinic with space group $C2/c$. Specimens from Minasragra, Peru with $x \sim 0.1$ have a unit cell with $a = 6.839(2)$, $b = 7.582(2)$, $c = 7.474(2)$ Å, and $\beta = 117.85(2)^\circ$. The six strongest lines of the powder pattern are: 3.342 ($\bar{1}12$, 100), 4.732 (110, 70), 3.024 (200, 70), 4.754 ($\bar{1}11$, 50), 3.293 (021, 35), 2.491 (022, 35). The mineral occurs as fine grained white aggregates associated with vanadium sulphide ores containing patronite and bravoite, mixed with other oxidation products. New unit cell data for the synthetic end-member compounds $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, and new X-ray powder data for retgersite ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) are provided.

THE monoclinic kieserite group of minerals is summarized by Strunz (1977) as:

kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$,
szomolnikite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$,
szmikite	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$,
gunningite	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$,
poitevinite	$(\text{Cu,Fe,Zn})\text{SO}_4 \cdot \text{H}_2\text{O}$

To these we now add a new nickel sulphate monohydrate, dwornikite, $(\text{Ni,Fe})\text{SO}_4 \cdot \text{H}_2\text{O}$. The new mineral was found with patronite (VS_2) and various sulphates, sulphur, and bitumen in a sample of vanadium sulphide ore from Minasragra, Peru. This material was probably collected in 1906 by D. Foster Hewett (see Hewett, 1910) and is now in the collections of the George Washington University, Washington, DC. We have named the mineral in honour of Edward J. Dwornik, mineralogist with the US Geological Survey, who has made extensive studies of vanadium minerals from Arkansas and Peru. The name has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Physical properties. Dwornikite is snowy white, sometimes with a faint greenish tint perhaps imparted by admixed impurities. It forms aggregates of very fine-grained particles mixed with other minerals, from which it is practically impossible to separate completely. Fig. 1 presents scanning electron microscope images of a typical grain of dwornikite, which show a somewhat fused appearance and the lack of any but the vaguest crystalline morphology. Even the smallest grains that could be examined microscopically showed some slight contamination.

Because of the extremely small grain size of the particles in the dwornikite aggregates, optical measurements could not be made with any certainty; the best obtainable indicate fairly strong birefringence, with a mean index about 1.63. According to Mandarino (1976), the specific refractivities of FeO and NiO are similar (0.188 and 0.176, respectively) so that the optical parameters should not be very different from those of szomolnikite (Palache *et al.*, 1951). The mean index of the latter is 6.626. The Gladstone-Dale relationship predicts a mean refractive index of 1.621 for szomolnikite and 1.654 for dwornikite. The density calculated from the composition and crystallography of dwornikite is 3.34 g/cm^3 . The qualities of hardness and fracture could not be measured, but may be expected to be similar to those of szomolnokite (Palache *et al.*, 1951).

Crystallography. Because of the lack of sizeable single crystals, the crystallographic properties of dwornikite have had to be derived from X-ray powder patterns. The similarity of the powder data to those of synthetic nickel and iron analogues published by Pistorius (1960) was recognized soon after the approximate composition of dwornikite

TABLE I. X-ray powder data for dwornikite and synthetic nickel and iron analogues

(a) <i>hkl</i>	Dwornikite (b)			NiSO ₄ · H ₂ O (c)			FeSO ₄ · H ₂ O (c)			(d) <i>I</i> _{calc.}
	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> _{obs.}	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> _{obs.}	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> _{obs.}	
111	4.753	4.754	50	4.750	4.743	50	4.859	4.850	30	38
110	4.728	4.732	70	4.728	4.732	65	4.789	4.79	15	52
020	3.791	3.792	25	3.796	3.790	10	3.742	3.73	6	18
112	3.341	3.342	100	3.335	3.333	100	3.455	3.444	100	100
111	3.315	3.318	12	3.312	3.314	30	3.379	3.373	24	23
002	3.304			3.296			3.422			1
021	3.289	3.293	35	3.290	3.289	35	3.283	3.283	21	27
202	3.051			3.045			3.195			0
200	3.023	3.024	70	3.021	3.020	45	3.115	3.116	42	43
221	2.5392	2.5399	18	2.539	2.539	16	2.577	2.579	27	16
022	2.4910	2.4912	35	2.489	2.488	40	2.525	2.521	37	46
222	2.3767			2.375	2.376	2	2.430	2.432	6	1
220	2.3638			2.364	2.365	2				2
113	2.3526			2.347			2.440			1
112	2.3370	2.3342	25	2.334	2.332	15	2.396	2.394	4	3
131	2.3350			2.337			2.324	2.326	9	0
130	2.3320			2.334			2.316	2.312	7	11
312	2.1575	2.1581	18	2.155	2.154	15	2.239	2.242	16	19
311	2.1503			2.149			2.218			1
132	2.0910	2.0906	12	2.091	2.087	7	2.101	2.103	10	8
131	2.0844			2.085			2.083			4
223	2.0213	2.0218	18	2.018	2.018	9	2.081	2.080	20	10
221	2.0055			2.005	2.005	2	2.004			1
313	1.9643			1.961			2.048			0
310	1.9480	1.9479	25	1.947	1.947	12	2.001	2.001	15	13
023	1.9047			1.902	1.902	2	1.948			2
040	1.8956	1.8949	6	1.898	1.898	4	1.871			3
204	1.8611	1.8616	6	1.856	1.856	5	1.947			4
202	1.8427			1.840			1.894			0
041	1.8221			1.824			1.805			0
114	1.7745	1.7741	9	1.770	1.769	6	1.842			8
133	1.7683			1.767	1.767	4	1.794	1.795	3	0
113	1.7651			1.762	1.762	2	1.815	1.818	3	1
132	1.7616			1.761			1.776			1
402	1.7097	1.7093	4	1.708	1.708	2	1.777	1.776	3	2
314	1.6920			1.688			1.768			1
332	1.6808			1.681			1.709			1
331	1.6774			1.678			1.700			0
311	1.6747			1.673			1.718			0
224	1.6707			1.667	1.668	4	1.727			5
241	1.6579			1.659			1.656			0
222	1.6573	1.6579	25	1.656	1.656	10	1.690	1.686	18	13
004	1.6521			1.648			1.711			2
042	1.6443			1.645	1.645	6	1.642	1.642	4	10
242				1.611	1.610	6	1.615	1.615	12	10
240				1.607	1.607	2	1.604			0
333				1.583			1.620	1.621	12	2
330				1.576	1.576	6	1.596			11
422				1.558	1.588	3	1.605	1.602	6	4
404				1.522	1.523	4	1.597	1.596	18	8
423				1.519	1.518	3	1.573	1.574	7	2
421				1.513			1.553	1.553	4	1
024				1.512	1.512	2	1.556	1.558	4	2

Notes:

- (a) All possible lines with $d > 1.64 \text{ \AA}$ have been listed.
 (b) This work: data from Guinier-Hagg pattern made with Cr-K α_1 radiation ($\lambda = 2.28962 \text{ \AA}$).
 (c) Data from Pistorius (1965), from diffractometer patterns made with Fe-K α radiation. Pistorius lists eighteen additional lines with $d < 1.51 \text{ \AA}$ for NiSO₄ · H₂O, which have not been indexed.
 (d) Powder intensities calculated from crystal structure of CoSO₄ · H₂O determined by Oswald (1968), used as an indexing guide.

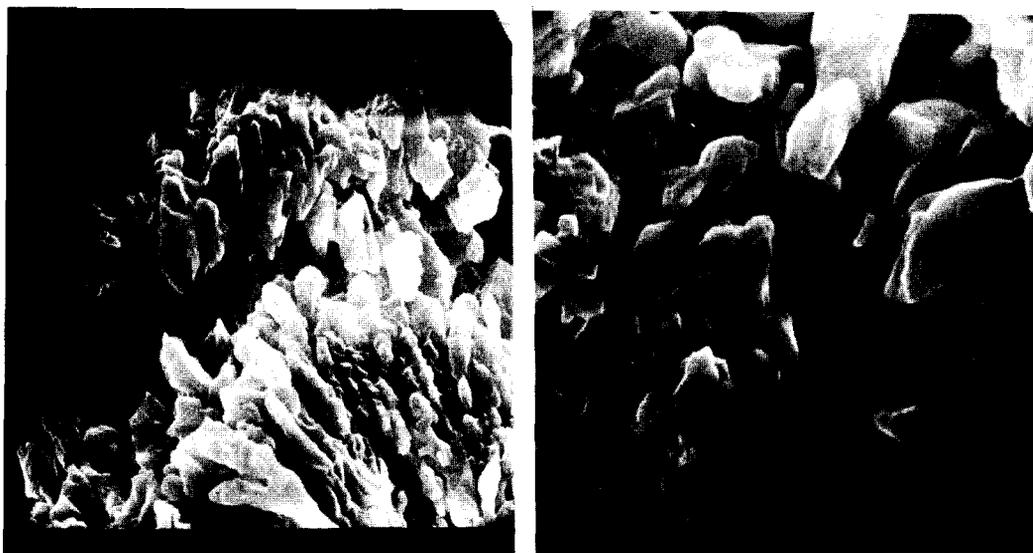


FIG. 1. Scanning electron microscope images of a typical grain of dwornikite. The right view shows the central area of the left view magnified three times. The bars represent $1\ \mu\text{m}$.

was ascertained. Oswald (1965), using Guinier focusing techniques, determined the monoclinic unit cell parameters for the synthetic sulphates and selenates of Mg, Mn, Fe, Co, and Ni, all members of the kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) group of compounds. Oswald determined an accurate crystal structure from the powder patterns of $\text{CoSO}_4 \cdot \text{H}_2\text{O}$, thus accounting completely for the observed intensities of the powder lines, as presented in detail in his paper. Unfortunately, he did not publish powder data for any of the other compounds, but Pistorius (1960) has given these for $\text{FeSO}_4 \cdot \text{H}_2\text{O}$

and $\text{NiSO}_4 \cdot \text{H}_2\text{O}$, based on X-ray powder diffractometer measurements using $\text{Fe-K}\alpha$ radiation. This information serves as a basis for the interpretation of our powder data.

We have made Debye-Scherrer patterns with $\text{Fe-K}\alpha$ radiation, but the best measurements come from Guinier-Hägg patterns made with $\text{Cr-K}\alpha_1$ radiation ($\lambda = 2.28962\ \text{\AA}$). The lines are somewhat broadened by the fine grain size, but nineteen lines used in a least-squares analysis have led to a conclusive result, shown in Table I (powder data, excluding a few impurity lines) and Table II (unit cell).

TABLE II. Crystallographic data for dwornikite, $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$.
Monoclinic, space group $C2/c$

	Dwornikite		$\text{NiSO}_4 \cdot \text{H}_2\text{O}$		$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	
	(a)	(b)	(c)	(d)	(c)	(d)
a \AA	6.839(2)	6.846	6.832(1)	6.84 ₉	7.112(3)	7.09 ₃
b \AA	7.582(2)	7.586	7.592(1)	7.57 ₉	7.485(4)	7.56 ₀
c \AA	7.474(2)	7.472	7.454(1)	7.47 ₃	7.812(7)	7.63 ₃
β deg.	117.85(2)	117.87	117.82(1)	117.95	118.82(4)	118.55
V \AA^3	342.7(1)	343.0	341.97(6)	342.7	364.3(3)	365.6
$D_{\text{calc.}}$ g/cm ³		3.346	3.355		3.098	

Notes:

- (a) This work: by least-squares analysis of data given in Table I.
- (b) Calculated assuming the composition $(\text{Ni}_{0.95}\text{Fe}_{0.05})\text{SO}_4 \cdot \text{H}_2\text{O}$.
- (c) By least-squares analysis of data from Pistorius (1965) given in Table I.
- (d) From Oswald (1968), by least-squares analysis of Guinier data, $\text{Fe-K}\alpha$ radiation (data not given).

The indexing of the powder data is not inherently straightforward, and Pistorius was unsuccessful in this process (lacking intensity information based on crystal structure), arriving at incorrect unit cells. The indexing must be controlled by reference to crystal structure information as presented by Oswald (1965) for $\text{CoSO}_4 \cdot \text{H}_2\text{O}$, which may be expected to be closely analogous to the Fe and Ni compounds. Table I shows our final interpretation of data of Pistorius (1960) and Table II the corresponding unit cell data derived by least-squares analysis, compared with those of Oswald (1965). Rather than the standardized unit cell setting with space group $A2/a$ used by Pistorius, we have here retained the $C2/c$ setting of Oswald and other workers.

LeFur *et al.* (1966), apparently unaware of Oswald's work, also determined unit cells and crystal structures for the Ni, Co, Zn, Fe, and Mn compounds, but did not publish their data or details of their X-ray powder techniques. For the Fe and Ni compounds, the data of Pistorius appear to be better controlled, and superior to those of either Oswald or LeFur *et al.*

None of our patterns was free of extra lines presumably associated with admixed impurities. A line of moderate intensity at 4.25 and weaker lines at 4.65, 4.57, 3.768, 3.392, 2.964, 2.721, 2.571, 2.125, and 1.755 Å all correspond closely to those of retgersite, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Table IV). In addition, weak lines at 4.84, 3.416, and 3.082 Å may be associated with szomolnikite, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ with some Ni replacing Fe. The relative amounts of these phases cannot be estimated from intensity relationships because of their varying qualities of crystallinity.

Chemistry. The composition of dwornikite was determined by means of an ETEC scanning electron microscope equipped with an EDAX 9100 X-ray fluorescence analyser. The X-ray spectrum showed lines only for Ni, Fe, and S. Background-subtracted net peak intensities for Ni, Fe, and S were extracted from the spectrum and percent compositions determined by means of a standard ZAF correction. The results of this procedure applied to four separate grains, including three from the specimen used for the Guinier-Hägg pattern, are shown in Table III. If the general formula is assumed to be $(\text{Ni}_{1-x}\text{Fe}_x)\text{SO}_4 \cdot \text{H}_2\text{O}$, the semiquantitative X-ray fluorescence results so obtained are consistent with $x = 0.2$. On the other hand, a linear interpolation of all the parameters of Table II between $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ will predict the observed values for dwornikite very closely when $x = 0.05$. While the accuracy of the fluorescence analysis is not great, it indicates the presence of an amount of iron much greater than that predicted

by the crystallography. The X-ray diffraction studies always showed impurities to be present in the dwornikite grains, including retgersite and szomolnikite as shown above. Other amorphous impurities, such as iron hydroxide, may also be present. The dwornikite itself evidently contains less than 10 mol% Fe replacing Ni, but this amount is probably variable.

Bravoite $(\text{Ni,Fe})\text{S}_2$, a member of the pyrite group, has been reported in small amounts with the main ore mineral (Hewett, 1910; Paist and Pings, 1970). Oxidation of bravoite is a likely source of dwornikite, and may continue after the material has been collected. A similar relationship clearly obtains between patronite (VS_2) and minasragrite, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (Smith and Marinenko, 1973) and other as yet undescribed weathering products (at least five different synthetic VOSO_4 hydrates are known).

Retgersite. For reference purposes, a Guinier-Hägg X-ray powder pattern was made of synthetic retgersite, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Merck Reagent crystals were used, which were stated to contain the following impurities in wt. %: Co, 0.10; Zn, 0.05; Cu, 0.01; Fe, 0.01; alkalis and alkaline earths, 0.3. The pattern was made at 24°C using $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54052 \text{ \AA}$), and CaF_2 as an internal standard. Of the 220 possible reflections accessible in the 2 θ range 5 to 87 degrees, 88 were observed, and the standard deviation of measurement of 2 θ as derived by least-squares analysis was 0.014°. This data set is about twice as extensive as that reported by Swanson *et al.* (1957), and is set out in Table IV. The tetragonal unit cell parameters (space group $P4_12_12$) found by least-squares analysis are compared with other previously published values:

	<i>a</i>	<i>c</i> (Å)
This work	6.7848(3)	18.2827(14)
Swanson <i>et al.</i> (1957)	6.782	18.28
O'Connor and Dale (1966)	6.790(3)	18.305(4)

TABLE III. X-ray fluorescence analysis of dwornikite

	Analyses, wt. %					
	1	2	3	4	Avg.	Calc. (b)
NiO	39.5	38.7	39.9	37.0	39.0	34.7
FeO	9.0	9.4	9.0	9.7	9.3	8.3
SO ₃	41.6	42.1	41.1	44.8	42.4	46.4
H ₂ O						10.6
Sum	90.1	90.2	90.7	91.5	90.7	100.0

Notes:

- (a) Estimated error is $\pm 10\%$ of each determination.
 (b) Based on the composition $(\text{Ni}_{0.8}\text{Fe}_{0.2})\text{SO}_4 \cdot \text{H}_2\text{O}$.

TABLE IV. X-ray powder data for retgersite, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Tetragonal, space group $P4_12_12$, a 6.7848, c 18.283 Å. Guinier-Hägg method, Cu- $K\alpha_1$ radiation, $\lambda = 1.54052$ Å

$h k l$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	I	$h k l$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	I	$h k l$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	I
1 0 1	6.361	6.359	9	2 0 8	1.8954	1.8952	9	3 3 5	1.4652	1.4649	2
1 1 1	4.640	4.637	25	3 2 0	1.8818	1.8819	6	2 1 11	1.4577	1.4569	1
0 0 4	4.571	4.578	50	3 2 1	1.8719	1.8717	2	4 2 4	1.4399	1.4397	1
1 1 2	4.248	4.257	100	1 1 9	1.8706			4 0 7	1.4225	1.4229	2
1 1 3	3.770	3.771	6	3 1 5	1.8505	1.8512	9	4 2 5	1.4013	1.4013	4
2 0 0	3.392	3.393	13	3 2 2	1.8431	1.8431	2	3 1 10	1.3916	1.3916	2
2 0 1	3.335	3.336	9	2 1 8	1.8255	1.8256	4	2 0 12	1.3898	1.3900	3
2 0 2	3.180	3.181	4	3 2 3	1.7980	1.7978	1	3 2 9	1.3805	1.3803	1
2 1 0	3.034	3.035	4	1 0 10	1.7653	1.7666	1	4 0 8	1.3620	1.3616	2
2 0 3	2.9641	2.9641	35	3 1 6	1.7543	1.7544	13	2 1 12	1.3616		
1 1 5	2.9082	2.9078	4	1 1 10	1.7084	1.7085	9	4 3 0	1.3570	1.3572	3
2 1 2	2.8797	2.8811	4	4 0 1	1.6889	1.6888	13	4 3 1	1.3532	1.3531	1
1 0 6	2.7797	2.7786	3	2 1 9	1.6880			1 1 13	1.3496	1.3497	1
2 0 4	2.7241	2.7247	35	3 1 7	1.6579	1.6579	3	4 3 2	1.3422	1.3433	3
1 1 6	2.5722	2.5727	25	2 2 8	1.6546	1.6549	9	5 1 1	1.3271	1.3273	2
2 1 4	2.5279	2.5288	9	4 1 1	1.6389	1.6390	3	3 1 11	1.3139	1.3138	1
2 1 5	2.3350	2.3359	25	4 0 3	1.6341	1.6342	6	3 2 10	1.3113	1.3120	2
1 1 7	2.2939	2.2938	1	3 3 1	1.5931	1.5929	3	5 1 3	1.3000	1.3001	4
3 0 1	2.2445	2.2435	2	4 0 4	1.5902	1.5904	2	2 2 12	1.2861	1.2851	2
1 0 8	2.1658	2.1655	3	4 1 3	1.5887	1.5884	2	1 1 14	1.2601	1.2600	4
3 1 0	2.1455	2.1477	1	3 3 2	1.5753	1.5753	3	5 2 1	1.2569	1.2566	1
3 1 1	2.1309	2.1310	25	2 1 10	1.5660	1.5655	1	3 3 9	1.2565		
2 2 4	2.1240	2.1243	9	4 0 5	1.5387	1.5389	4	5 1 5	1.2504	1.2501	3
3 0 3	2.1203	2.1211	6	3 2 7	1.5268	1.5270	2	4 2 9	1.2155	1.2152	2
3 1 2	2.0888	2.0893	9	0 0 12	1.5236	1.5240	4	5 2 4	1.2146		
1 1 8	2.0632	2.0633	1	4 2 0	1.5171	1.5172	3	4 4 2	1.1892	1.1894	6
3 0 4	2.0270	2.0263	4	4 2 1	1.5119	1.5121	6	5 1 7	1.1856	1.1856	4
3 1 3	2.0238	2.0238	6	3 3 4	1.5095	1.5093	1	4 4 3	1.1768	1.1766	3
2 2 5	2.0057	2.0072	1	4 2 2	1.4966	1.4965	2	3 1 13	1.1762		
2 1 7	1.9795	1.9798	6	3 1 9	1.4751	1.4751	3	0 0 16	1.1427	1.1426	3
3 1 4	1.9422	1.9412	3	4 2 3	1.4722	1.4715	3	5 3 4	1.1276	1.1275	4
3 0 5	1.9234	1.9247	3								

The structure as determined in a neutron diffraction study by O'Connor and Dale (1966) was used to calculate reflection intensities as an aid to index the observed powder pattern.

Acknowledgements. We are grateful to Dr Michael Fleischer, Mary E. Mrose, and Richard C. Erd of the US Geological Survey and to Dr Daniel E. Appleman of the Smithsonian Institution for valuable comment and criticism of this work.

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[Revised manuscript received 28 September 1981]