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THE AHLFELDITE-COBALTOMENITE SERIES

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ABSTRACT

Study of synthetic ahlfeldite ($NiSeO_3 \cdot 2H_2O$) and synthetic cobaltomenite ($CoSeO_3 \cdot 2H_2O$) gave the following data:
Ahlfeldite: Colour green, density (calc.) 3.51. Crystals long, prismatic elongated parallel to [001] with forms {110} and {$\bar{1}$01}. Unit cell dimensions calculated from x-ray powder diffraction data: a = 7.519, b = 8.751, c = 6.448Å, β = 99°00′. The six strongest lines in the x-ray powder diffraction pattern: 5.66(100) (110), 3.415(70) (210), 2.989 (65) (012), 3.77(50) (120), 2.715(50) (130), 2.188 (45) (040). Optical data: α = 1.703, β=1.744, γ = 1.786, optically negative, $2V$ = 87°, $c\Lambda\gamma$ = -12°. Weak pleochroism, γ = green, β = pale green, α = very pale green with absorption $\gamma > \beta > \alpha$.
Cobaltomenite: Colour red, density (calc.) 3.42. Crystals either long prismatic elongated parallel to [001] or tabular flattened parallel to {$\bar{1}$01}. Unit cell dimensions calculated from x-ray powder diffraction data: a=7.615, b=8.814, c=6.499Å, β= 98°51′. The six strongest lines in the x-ray powder diffraction pattern: 5.72(100) (110), 3.46(70) (210), 3.017(55) (012), 3.80(50) (120), 2.738(45) (130), 2.378(40) ($\bar{3}$11). Optical data: α=1.681, β= 1.728, γ = 1.769. Optically negative, $2V$ = 83°, $c\Lambda\gamma$ = -13°. Weak pleochroism, γ = red, β = pink, α=pale pink, absorption $\gamma > \beta > \alpha$.

The composition of intermediate members of the series can be estimated by measurement of selected d-spacings.

INTRODUCTION

An excellent review of the historical background of ahlfeldite and cobaltomenite was given by Aristarain & Hurlbut (1969). A very brief summary is as follows. Ahlfeldite ($NiSeO_3 \cdot 2H_2O$) and cobaltomenite ($CoSeO_3 \cdot 2H_2O$) are isostructural (space group $P2_1/n$), and apparently form an isomorphous series. The x-ray powder patterns are considered essentially identical and the only practical means of distinguishing members in the series is by chemical analysis.

The present study was undertaken to determine the practicality of other techniques for identification. Through the kindness of Prof. Dr. G. Gattow of the Universtät Göttingen, samples of synthetic ahlfeldite and synthetic cobaltomenite were made available. From these samples, optical, crystallographic, and chemical data were obtained. These data were applied to the identification of two natural specimens.

COLOUR AND DENSITY

The colour of synthetic ahlfeldite is pale green and the streak is very pale green. Synthetic cobaltomenite is pink with a pale pink streak. In natural specimens, only a small amount of cobalt need be present to give a dominant pink colour.

The densities of the synthetic material used in this study were not measured because of the very small sample size and grain size. All known densities (calculated and measured) for the two compounds are given in Table 1.

TABLE 1. CELL PARAMETERS AND DENSITIES OF AHLFELDITE AND COBALTOMENITE

Substance	aÅ	bÅ	cÅ	β	ρ(meas)	ρ(calc)	Ref.
Ahlfeldite (synthetic)	7.55	8.75	6.46	99°	3.416	3.49_3	1
Ahlfeldite Pacajake, Bolivia ($(Ni_{0.90}Co_{0.10})SeO_3 \cdot 2H_2O$)	7.53	8.76	6.43	99°05'	3.37±0.02	3.51	2
Ahlfeldite Pacajake, Bolivia					3.4		3
Ahlfeldite (synthetic)	7.519	8.751	6.448	99°00'		3.51	4
Cobaltomenite (synthetic)	7.640	8.825	6.515	98°36'	3.410	3.40_2	1
Cobaltomenite (synthetic)	7.615	8.814	6.499	98°51'		3.42	4

1. Lieder & Gattow (1967), with a and c reversed from original data. The cell data of Lieder & Gattow for ahlfeldite and cobaltomenite listed by Strunz (1970) are in error. Those listed for ahlfeldite are really for cobaltomenite and *vice versa*.
2. Aristarain & Hurlbut (1969).
3. Gonī & Guillemin (1953).
4. This study (cell dimensions calculated from x-ray powder data).

CRYSTALLOGRAPHIC DATA

Crystals of both synthetic selenites were very small, averaging 0.002 mm by 0.005 mm. Typical crystals of either synthetic cobaltomenite or synthetic ahlfeldite have only the forms {110} and {$\bar{1}$01}. Most of the crystals are elongated parallel to [001] although an occasional crystal of synthetic cobaltomenite is found as a tabular crystal flattened parallel to {$\bar{1}$01}.

X-ray powder diffraction patterns of the two materials were obtained using Debye-Scherrer cameras (114.6mm diameter) and Mn-filtered Fe radiation. The programme written by Evans *et al.* (1963) was used to index the patterns and to calculate the unit cell parameters from the measured *d*-spacings. These data are compared to those obtained by Lieder & Gattow (1967) and Aristarain & Hurlbut (1969) in Table 1. The present writers have followed the orientation of Aristarain & Hurlbut (1969) where *c* is taken as the axis of elongation.

Superficially, the powder patterns of synthetic ahlfeldite and synthetic cobaltomenite are identical with respect to *d*-spacings and intensities. Measurements, however, show that there are slight differences in *d*-spacings due to the slightly different unit cell parameters. The *x*-ray powder diffraction data for synthetic ahlfeldite and for synthetic cobaltomenite are listed in Table 2.

TABLE 2. *X*-RAY DIFFRACTION DATA FOR SYNTHETIC AHLFELDITE AND SYNTHETIC COBALTOMENITE (Camera diameter 114.6 mm, Fe*K*α).

ahlfeldite				cobaltomenite			
I	d_{meas}Å	d_{calc}Å	*hkl*	*I*	d_{meas}Å	d_{calc}Å	*hkl*
100	5.66	5.662	100	100	5.70	5.722	110
15	5.25	5.257	$\bar{1}01$	10	5.30	5.304	$\bar{1}01$
10	4.49	4.507 4.499	$\bar{1}11$ 101	15	4.55	4.551 4.546	101 $\bar{1}11$
20	4.38	4.375	020	20	4.40	4.407	020
30	4.00	4.001	111	30	4.04	4.044	111
50	3.77	3.770	120	50	3.80	3.803	120
70	3.415	3.418	210	70	3.46	3.460	210
10	3.214	3.211	$\bar{2}11$	10	3.246	3.244	$\bar{2}11$
7	3.137	3.137	121	7	3.162	3.166	121
65	2.989	2.992	012	55	3.017	3.017	012
7	2.927	2.929	$\bar{1}12$	10	2.951	2.951	$\bar{1}12$
50	2.715	2.715	130	45	2.738	2.737	130
10	2.651	2.652	031	b 15	2.686	2.672	031
10	2.630	2.629	$\bar{2}02$				
10	2.534	2.533	$\bar{1}22$	10	2.552	2.553	$\bar{1}22$
30	2.481	2.480	221	30	2.509	2.507	221
7	2.440	2.440	$\bar{3}01$	7	2.469	2.468	$\bar{3}01$
35	2.349	2.350	$\bar{3}11$	40	2.378	2.377	$\bar{3}11$
1	2.290	2.294	230	1	2.314	2.315	230
2	2.247	2.253 2.250	$\bar{2}22$ 202	2	2.273	2.276 2.272	202 $\bar{2}22$
5	2.228	2.228	$\bar{2}31$	5	2.246	2.247	$\bar{2}31$
				5	2.222	2.223	301
45	2.189	2.188	040	20	2.206	2.203	040
5	2.151	2.151	032				
10	2.127	2.128 2.127	311 $\bar{1}32$	5	2.158	2.156 2.154	311 $\bar{3}21$
				1	2.144	2.143	$\bar{1}32$
5	2.062			2	2.096		
5	2.017						
5	2.006						
10	2.000			b 5	2.014		
10	1.9618			2	1.9960		
b 5	1.9105			5	1.9280		
10	1.7880			1	1.8018		
7	1.7669			2	1.7859		
10	1.7508			5	1.7694		
35	1.7141			35	1.7340		
5	1.6962			5	1.7160		
15	1.6808			10	1.6950		
15	1.6285			15	1.6436		
10	1.5825			10	1.5957		
7	1.5480			5	1.5650		
10	1.5326			15	1.5440		
				5	1.5210		
b 7	1.4981			5	1.5148		
2	1.4872						
15	1.4776			15	1.4950		
5	1.4587			5	1.4684		
10	1.4196			10	1.4340		
5	1.3658			7	1.3810		
10	1.3461			10	1.3580		
2	1.3199			1	1.3390		
10	1.2863			5	1.2963		
1	1.2711			2	1.2830		
7	1.2453			5	1.2594		
5	1.2372						
5	1.2197			5	1.2330		
				7	1.2230		
5	1.1749						
15	1.1380			10	1.1500		
b 15	1.1126			b 10	1.1244		
10	1.0280			5	1.0394		
7	1.0093			7	1.0184		
5	1.0020			7	1.0110		
10	0.9865			2	0.9940		
10	0.9756			10	0.9839		

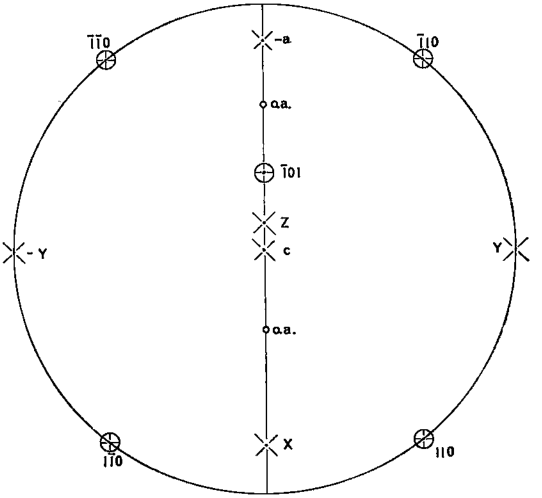

FIG. 1. Stereogram (upper hemisphere) of synthetic ahlfeldite and synthetic cobaltomenite showing crystallographic and optical elements.

OPTICAL DATA

The orientation of the principal vibration directions, optic axes, and crystal faces of both synthetic compounds were determined with a four-axis universal stage. The average grain size of the samples was 0.002mm by 0.005mm with an occasional grain reaching a length of 0.02mm. This small grain size coupled with the tendency of the crystals to lie on prism faces hampered the determination of the optical constants. The orientation of the indicatrix is shown in Figure 1, which serves equally well for both compounds.

The principal indices γ and α were determined from grains which were supported or tilted by other grains so that they were not lying on crystal faces. The principal index β was calculated from γ, α and $2V$. On several crystals of cobaltomenite flattened on ($\bar{1}01$) it was possible to measure β directly. Such flattened crystals were not found in synthetic ahlfeldite.

Finally, on crystals lying on (110), indices γ' and α' were determined. It was then possible to calculate β from these values by the method outlined by Sturman (1973). For synthetic cobaltomenite the measured value of β is 1.727; the value calculated from γ, α, and $2V$ is 1.728; and the value calculated from γ' and α' is 1.728. For synthetic ahlfeldite, where β could not be measured directly, the two calculated values are, respectively, 1.745 and 1.743.

Table 3 lists all the optical data obtained in this study.

TABLE 3. OPTICAL DATA FOR SYNTHETIC AHLFELDITE AND SYNTHETIC COBALTOMENITE

	ahlfeldite	cobaltomenite		ahlfeldite	cobaltomenite
α	1.703	1.681		*Crystals lying on (110)*	
β	1.744	1.728	γ'	1.784	1.766
γ	1.786	1.769	α'	1.725	1.710
$2V_\alpha$ (meas.)	87°	83°	$c \wedge \gamma'$	11°	12°
$2V_\alpha$ (calc.)	88°	83°			
Dispersion	$r<v$	not observed		*Crystals lying on ($\bar{1}01$)*	
$c \wedge \gamma$	-12°	-13°	β		1.728
$\beta \wedge (110)$	47°	51°	α'		1.693
$c \wedge (\bar{1}01)$	33°	35°		symmetrical extinction	
Pleochroism (weak)					
γ	green	red			
β	pale green	pink			
α	very pale green	pale pink			
absorption	$\gamma>\beta>\alpha$	$\gamma>\beta>\alpha$			

DETERMINATION OF INTERMEDIATE MEMBERS

In any isomorphous series it is desirable to have a physical method for determination of the chemical composition of intermediate members. In the series ahlfeldite-cobaltomenite, because of the difficulties of analysis due to the small grain size, several possibilities present themselves, namely, refractive indices, density, unit cell parameters, colour and *d*-spacings.

Of these, colour is most unreliable, as illustrated by the ahlfeldite of Pacajake, Bolivia. Although Aristarain & Hurlbut (1969) found that the formula for this mineral is $(\mathrm{Ni}_{0.90}\mathrm{Co}_{0.10})\mathrm{SeO}_3{\cdot}2\mathrm{H}_2\mathrm{O}$, the mineral is brownish-pink to red rather than the expected green.

The use of density and refractive indices is ruled out by the grain size of most specimens. For the same reason (plus the time involved) determination of unit cell parameters by *x*-ray single-crystal methods does not provide a practical means of identification. Directly related to the unit cell parameters are the *d*-spacings of the powder diffraction data.

Unit cell parameters can be calculated most accurately from the back reflections. Unfortunately, the back reflections are very weak for cobaltomenite and ahlfeldite and cannot be indexed because of the monoclinic symmetry and relatively large cell dimensions of the crystals. Thus, 9 lines were chosen with as small *d*-spacings as possible but where corresponding lines can still be easily recognized in powder patterns of cobaltomenite and ahlfeldite. The differences in *d*-spacings for these particular lines range from 0.020 to 0.011 Å (Table 4). Any intermediate member of the series should have *d*-spacings within this range. The composition of such an intermediate member is determined by a simple proportion assuming a linear relationship between *d*-spacings and composition. For example using Line 4, on Table 4, synthetic cobaltomenite has a *d*-spacing of 1.6436 and synthetic ahlfeldite has a *d*-spacing of 1.6285. This difference is 0.0151. An intermediate member with a *d*-spacing of 1.6416 for this line would have a composition of $(\mathrm{Ni}_{0.13}\mathrm{Co}_{0.87})\mathrm{SeO}_3{\cdot}2\mathrm{H}_2\mathrm{O}$. The value of 0.13 is determined from the ratio 0.0020/0.0151 where 0.0020 is the difference between the *d*-spacing of the intermediate member and that of cobaltomenite.

Ideally, all nine *d*-spacings should give the same composition for an intermediate member, but because of the error in measurement of 2θ, the results will be different. Using a large diameter camera (114.6mm) and Fe$K\alpha$ radiation, an error of $\pm0.05°$ 2θ will result in an error of ±5% in the composition.

To indicate the accuracy which can be obtained, two sets of measurements were made on a specimen of cobaltomenite (ROM No. M28049). These are given in Table 4. The % of the nickel end-member calculated from the individual measurements ranges from 8% to 26%. The mean is 16% with a standard deviation of 5%. Table 4 also includes data for another cobaltomenite specimen (ROM No. M27654) which results in a % of the Ni end-member of 16%. Using the data of Aristarain & Hurlbut (1969) for ahlfeldite, the method gives a composition of $(\mathrm{Ni}_{0.89}\mathrm{Co}_{0.11})\mathrm{SeO}_3{\cdot}2\mathrm{H}_2\mathrm{O}$ which agrees favorably with their empirical formula $(\mathrm{Ni}_{0.90}\mathrm{Co}_{0.10})\mathrm{SeO}_3{\cdot}2\mathrm{H}_2\mathrm{O}$.

X-ray fluorescence analyses were carried out in an attempt to check the calculated compositions of specimens M28049 and M27654. Both specimens consisted of very small grains of cobaltomenite scattered on fracture surfaces in sandstone. Sections could not be prepared for

TABLE 4. DETERMINATION OF THE Ni-CONTENT OF THE AHLFELDITE-COBALTOMENITE SERIES BY MEASUREMENT OF SELECTED *d*-SPACINGS (see text)

	Cobaltomenite (Synthetic)	Ahlfeldite (Synthetic)		Cobaltomenite M28049, Yellow Cat District, Grand Co., Utah								Cobaltomenite M27654 Temple Mt., Emery Co., Utah			Ahlfeldite (Aristarain & Hurlbut 1969)		
				I Reading				II Reading									
I	*d*	*d*	Δd	2θFe *K*α	*d*	Δd	% Ni comp	2θFe *K*α	*d*	Δd	% Ni comp	*d*	Δd	% Ni comp	*d*	Δd	% Ni comp
35	1.7340	1.7141	0.0199	68.05	1.7311	0.0029	15	68.10	1.7300	0.0040	20	1.7309	0.0031	16	1.718	0.0160	81
5	1.7160	1.6962	0.0198	68.95	1.7112	0.0048	24	68.90	1.7123	0.0037	19	1.7121	0.0039	20			
10	1.6950	1.6808	0.0142	69.78	1.6934	0.0016	11	69.80	1.6930	0.0020	14	1.6941	0.0009	6	1.682	0.0130	92
15	1.6436	1.6285	0.0151	72.32	1.6416	0.0020	13	72.34	1.6413	0.0023	15	1.6413	0.0023	15	1.629	0.0146	97
10	1.5957	1.5825	0.0132	74.81	1.5946	0.0011	8	74.82	1.5944	0.0013	10	1.5939	0.0018	14	1.584	0.0117	89
5	1.5650	1.5480	0.0170	76.59	1.5631	0.0019	11	76.71	1.5610	0.0040	24	1.5624	0.0026	15	1.549	0.0141	83
15	1.5440	1.5326	0.0114	77.81	1.5423	0.0017	15	77.89	1.5410	0.0030	26	1.5418	0.0022	19	1.533	0.0110	95
15	1.4950	1.4776	0.0174	80.91	1.4929	0.0021	12	81.00	1.4915	0.0035	20	1.4913	0.0037	21	1.479	0.0160	92
10	1.4340	1.4196	0.0144	85.18	1.4317	0.0023	16	85.20	1.4310	0.0020	14	1.4316	0.0024	17	1.422	0.0120	83
							$\bar{x} = 14$ $\sigma = 5$				$\bar{x} = 18$ $\sigma = 5$			$\bar{x} = 16$ $\sigma = 4$			$\bar{x} = 89$ $\sigma = 6$

electron probe analysis because of the planar arrangement and scattered distribution of the very small grains of weakly-adhering cobaltomenite. A microscopically pure sample of cobaltomenite was obtained from M28049, but the only sample obtainable from M27654 contained other (unidentified) phases. *X*-ray fluorescence analysis on M28049 gave 17% of the Ni end-member compared to the calculated figure of 16%. Analysis of three impure fractions from M27654 gave 28%, 30%, and 38% Ni end-member compared to the calculated figure of 16%. The writers feel that the discrepancy in M27654 is due to admixed impurities in the analyzed samples rather than any real difference in composition.

In conclusion, it is proposed that careful measurement of the powder diffraction pattern provides the most practical means of identification of intermediate members. In the case of larger crystals, optical constants could be used but the accuracy would be no greater.

It is important to point out that linear variation of the optical and crystallographic constants with respect to composition is assumed. This is supported by the data for the two end-members and the cobaltomenite (M28049) with 17% of the Ni end-member and the ahlfeldite with 90% of the Ni end-member. However, it cannot be proved until data from other intermediate members are available.

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