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AHLFELDITE FROM PACAJAKE BOLIVIA; A RESTUDY[1]

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ABSTRACT

Ahlfeldite $(Ni,Co)SeO_3 \cdot 2H_2O$ is found at Pacajake, Bolivia, as an alteration product of penrosite. It occurs in crystalline crusts and rarely in well-formed crystals ranging from 1/4 to 1 mm in length, elongated along the c axis or tabular flattened on $\{110\}$. The forms present are: $\{110\}$, $\{011\}$, $\{032\}$, $\{103\}$ and $\{\bar{1}01\}$. The mineral is monoclinic, $2/m$; space group $P2_1/n$; $a=7.53$, $b=8.76$, $c=6.43$ Å, $\beta=99°05'$; $a{:}b{:}c=0.8596{:}1{:}0.7340$; volume 418.8 Å^3, $Z=4$. Strongest lines in X-ray powder photographs are in Å: 5.69 (100), 3.426(80), 2.992(75), 3.772(60) and 2.719(60).

Ahlfeldite is optically biaxial $(-)$; $\alpha=1.709$, $\beta=1.752$, $\gamma=1.787$; $2V=85°$; $r<v$ strong; $Y=b$, $Z\wedge c=-16°$; pleochroism X=pale green, Y=pale pink, Z=pink. The hardness is 2–2 1/2; density 3.37 (meas.), 3.51 (calc.). Cleavage $\{110\}$ and $\{103\}$ fair. Color brownish varying toward red with increasing Co content. A water determination and the interpretation of a microprobe analysis yield the following: NiO 30.24, CoO 3.55, SeO_2 50.01, H_2O 16.2 Total 100, wt %. Variation in Ni:CO ratio indicated a solid solution series. It is proposed to use ahlfeldite when Ni>Co and cobaltomenite when Co>Ni.

HISTORICAL REVIEW AND INTRODUCTION

In 1882 Bertrand published the results of a study of secondary selenium minerals from Cacheuta, Provincia de Mendoza, Argentina (erroneously indicated as La Plata). He described briefly a *cobalt selenite*, associated with a lead and cobalt selenide, for which he proposed the name cobaltomenite. He indicated that the crystals are monoclinic, negative, with optic plane parallel to their elongation and with the acute bisectrix perpendicular to the elongation; the color is pink. No other characteristics are given.

In 1935 Ramdohr stated that Herzenberg had proposed the name ahlfeldite for a *nickel selenate* mineral found at Calquechaca, Bolivia. Later, Herzenberg and Ahlfeld (1935) reported the mineral to be brown and in crystals ranging from 0.5 to 2 mm, but gave no further information. In April 1935, Dr. Ahlfeld sent Professor Palache of Harvard University specimens of ahlfeldite which he said were "not yet well described and analyzed", although the name was already in print. In reply, (July 8, 1935) Palache said, "Dr. Berman has obtained preliminary characteristics which are certainly different from those of any known mineral . . . crystals are probably triclinic. Better measurements than we have yet obtained are essential to any adequate understanding of them".

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Later (Aug. 16, 1935), Ahlfeld wrote Palache, "The rose-colored mineral Dr. Herzenberg determined as a seleniate of nickel, I think it can be identical with Bertrand's cobaltomenite from Cacheuta, for which, however there is also no analysis." In another letter (Feb. 28, 1936), Ahlfeld felt even more strongly and wrote "The name 'Ahlfeldite' given by Herzenberg is erroneous, since it gives with blowpipe only cobalt and selenium reactions is therefore identical with cobaltomenite from Cacheuta." In September of the same year Ahlfeld reported "that the mine is completely exhausted, and therefore no other specimens have been found."

In a paper published in 1937 Palache said that the "red mineral regarded as new and named ahlfeldite . . . " was " . . . later recognized as cobaltomenite." In the same year Block and Ahlfeld in describing the Pacajake Mine, where ahlfeldite was found, indicate that the mineral is cobaltomenite. This is also repeated by Ahlfeld and Muñoz Reyes (1938, p. 62).

Herzenberg (1944, 1945), in identical papers, said that Ahlfeld, during a trip to Argentina, was unable to find specimens of cobaltomenite in museums and that the mine was inaccessible. In these papers he now decribes ahlfeldite as greenish to yellowish and said the red is due to an outside coating. He also stated that an analysis of a solution of ahlfeldite gives no indication of cobalt and indicates it to be a *hydrated nickel selenate.* In quoting Palache's letter (July 8, 1935) he mentions the mineral is "probably triclinic." In summarizing this paper Fleischer (1946) concluded that, "Ahlfeldite is therefore a valid species."

In 1953 Goñi and Guillemin presented the first adequate description of ahlfeldite from Bolivia indicating the mineral is a monoclinic *hydrated nickel selenite* with a brownish-pink color. Also optical and X-ray powder data are given. They state that the properties observed on cobaltomenite by Bertrand could perfectly well be applied to ahlfeldite. For this reason they concluded that the two minerals could be identical, although the type cobaltomenite was not available for comparison.

In Dana's System of Mineralogy (1951) cobaltomenite is listed as a selenite ($CoSeO_3 \cdot 2H_2O$?) and ahlfeldite as a selenate ($NiSeO_4 \cdot 6H_2O$?). Sindeeva (1964) also considered both minerals to be valid species.

Gattow and Lieder (1963) studied cobaltomenite[1] and ahlfeldite,[2] both from Pacajake, Bolivia. They found the X-ray powder patterns of the minerals to be identical and also identical with those of synthetic $CoSeO_3 \cdot 2H_2O$ and $NiSeO_3 \cdot 2H_2O$. Using X-ray spectrographic methods

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[1] U. S. Nat. Mus. Specimen No. 114452.

[2] U. S. Nat. Mus. Specimen No. R7758 and Lab. Min. Sorbonne, Paris, Specimen No. 1947.

they found the ratio of Ni:Co is 1:1 for cobaltomenite and 4:1 for ahlfeldite. They, therefore, conclude that ahlfeldite is merely a nickel-rich variety of cobaltomenite. Fleischer (1963) in discussing this paper remarks, "The existence of a mineral in this series with Co>Ni has not yet been proved, but it is certainly probable and it would seem more logical to keep both ahlfeldite, for members with Ni>Co and cobaltomenite, for those with Co>Ni."

In studying ahlfeldite from Pacajake we observed that at this locality the color of the crystals varied from brown through brownish-pink to red. The red color, resembling that of erythrite, as pointed out by Bertrand in his original description of cobaltomenite, undoubtedly results from a high cobalt content. This red mineral has a ratio of Ni:Co= 50:50, (Gattow and Lieder 1963). Electron microprobe analyses of the brownish-pink crystals made during this study yielded ratios of Ni:Co of 90:10 and 86:14. In his description of ahlfeldite, Herzenberg (1944) analyzed yellow to green crystals with a reddish-brown coating and found no cobalt.

These various analyses on samples from the same deposit suggest that solid solution exists between Ni and Co which is reflected in the color of the mineral. We, therefore, agree with Fleischer that the name cobaltomenite, even though none of the original material is available, be retained as the name for the cobalt-rich members of the series and that ahlfeldite be used for the nickel-rich members. The U. S. National Museum Specimen (No. 114452) labeled cobaltomenite is actually in the middle of the series.

OCCURRENCE

Ahlfeldite was found in Bolivia in the Pacajake silver mine near Hiaco, about 24 km ENE of Colquechaca on the eastern slope of the Central Cordillera. The deposit was described by Block and Ahlfeld (1937) as a vein striking N 30° W and dipping 65° SW, inclosed in Devonian sandstone. The primary vein minerals are penrosite (=blockite, (Ni,Cu,Pb)-Se_2) pyrite, clausthalite (PbSe), naumannite (Ag_2Se), tiemannite (HgSe), with barite, siderite, hematite and calcite. The secondary minerals include cerussite, anglesite, wulfenite, limonite and the rare silenium minerals, chalcomenite ($CuSeO_3 \cdot 2H_2O$), molybdomenite ($PbSeO_3$), ahlfeldite, native selenium and $Pb(SeS)O_4$.[1]

Ahlfeldite, an alteration product of penrosite, is found in crystalline crusts 1–1.5-mm thick covering areas of only a few square millimeters or filling small solution cavities. Rarely it is present in well formed individual crystals ranging in length from 0.25–1 mm.

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[1] A report on this mineral is in preparation.

MORPHOLOGY

Five relatively well formed crystals were measured on the two-circle goniometer; four, elongated on the *c* axis, present a rhomboidal cross-section and have similar forms at both ends. The ratios of length: width: thickness are approximately 3:1:1. The habit of these crystals is represented in Figure 1. The fifth crystal was tabular flattened on {110}. The angular measurements of the observed forms are given in Table 1.

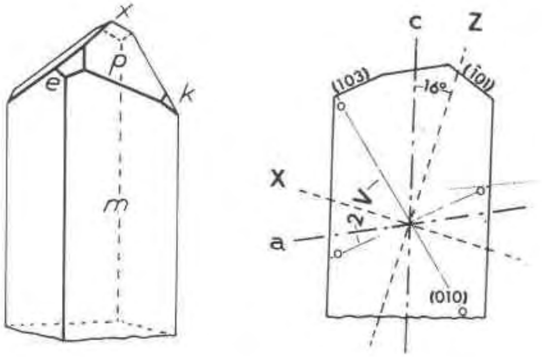

FIG. 1. Crystal drawing of ahlfeldite elongated along c axis (left); Optical orientation of ahlfeldite (right).

TABLE 1. AHLFELDITE ANGLE TABLE

Monoclinic; prismatic $2/m$

$a:b:c=0.8630:1:0.7322$; $\beta=99°05'$; $p_0:q_0:r_0=0.8484:0.7230:1$; $r_2:p_2:q_2=1.3831:1.1734:1$; $\mu=80°55'$; p_0' 0.8592; q_0' 0.7322; x_0' 0.1599

Forms		ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
m	110	49°34′	90°00′	0°00′	49°34′	83°06′	40°26′
p	011	12 19	36 51	80 55	54 08	35 52	82 42
k	032	8 17	47 59	80 55	42 40	47 20	83 53
e	103	90 00	23 52	66 08	90 00	14 47	66 08
x	$\bar{1}01$	−90 00	34 58	−55 02	90 00	44 03	55 02

PHYSICAL AND OPTICAL PROPERTIES

Ahlfeldite has two fair cleavages: {110} and {103}; it is brittle with a hardness of 2–2.5. The crystals are transparent with vitreous luster and the color is brownish-pink to red. The specific gravity, measured by suspension in an aqueous solution of thallium malonate-formate, was determined as 3.37 ± 0.02. This is considerably less than the calculated density, 3.51. This difference can be interpreted as resulting from numerous small inclusions and voids along cleavages or from cracks and impurities, since the crystal fragments available for specific gravity measurements were far from perfect. Goñi and Guillemin (1953) report a value of 3.4±0.05 for material from the type locality. Gattow and Lieder (1963) gave 3.416±0.004 for synthetic $NiSeO_3 \cdot 2H_2O$ and 3.410±0.001 for synthetic $CoSeO_3 \cdot 2H_2O$.

The optical properties are given in Table 2 and the optical orientation is represented in Figure 1.

TABLE 2. OPTICAL PROPERTIES OF AHLFELDITE

Indices:	Pleochroism
$\left.\begin{array}{l}\alpha=1.709\\ \beta=1.752\end{array}\right\}$ Na light ±0.001 $\gamma=1.787$ ±0.002	X=pale green Y=pale pink Z=pink
Opt. (−) $2V=85°$ $r<v$ strong	$Z\wedge c=-16°$ $Y=b$

X-RAY STUDY

The unit-cell data of ahlfeldite are given in Table 3. These values were determined with X-ray precession photographs (Mo/Zr) taken with b (0, 1st, 2nd layers) and a (0 layer) as precession axes. They were refined with data from X-ray powder photographs.

The most nearly orthogonal cell with $c<a$ was chosen whose general conditions for reflections are: $h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$; $h0l$, $h+l=2n$. The extinctions lead to the unique space group $P2_1/n$. In addition this seems preferable to the alternate designation $P2_1/c$, for in this orientation most of the well-formed crystals are elongated on c. With $P2_1/c$ as

TABLE 3. UNIT CELL DATA FOR AHLFELDITE

$a=7.53\pm0.01$ Å $b=8.76\pm0.02$ Å $c=6.43\pm0.01$ Å	Space group $P2_1/n$ Measured specific gravity, 3.37±0.02
$\left.\begin{array}{l}\beta=99°05'\\ \mu=80°55'\end{array}\right\}\pm15'$	Calculated density, 3.51 for empirical formula $(Ni_{0.90}Co_{0.10})SeO_3 \cdot 2H_2O$
$a:b:c=0.8596:1:0.7340$ Cell vol.=418.8 Å^3 $Z=4$	

TABLE 4. X-RAY POWDER DATA FOR AHLFELDITE

(CuKα=1.54178; CuKα_1=1.54051; Ni filter)
Camera diameter 114.59 mm

This Study				Goñi and Guillemin (1953)	
I[a]	d (obs)	d (calc)[b]	hkl	I	d (obs)
100	5.69	5.669	110	100	5.72
5	5.27	5.256	$\bar{1}01$	15	5.26
20	4.49	4.491	101	15	4.43
20	4.38	4.380	020		
40	4.01	3.996	111	25	4.00
60	3.772	3.774	120	40	3.77
80	3.426	3.422	210	50	3.40
30	3.214	3.214	$\bar{2}11$		
30	3.128	3.136	121		
75	2.992	2.985	012	80	2.98
20	2.930	2.924	$\bar{1}12$		
60	2.719	2.718	130	25	2.72
30	2.655	2.653	031	10	2.63
30	2.533	2.531	$\bar{1}22$	15	2.53
40	2.482	2.480	221	15	2.47
20	2.439	2.443	$\bar{3}01$		
50	2.354	2.353	$\bar{3}11$	25	2.35
5	2.299	2.296	230		
20	2.230	2.246	202		
		2.230	231		
75	2.190	2.190	040	50	2.20
20	2.148	2.149	032		
20	2.127	2.129	311		
		2.126	$\bar{1}32$		
10	2.062	2.066	$\bar{1}13$		
		2.063	$\bar{3}12$		
20	2.008	2.008	132		
15	1.958	1.962	321		
		1.956	103		
15	1.909	1.910	$\bar{3}22$		
		1.909	113		
		1.906	023		
1	1.875	1.874	$\bar{3}31$		
2	1.789	1.803	042		
		1.789	$\bar{1}42$		
2	1.766	1.770	241		
2	1.751	1.752	303		
		1.754	331		

[a] Visual estimation.

[b] The calculated *d* values were obtained and indiced on an IBM 7094 Computer using a program for calculations of all possible spacings.

TABLE 4.—(*Continued*)

This Study				Goñi and Guillemin (1953)	
I^a	d (obs)	d (calc)^b	hkl	I	d (obs)
50	1.718	1.719	$\bar{1}33$		
		1.718	$\bar{3}13$		
		1.717	$\bar{3}32$, 142		
		1.716	$\bar{4}21$		
25	1.682	1.681	411		
		1.682	$\bar{2}42$		
30	1.629	1.627	$\bar{3}23$		
		1.631	$\bar{3}41$		
		1.632	151		
30	1.584	1.587	004		
		1.585	250		
10	1.549	1.551	$\bar{2}04$		
20	1.533	1.534	025		
15	1.503	1.504	402		
		1.502	$\bar{5}01$		
20	1.479	1.480	$\bar{5}11$, 152		
		1.476	313		
		1.477	431		
15	1.460	1.460	060		
		1.459	143		
20	1.422	1.423	061		
		1.420	$\bar{4}41$		

space group the cell volume remains the same but $c > a$ and $\beta = 124° 26'$. The transformation formula from the n glide to the c glide position is $00\bar{1}/010/101$.

X-ray powder photograph data are presented in Table 4 with corresponding values obtained by Goñi and Guillemin (1953) for comparison. The two sets of values agree well with one another and with those given by Gattow and Lieder (1963) for synthetic $NiSeO_3 \cdot 2H_2O$ and for the cobalt analogue.

CHEMISTRY

The chemical composition of ahlfeldite has been determined as $(Ni,Co)SeO_3 \cdot 2H_2O$ (Goñi and Guillemin 1953; Gattow and Lieder, 1963). During this study brownish-red crystals from Pacajake were analyzed. The water was determined by Mr. William Sabine using a highly sensitive technique. This involved heating the sample at a uniform rate in a stream of dry nitrogen and measuring the evolved water with a P_2O_5 electrolysis cell. The mineral dehydrated in two stages with maxima at

236°C and 440°C. The amount of water was determined as 16.2 percent, which agrees almost exactly with the theoretical amount in $NiSeO_3 \cdot 2H_2O$. (See Table 5.)

Using the electron microprobe and NiSe and metallic cobalt as standards, the crystals were analyzed for Ni,Co and Se by Dr. John Drake. Because the sample partially dehydrated under the electron beam the values obtained and the oxides percentages derived from them, were higher than had the mineral been fully hydrated. These percentages were then reapportioned including the 16.2 weight percent water, obtaining the figures given in column 1, Table 5. They result in the empirical formula, $(Ni_{0.90}Co_{0.10})SeO_3 \cdot 2H_2O$. The recalculated values are very close to those of the synthetic compounds (see Table 5) in spite of the fact that the method involves an error of ±5 percent. An electron microprobe analysis of another ahlfeldite crystal gave a ratio of Ni:Co=86:14.

Table 5. Chemical Analysis of Ahlfeldite from Pacajake, Bolivia

	Ahlfeldite[a]			Synthetic		
	Wt%	Atomic proportions when Se=1			$NiSeO_3 \cdot 2H_2O$ Wt%	$CoSeO_3 \cdot 2H_2O$ Wt%
NiO	30.24	Ni	0.898	NiO	33.70	—
CoO	3.55	Co	0.105	CoO	—	33.77
SeO_2	50.01	Se	1.000	SeO_2	50.05	50.00
$H_2O(+)$	16.20	H	3.992	H_2O	16.25	16.23
$H_2O(-)$	0.06	O	4.998			
	100.06				100.00	100.00

[a] NiO, CoO and SeO_2 electron microprobe analysis by Dr. John Drake; H_2O by Mr. William Sabine.

Because of the close similarity of Co and Ni in ionic radius and atomic weight, the substitution of one element for the other causes only slight difference in optical properties, *d* or density. It is thus only through a chemical determination of the ratio of Ni:Co that members of the series can be distinguished. However, in a qualitative way the color gives a clue to the composition: the deeper the red the greater the cobalt.

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