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COSTIBITE (CoSbS), A NEW MINERAL FROM BROKEN HILL, N.S.W., AUSTRALIA[1]

L. J. CABRI, D. C. HARRIS AND J. M. STEWART,
Mines Branch, Dept. of Energy, Mines and Resources, Ottawa, Canada.

ABSTRACT

Costibite from the Consols Mine, Broken Hill, New South Wales is a new mineral having the composition CoSbS, essentially the same as paracostibite from Red Lake, Ontario, Canada, but with a different space group and crystal structure. Costibite is orthorhombic with $a=3.603$, $b=4.868$, $c=5.838$Å, $Z=2$, space group $Pmn2_1$, calc. $\rho=6.89$ g/cc. The strongest lines of the X-ray powder pattern are: 4.86(5) (010), 2.90(6) (110), 2.596(10) (111), 2.503(9) (012), 1.908(8) (121), 1.803(4) (200), 1.714(4) (103), 1.616(4) (113), and 1.463(4) (212).

In reflected light the mineral is greyish in color, very similar to paracostibite, it is weakly bireflecting and weakly anisotropic. Its microhardness value is 781 kg/mm^2 with a 15 g load.

INTRODUCTION

Subsequent to discovering the new mineral paracostibite in ore from the Red Lake area, Ontario, we were fortunate to obtain what appeared to be a type willyamite specimen for a reexamination by modern techniques; this led to our discovery of the new mineral costibite. Paracostibite (CoSbS) is orthorhombic with space group *Pbca* (Cabri *et al.*, 1970a); willyamite, as redefined (Cabri *et al.*, 1970b), is the portion of the pseudocubic (Co, Ni)SbS series where Co$>$Ni.

The optical properties of paracostibite and costibite are nearly identical. The composition of these two minerals, as well as those of the hypothetical cobalt end-member of the willyamite solid solution series, are also nearly identical. This created the remarkable situation whereby two, and possibly three polymorphs of CoSbS have been discovered within the space of a few months, where previously none were known.

MATERIALS AND METHOD OF INVESTIGATION

The museum sample examined was obtained from the Smithsonian Institution, Washington, D.C., and bore the U.S. National Museum number R849, labelled "Willyamite, Consols Lode, Broken Hill, N.S.W." The sample came from the Roebling collection with the following note attached: "from George Smith, chemist at the mine, only specimen found, $10., near ullmannite, W. A. Roebling." Dr. J. S. White, Jr., who kindly sent us the specimen, feels that this can be regarded as the type specimen from willyamite since it was Smith who had found the "willyamite" described by Pittman (1893); we share this opinion. This specimen will also become the type for costibite, and is preserved at the Smithsonian Institution. A polished section cut from the specimen is preserved at the National Mineral Collection, Ottawa.

The sample was studied by ore microscopy, X-ray diffraction analysis, and electron-

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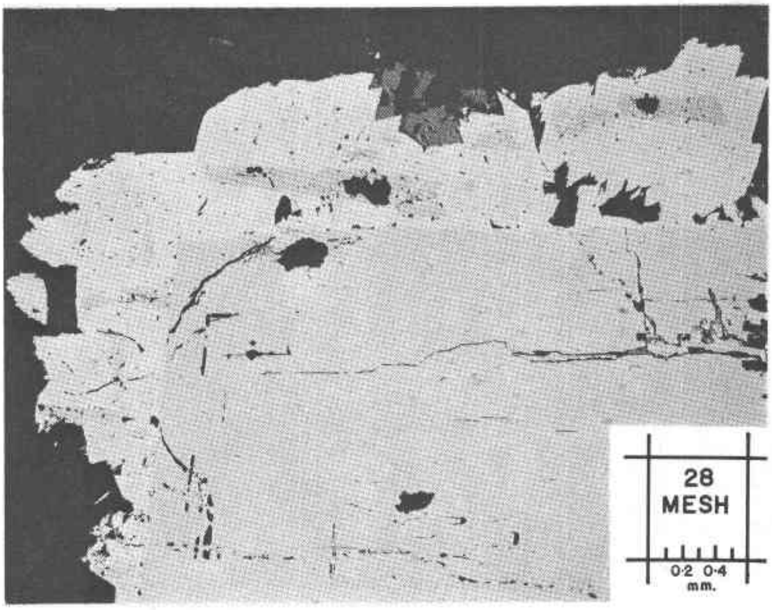

FIG. 1. Photomicrograph of large ullmannite-willyamite zoned crystal (gray) surrounded by lollingite (white) containing lamellae of costibite (gray). Four of the black areas are holes from which material was removed for X-ray powder diffraction analysis. The gangue mineral (black) surrounding the löllingite is siderite. The large costibite lamella showing a hole, in the upper right portion of the photomicrograph, was subsequently dug out of the single-crystal work.

probe microanalysis. The X-ray powder data were obtained by the film method using 114.6-diameter Debye-Scherrer powder cameras. Film shrinkage corrections were applied, and the unit-cell parameters were refined by a least-squares computer program. The single-crystal work was done by the precession method.

The composition of costibite was determined using a Materials Analysis Company (MAC) model 400 electron-probe microanalyser. Synthetic CoSbS, NiSb, and FeAs, synthesized from high purity elements, were used as standards. The techniques employed in synthesizing some of these are reported in Cabri *et al.* (1970a).

The ore microscopy, including reflectivity measurements and microhardness determinations, were performed on samples mounted, polished, and finally buffed as described by Cabri *et al.* (1970a). The apparatus and techniques used for reflectivity measurements and microhardness indentations are those described by Cabri and Traill (1966) except that a 16 5:1 objective with a numerical aperature of 0.40 was used.

GENERAL MINERALOGY

A section from sample R849 consisted of a zoned crystal of willyamite-ullmannite surrounded by a rim of löllingite. This löllingite contains costibite lamellae (up to 0.2×1.4 mm) that appear to be oriented parallel to the sides of a large willyamite-ullmannite zoned crystal (Fig. 1). Figure

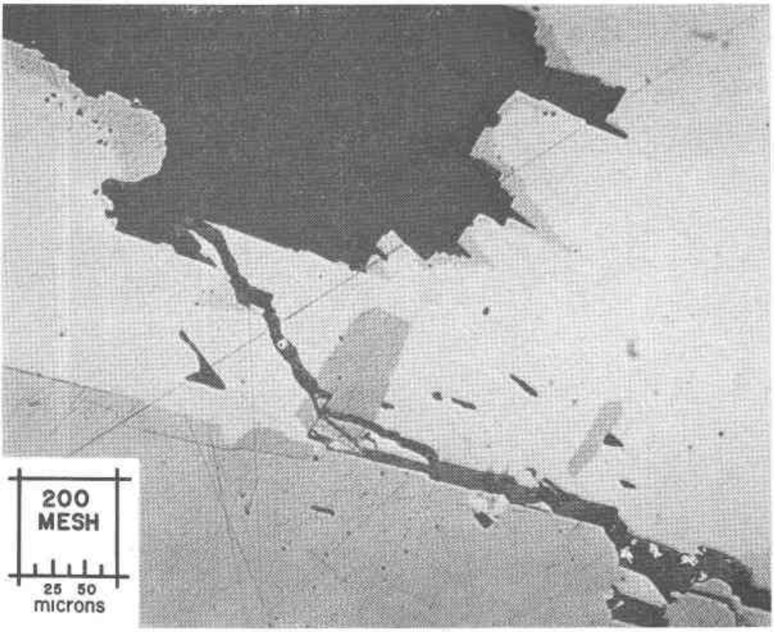

FIG. 2. Photomicrograph of two costibite lamellae (grey) in lollingite (white) near the edge of an ullmannite-willyamite crystal (grey). A vein of pyrargyrite cuts across the costibite. A rim of cobaltite (light grey) can be seen at the boundary between the löllingite and siderite (large black area).

2 shows other costibite lamellae at a greater magnification which permits the sharp contact with löllingite to be seen more clearly. It is noteworthy that, although some of the costibite lamellae are very nearly in contact with willyamite, there is either löllingite or pyrargyrite between them.

PHYSICAL, OPTICAL, AND CHEMICAL PROPERTIES

In reflected light the mineral is very similar to paracostibite and willyamite. Like paracostibite, but unlike willyamite, it is weakly bireflecting and weakly anisotropic. It is greyish in color in air and in oil immersion in contrast to the surrounding löllingite. The reflectivity spectrum for two grains, using a calibrated silicon standard, was measured from 440 to 650 nm but was found to be rather featureless. The values at four wavelengths are given in Table 1; those for paracostibite, willyamite and ullmannite are also given, for comparison purposes.

The VHN microhardness gave an average value of 781 kg/mm^2 (range 695–1009, 12 indentations on four grains) for a 15 g weight, in contrast to 1009 kg/mm^2 and a narrower range obtained for paracostibite using

TABLE 1. REFLECTIVITIES, IN PERCENT

Wavelength nm	Costibite Consols lode, N.S.W. U.S.N.M. #R 849 Average	Paracostibite Red Lake, Ontario Max.	Min.	Willyamite Consols lode, N.S.W. U.S.N.M. #R 849	Ullmannite Consols lode, N.S.W. R.O.M. #E-1768
470	44.4	47.8	46.9	47.2	46.5
546	45.9	48.1	47.5	47.7	46.4
589	45.5	48.4	47.7	46.7	46.4
650	47.8	48.8	48.0	48.9	48.9

The small differences between these values can be attributed to errors in measurement due to the differences in the surface polish.

the same weight. We have no explanation for the relatively large range of values obtained, but the average value suggests that costibite is softer than paracostibite.

Electron-probe microanalyses of three large grains from a polished section gave: Co 26.5–26.9, Fe 0.3–0.8, Ni 0.0–0.6, Sb 56.6–57.3, As 0.3–0.4, and S 15.0–15.1 percent; averages: Co 26.7±0.5, Fe 0.6±0.05, Ni 0.2 ±0.05, Sb 57.0±0.5, As 0.3±0.1, S 15.1±0.5 percent, for a total of 99.9 percent, giving $(Co, Fe, Ni)_{0.98}(Sb, As)_{1.0}S_{1.0}$; therefore equivalent to CoSbS.

The electron back scatter and X-ray images for various elements of a small area in Figure 2 showing a tabular costibite crystal in löllingite is illustrated in Figure 3. The FeK_α, CoK_α and NiK_α images clearly distinguishes cobaltite rimming löllingite, which, in turn, is surrounded by the siderite gangue.

We were able to obtain X-ray diffraction patterns free of any other phases, and one such pattern is listed in Table 2. The X-ray powder pattern for costibite is compared to that of rammelsbergite in Figure 4. The two patterns exhibit some similarity, but close examination shows that there are significant differences. A fragment of costibite was removed for single-crystal work with a precession camera. The space group ($Pmn2_1$ or $Pmmn$) could not be uniquely determined by the precession method. Dr. E. J. Gabe, of our Division, who is working on the structure of costibite as well as that of synthetic paracostibite, has informed us that the three dimensional Patterson map indicates that the space group for costibite is $Pmn2_1$. These structures will be reported at a later date. The cell dimensions given in Table 2 are taken from single-crystal diffractometer measurements and agree closely with values calculated from the powder film. On the basis of $Z=2$, the calculated density is 6.89 g/cc.

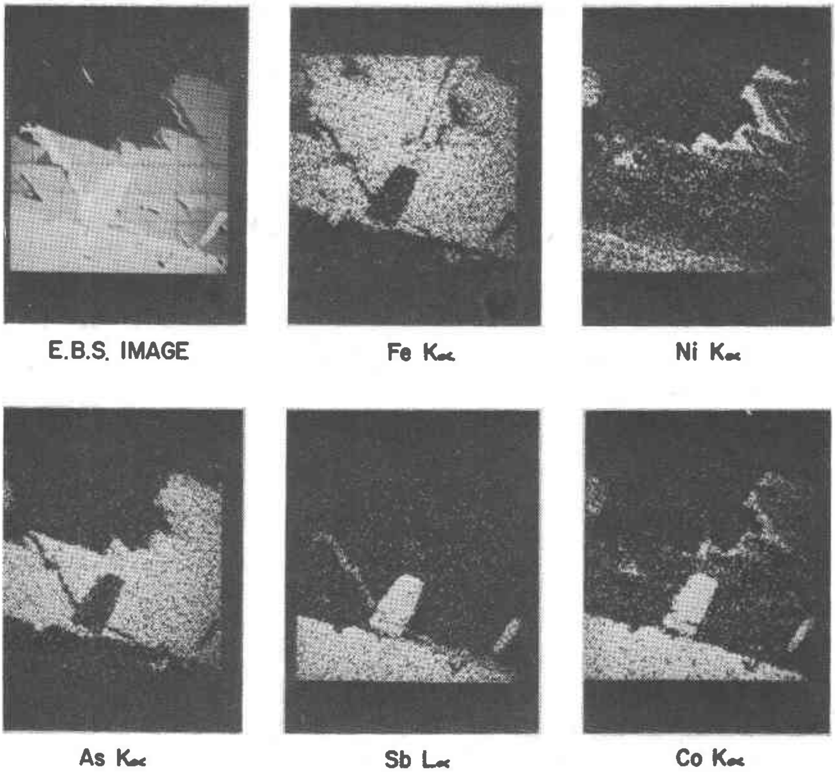

FIG. 3. Part of the area of Figure 2 showing electron back-scatter and as element fluorescent X-ray images. This permits all the minerals occurring in this photomicrograph to be distinguished, and the noncontact of costibite and willyamite to be delineated.

The name costibite (KŌ-STĬB-AIT), is for the composition (CoSbS). It has been approved by the Commission on New Minerals and Mineral Names, I.M.A.

Discussion

Costibite and paracostibite can both be considered as polymorphs of composition CoSbS, and willyamite, could possibly be yet a third polymorph. The pure CoSbS end-member for willyamite has not yet been found (Cabri *et al.*, 1970b), but there is no theoretical reason why it should not occur. The relationship between these polymorphs, and their thermal stabilities, is of interest because of the clues it provides about the genesis of the ore deposits in which they occur.

Synthetic preparations of CoSbS by "dry fusion" (Cabri *et al.*, 1970a) have only produced paracostibite. Bayliss (1969) reports the production

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR COSTIBITE
FE-FILTERED CO RADIATION

$a=3.603\pm0.002$, $b=4.868\pm0.002$, $c=5.838\pm0.002$Å

I(est.)	*d*(meas.)Å	*hkl*	*d*(calc.)Å	*I*(est.)	*d*(meas.)Å	*hkl*	*d*(calc.)Å
5	4.864	010	4.8680	1	1.2776	213	1.2758
2	3.738	011	3.7388	3	1.2501	024	1.2517
4	3.075	101	3.0661	4	1.1792	231	1.1808
6	2.902	110	2.8960			133	1.1778
10	2.596	111	2.5944	1	1.1628	223	1.1617
9	2.503	012	2.5034	2	1.1452	311	1.1435
1	2.430	020	2.4340	1	1.1353	015	1.1354
3	2.245	021	2.2466	3b	1.1137	232	1,1144
3	2.055	112	2.0559	1	1.1036	214	1.1045
8	1.908	121	1.9063	3	1.0840	034	1.0851
2	1.866	022	1.8694	3	1.0728	142	1.0724
5	1.8032	200	1.8015	3	1.0607	321	1.0592
4	1.7147	103	1.7122	4	1.0387	134	1.0390
<1	1.6907	210	1.6895	5	1.0289	224	1.0279
3	1.6569	122	1.6593	3	1.0090	240	1.0085
4	1.6167	113	1.6152	1	1.0014	313	1.0002
3	1.5641	031	1.5634	3	0.9919	143	0.9920
1b	1.5348	202	1.5330	3	0.9612	215	0.9605
<1	1.5202	023	1.5199			051	0.9603
4	1.4634	212	1.4622	3	0.9538	016	0.9541
1	1.4356	131	1.4342			242	0.9532
1	1.4152	032	1.4183			331	0.9524
3	1.4006	123	1.4004	2	0.9425	323	0.9423
1	1.3230	132	1.3197	2	0.9170	135	0.9166
2	1.2973	222	1.2972			332	0.9165

Intensities estimated visually, b signifies broad.

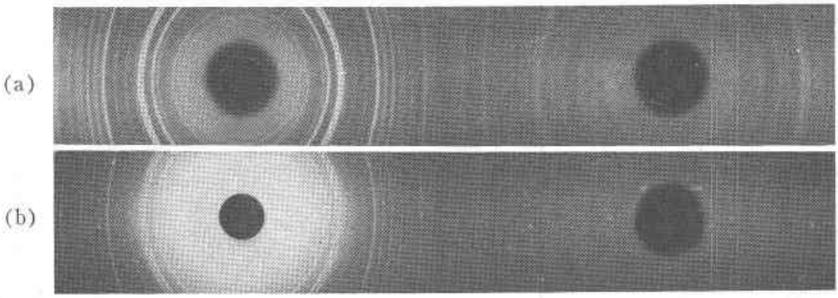

FIG. 4. X-ray powder diffraction patterns of (a) rammelsbergite and (b) costibite. Fe-filtered Co radiation, 57.3-mm Debye-Scherrer camera. The low-angle reflections for costibite cannot be seen in this reproduction. The rammelsbergite is No. 511 from the mine of Siscoe Metals of Ontario, Gowagnda, and has a composition, as determined by electron-probe microanalysis, of Ni 25.0, Co 3.3, Fe 0.0, As 67.0, S 1.7; total 97.0%.

of non-cubic CoSbS at 550°C using a LiCl-KCl flux, but it is not known whether he had costibite or paracostibite. Paracostibite is stable up to 876 ± 5°C and annealing experiments on synthetic material produced no change down to 100°C (Cabri *et al.*, 1970a), which were annealed for three days. These data suggest that costibite is a lower temperature polymorph.

We performed experiments to determine the temperature at which CoSbS reacts with synthetic $FeAs_2$ by grinding mixtures of the two and annealing at various temperatures. The temperature at which the reaction occurs to form $(Fe, Co)As_2 + FeS + Sb$ was determined to be 445 ± 10°C. This gives an upper temperature limit for the costibite lamellae in löllingite found in the Australian Broken Hill Consols Lode. Longer term experiments, longer than 7 to 17 days, may give a more precise temperature.

The difference between the mineralogy of the A. B. H. Consols lode and the "Thackaringa" sulphide ores has been discussed by Markham and Lawrence (1962) and Lawrence (1967, 1968). Although they suggest that both types of deposits are due to a certain amount of remobilization and redeposition, they imply that the A. B. H. Consols ore must have had a different genesis than the more numerous "Thackaringa"-type deposits in the Broken Hill area. Their arguments are based on the kind of mineralogy and the greater complexity of the Consols ore; they also suggest a similarity between the Consols and St. Andreasburg ores.

The A. B. H. Consols ore contains other mineral pairs that are thought to be dimorphous, such as argentopyrite-sternbergite ($AgFe_2S_3$) and pyrostilpnite-pyrargyrite (Ag_3SbS_3) (Markham and Lawrence, 1962). The apparently non-reversible reaction, pyrostilpnite→pyrargyrite, was given as $<197°C$ (Chang, 1963), and the breakdown of both argentopyrite and sternbergite to form, initially, acanthite, monoclinic pyrrhotite, pyrite, and vapor, (a metastable assemblage) was determined to occur, as low as 152 ± 3°C (Taylor, 1969). Although we were unable to find either argentopyrite or pyrostilpnite in our sample, their presence in other parts of the Consols fissure vein suggests that the ore-forming processes were still in operation below 152°C together with low values for sulfur fugacity (Czamanske, 1969). A more detailed presentation of the chemical identity of argentopyrite and sternbergite is presented by Murdock and Berry (1954), Czamanske and Larson (1969). The presence of the costibite-lollingite mineral pair in our specimen gives an upper temperature limit of 455°C for the crystallization of the assemblage of these minerals. We have no evidence, at present, on the upper stability limit of the zoned willyamite.

It is, of course, very difficult to present a more detailed discussion of the genesis of the Consols ore on the basis of one sample. The number and variety of the polymorphic mineral pairs found in this ore warrants a detailed reexamination of the mineralogy by modern methods. This would be of help for the eventual elucidation of the phase chemistry of the ore by laboratory experiments.

ACKNOWLEDGMENTS

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