A REEXAMINATION OF THE LEAD SULPHOSALT KEELEYITE FROM BOLIVIA[1]

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The mineral keeleyite, a sulphosalt of lead from the Oruro district of Bolivia, was originally described by Mr. S. G. Gordon[2] as a new species having the formula $2PbS \cdot 3Sb_2S_3$. The first analysis, which was made by Whitfield, was corrected on the assumption that the contaminating sulphide was principally chalcopyrite. Later it was found that the so-called chalcopyrite was in reality stannite. The first formula as above deduced was $2PbS \cdot 3Sb_2S_3$. Since the tin present would be included and weighed with the antimony, there was opportunity for a considerable error in the important relation existing between basic and acid sulphides in the compound, and some doubt was entertained as to the correctness of the formula derived for the mineral. Some reviewers questioned the validity of the mineral as a distinct species and, in fact, one of the present writers allowed a review of the original description to be published over his name (E.V.S.)[3] questioning the reliability of the formula adduced. In a commendable effort to further establish or discredit his species, Mr. Gordon has encouraged and assisted continued work on this mineral. The single original specimen, measuring $3\times5\times7$ inches[4] was not obtained in place but was found on the *cancha* of the San José mine at Oruro. Mr. Gordon had hoped, on his second visit to Bolivia in 1925, to obtain more material for a more thorough and extended investigation of the mineral. As these hopes were not realized, a new analysis and mineralographic examination was made on the original specimen.

As originally described by Gordon the specimen was a mass of cavernous quartz studded with small, white, quartz crystals. The cavities contain sheaf-like aggregates of acicular, dark metallic gray crystals of keeleyite, some pyrite and small twinned crystals of

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[2] Samuel G. Gordon, Keeleyite, a new lead sulfantimonite from Oruro, Bolivia. *Proc. Acad. Nat. Sci., Philadelphia*, vol. **74**, p. 101 (1922).

[3] *Amer. Mineralogist*, vol. **8**, p. 167, Sept. 1923.

[4] This specimen has since been broken into two pieces, one of which is in the collection of Mr. George Vaux, Jr., of Bryn Mawr, Pa.

stannite. The keeleyite crystals are deeply striated and furrowed, due in part, to parallel and subparallel growth. No measurable crystals were found.

The sample for reexamination, prepared for analysis by Mr. Gordon and turned over to the writers for investigation, consisted of approximately a half gram of acicular crystals which had been individually selected under a microscope and freed from all visible impurities. A mineralographic examination showed this material to be unusually pure. A further result of the microscopic work was to demonstrate that keeleyite is distinctly different from zinkenite in both color and microchemical reactions and that this mineral does not agree with any lead sulphantimonite for which data are at hand. The microchemical and other properties are given below and compared with zinkenite:

	Zinkenite	Keeleyite
1:1 HNO_3	Quickly tarnishes brown to black with slow effervescence; rubs to iridescent gray	Negative
1:1 HCl	Negative; fumes tarnish slowly; rubs faint.	Negative
20%KCN	Negative	Negative
20% $FeCl_3$	Negative	Negative
40% KOH	Slowly develops grain structure	Stains dark gray
5% $HgCl_2$	Negative	Negative
Aqua regia	Quickly stains black	Stains iridescent.
Hardness	Soft	Soft or medium
Color	Grayish white	Gray
Anisotropism	Moderate	Moderate
Form	Prismatic	Prismatic

The data given above for zinkenite are those of Davy and Farnham.[5] These were confirmed in their entirety on a specimen of zinkenite from Wolfsberg (in the Harz) in the National Museum collection (Cat. No. 83,982). Aside from the difference in action toward reagents, keeleyite is distinctly darker gray in color than any of the other sulphantimonites of lead as seen in polished surface under the microscope. A specimen in the Museum collection (Cat. No. 94,618) labelled "keeleyite, not from type" which as received from Mr. Gordon consists of gray needles thickly and firmly embedded in a white clay. This gray mineral was found to be identical mineralographically with the analyzed keeleyite.

[5] Microscopic examination of the ore minerals. McGraw-Hill Book Co., 1920, page 62.

The analysis of the pure mineral, carried out by standard methods, gave the following results:

Constituents	Per cent			Ratios
Insoluble	0.60			
Lead (Pb)	29.80	.144		
Silver (Ag_2)	0.52	.002		
Iron (Fe)	0.84	.015	.190	$.038 \times 5$
Zinc (Zn)	1.24	.019		
Copper (Cu)	0.64	.010		
Tin (Sn)	0.18	.002		
Arsenic (As)	0.27	.004	.366	$.037 \times 10$
Antimony (Sb)	43.32	.360		
Sulphur (S)	23.02	.717	.717	$.036 \times 20$
	100.43			

The above results and ratios indicate the formula $5RS \cdot 5Sb_2S_3$, or $PbS \cdot Sb_2S_3$ with the lead in part replaced by small amounts of zinc, iron, copper and silver in the order named. In view of the ideal purity of the analyzed sample there is no possibility of eliminating the miscellaneous bases as due to admixtures. The sum of these various bases bears a ratio to the lead of 1:4, so that the formula can be more exactly made to represent the analytical results by expansion to

$$4PbS \cdot (Zn, Fe, Cu, Ag_2)S \cdot 5Sb_2S_3.$$

Such formulas are not unknown among the sulphosalts since Schaller's formula for jamesonite is $4PbS \cdot FeS \cdot 3Sb_2S_3$ and owyheeite has the formula $8PbS \cdot 2Ag_2S \cdot 5Sb_2S_3$. In spite of the mixed character of the accessory bases, it seems entirely probable that this formula expresses the difference between the composition of keeleyite and zinkenite.

In this connection it is well to reconsider the first analysis of keelyite made by Whitfield and published by Gordon in his original description of the mineral. Subsequent examination, by both Gordon and Shannon of the same keeleyite shows the impurities mixed with the mineral to be only pyrite and stannite, the pyrite being in coarse crystals, easily recognized on account of their color. The stannite, dark in color and not anticipated, probably did contaminate the sample to some extent. In interpreting the original results all of the iron and copper were deducted as extraneous and the formula derived from the relation between lead and antimony (the latter contaminated by the unrecognized tin) was 2PbS ·

$3Sb_2S_3$. The original analysis is given in column 1 of the following table. In column 2 are given the ratios of the original analytical figures while in columns 3 and 4 are given the residual ratios as nearly as possible after deducting 7.74% of stannite, all of the copper being used, by way of trial, as the only possible index to this constituent. It will be seen that the corrected ratios indicate the formula $4PbS \cdot FeS \cdot 5Sb_2S_3$.

	1	2	3	4
Lead (Pb)	25.80	.125	.125	.031× 4
Iron (Fe)	2.77	.049	.031	.031× 1
Copper (Cu)	2.25	.035		
Antimony (Sb)	43.46	.362	.344	.034×10
Sulphur (S)	24.54	.765	.693	.035×20
	98.82			

The only other explanation of the difference between keeleyite and zinkenite is that the formula commonly ascribed to zinkenite is wrong and that this mineral actually has the formula $2PbS \cdot 3Sb_2S_3$ or $3PbS \cdot 4Sb_2S_3$. However this may be, it is definitely established that keeleyite is different from the other sulphosalts of lead and can be accorded full species rank.

APATITE CRYSTALS FROM WIANT'S QUARRY, NEAR PILOT, MARYLAND

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In Mr. Samuel G. Gordon's paper on desilicated granitic pegmatites[2] of the vicinity of the Pennsylvania-Maryland state line he states that the albitite of Wiant's quarry, three quarters of a mile northeast of Pilot, Cecil County, Maryland, is filled with miarolitic cavities which are lined with minute, colorless, albite crystals. He further says that minute, transparent, greenish, highly modified beryl crystals occur rarely implanted on the albite while not infrequently the rest of the cavity is filled with matted masses of dark green actinolite needles.

[1] Published by permission of the acting Secretary of the Smithsonian Institution.
[2] *Proc. Acad. Nat. Sci. Philadelphia*, **1921**, part 1, page 179.