X-RAY INVESTIGATION OF COLUSITE, GERMANITE AND RENIÉRITE

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ABSTRACT

X-ray powder photographs of colusite, germanite and reniérite show them to be essentially isostructural. They are isometric or pseudo-isometric, some divergences from a truly isometric pattern being shown. Colusite and germanite are isotropic on the polished surface, but reniérite is strongly anisotropic, and also moderately magnetic. The color of reniérite is bronze brown, as contrasted with the grayish pink of germanite. Reniérite in addition shows more variation than germanite from the normal isometric pattern. The accumulated evidence indicates that germanite and reniérite should be considered separate species.

Average values for the cell edges of the three minerals are as follows:

colusite $a_0 = 10.608 \pm$ Å, germanite $a_0 = 10.58 \pm$ Å, reniérite $a_0 = 10.58 \pm$ Å.

Relative intensities of the diffraction lines correspond very closely, with the exception of those corresponding to the following group of spacings:

Form	Intensity		
	colusite	*germanite*	*reniérite*
(002)	2	1	½
(012)	2	½	½
(112)	2	2	2

Nearly all of the lines of the powder photograph of each can be indexed satisfactorily, but for all three minerals rather definite lines appear at about $11.6 \pm$ Å, that cannot be indexed from the assumed values of a_0.

HISTORICAL

Colusite was first noted as a probable new mineral, and called "bronze enargite" by Murdoch (10) in 1915, in the course of examination of specimens from Butte, Montana, for the Secondary Enrichment Investigation directed by Professor L. C. Graton. The presence of tin was recognized, and imperfect crystals were judged by Professor Palache to be isometric, but the only analysis was unfortunately abortive. The same mineral was later named "colusite" by Reno H. Sales of the Anaconda Copper Mining Company. It was studied in some detail by Landon and Mogilnor (6) and Zachariesen (18), in 1933, and considered to belong to the sphalerite group, with a unit cell edge of $5.30 \pm$ Å. Later work by Nelson (11), and Berman and Gonyer (1), in 1939 modified some of the earlier conclusions, and showed that the unit cell edge should be doubled, and that the structure was closely related to the tetrahedrite group.

Germanite was first observed from Tsumeb, Southwest Africa, by Schneiderhöhn (13), in 1920, and described as "Rosa Erz," an unknown, new copper iron sulfide. It was described by Pufahl (12) in 1922, with an analysis, and with recognition of the presence of germanium. Kriesel (4, 5) published further analyses. Thomson (15) in 1924 made a mineralographic study of germanite, and an additional analysis, in which all iron present was attributed to pyrite. [The writer has found a small amount of iron in germanite by a microchemical test on pure material from a polished surface.] De Jong (3) in 1930 attempted to determine the crystal structure by *x*-ray study. He found a value of 5.29± Å for the cell edge, but suggested that if a different structure were assumed, this value might be doubled.

Reniérite was first noted from the Prince Leopold mine, Kipushi, in the Belgian Congo, by Thoreau (16), in 1928. He observed it as small grains in the sulfide ores, resembling in color, hardness and chemical behavior the "orange bornite" of Murdoch (10). Le graye (7) in 1933 described the mineral more fully, and suggested it might be chalmersite. He determined moderate magnetism, and strong isotropism on the polished surface. His etch reactions with the standard reagents were all negative. Vaes (17) in 1948 redescribed this mineral, and named it reniérite. His analysis showed considerably more iron than germanite, [confirmed by microchemical test on pure material from a polished surface—J.M.] and recorded the presence of germanium, as well as of essential zinc and arsenic. He, too, noted magnetism, sometimes with polarity, and strong anisotropism, with occasional polysynthetic twinning on the polished surface. In addition, he found minute crystals of tetrahedral symmetry with positive forms (111), (*hll*) and (*hhl*) of good quality, and the negative form $(1\bar{1}1)$ curved and imperfect.

Dr. H. Lambot, at the University of Liège, has published a brief note (19) on reniérite, giving *x*-ray powder data in agreement with mine, and observing also from these that the unit cell edge should be doubled.

A new occurrence of reniérite was brought to the attention of the writer by F. W. Farwell of the American Cyanamid Company. The mineral was discovered by Dr. B. Geier of the Tsumeb Corp., Ltd., as disseminated grains intergrown with galena, pyrite, tennantite, germanite and bornite, in primary ore from the 2390 foot level of the Tsumeb mine, Tsumeb, Southwest Africa. He at first considered it a new mineral and tentatively designated it mineral *X*. However, the *x*-ray powder data show it to belong to the germanite-reniérite group, with physical and chemical properties nearly identical with those of reniérite. Accordingly, the find may be considered as a new locality for reniérite.

Dr. Geier and the Tsumeb Corporation have kindly consented to the incorporation of these new data in this paper, and the author hereby wishes to express his appreciation of this courtesy.

TABLE 1. *X*-RAY POWDER PHOTOGRAPHS
Average readings in Ångstrom units with CuKα and CoKα radiation

Colusite		Germanite		Reniérite		*hkl*
d/n	*I*	*d/n*	*I*	*d/n*	*I*	
11.88 Å	½	11.46 Å	½	11.72 Å	½	?
11.00 ?	½	10.13	½	10.25 ?	½	001
9.99 ?	½	8.77 ?	½	8.96 ?	½	?
7.46	½	7.50	1	7.50	1	011
6.80	½	7.02 ?	½			?
6.65 ?	½					?
		6.25 ?	½			?
6.07	½	6.11	½	6.05	½	111
5.30	2	5.31	1	5.30	½	002
4.75	2	4.74	½	4.80	½	012 ←
4.33	2	4.32	2	4.31	2	112
		3.73	½	3.75	½	022
				3.55	½	003
3.36	2	3.42	½	3.34		?
		3.34	½		1	013 ←
3.21	½					113
3.075	10	3.054	10	3.06	10	222
2.96	½	2.96	½	2.96	½	023
2.83	1	2.83	1	2.82	1	123
2.66	4	2.64	4	2.65	3	004
2.56	½			2.56	½	014
2.50	½	2.49	½	2.50	½	033, 114
2.476	½					?
2.41	½					133
2.38	½	2.37	½	2.386	½	024
2.32	½					124
2.26	1	2.255	1	2.255	½	233
		2.16	½	2.163	½	224
2.12	½			2.13	½	005
2.08	1	2.083	1	2.075	½	015, 134 ←
2.018	½			2.03	½	115
1.98	½					025, 234
1.88	8	1.87	8	1.87	8	044
				1.858	½	?
1.82	½			1.816	½	035, 334
		1.791	½			135
1.773	½	1.766	½			006, 244
1.72	½	1.72	½	1.722	½	116, 235
1.60	6	1.596	7	1.595	6	226
1.56	½	1.562	½	1.56	½	136
1.53	1	1.527	1	1.529	1	444
1.495	½	1.502 ?	½	1.497	½	017
		1.479 ?	½	1.473	½	117, 155

TABLE 1—(*Continued*)

Colusite		Germanite		Reniérite		*hkl*
d/n	*I*	*d/n*	*I*	*d/n*	*I*	
		1.442	½	1.444	½	127, 255, 336 ←
				1.435	½	?
				1.395	½	445, 037, 227
1.35	½	1.343	½			156, 237
1.323	2	1.323	2	1.325	1	008
				1.317		?
1.22	2	1.214	3	1.214	3	266
1.206	½					238
1.19	1	1.184	1	1.194	½	048
1.084	3	1.080	4	1.083	2	?
				1.080	1	448
1.023	2			1.022	1	159, 377 ←
		1.019	2	1.020	1	666, 2.2.10
				1.016	½	0.3.10
.9921 ?	½	1.005	2			
.9411	½					
.9394	1	.9369	1	.9395	½	
		.9358	1	.9360	½	
				.9340	½	
		.9287 (broad)	1			
.9245 (broad)	½					
		.9171 (broad)	1			
.8979 (broad)	2					
		.8950 (broad)	3	.8958 (broad)	½	
.8432 (broad)	½					
.8396	1					
.8108	½					
.8074	½	.8080	½			
		.8063	½			

Indexing based on a cubic unit cell with $a_0 = 10.608$ Å for colusite, $a_0 = 10.585$ Å for germanite, and $a_0 = 10.583$ Å for reniérite.

X-RAY STUDY

Colusite, germanite and reniérite are here considered together because they are essentially isostructural, with almost identical spacings and intensities of powder photograph lines. Certain minor variations serve to distinguish them, and in addition germanite and reniérite are characterized by important physical and chemical differences, which warrant their designation as separate species.

The material used in this study is from the type localities. The colusite is from one of the original specimens collected in 1914, from the 1400′

level of the Mountain View Mine, Butte, Montana. The germanite is from Tsumeb in Southwest Africa, and the reniérite from the Prince Leopold Mine, and from the Tsumeb Mine. As observed by earlier workers, these minerals are apparently isometric, hextetrahedral, space groups $\bar{4}3m$, crystals of colusite and reniérite confirming this determination. Germanite has not so far been observed in crystals. As seen in Table 1, spacings and intensities are nearly identical for all three. There are some differences, however, to which attention may be drawn. These are indicated by pointers in the right hand margin of Table 1. It is considered that they are significant. First, there is a small but consistent difference in the value of a_0 between colusite on one hand and germanite and reniérite on the other. Second, the relative intensities in the set of lines (002) (012) (112) for colusite varies distinctly from those

TABLE 2

	Colusite	Germanite	Reniérite
		Polished Surface Characteristics	
Color	pale bronze brown	pale grayish pink	orange bronze
Hardness	C	C	C
Optical behavior	isotropic	isotropic	strongly anisotropic dark brown to pale golden brown, or grayish yellow to gray blue [Le graye]
		Etch reactions	
HNO_3	stains brown	stains brown neg. [Schneiderhöhn, Murdoch]	neg. fumes tarnish slightly [Murdoch]
HCl	stains brown	neg.	neg.
KOH	neg.	neg.	neg.
$FeCl_3$	neg.	pos. neg. [Schneiderhöhn, Murdoch]	neg.
KCN	scratches develop, solution turns pink	neg.	neg.
$HgCl_3$	neg.	neg.	neg.
		Physical properties	
Specific Gravity	4.43±	4.46±	4.3±
Cleavage	none	none	none
H	3–4	4	4.5 Strongly magnetic

ANALYSES

	Colusite		Germanite			Reniérite		
	1	2	3	3*a*	4	5	6*a*	6*b*
Cu	47.99	46.9	42.12	41.57	45.39	41.63	41.18	43.81
Fe	1.09	3.6	7.8	8.39	4.56	13.73	12.80	12.08
Sn	6.71	5.8	—	—	—	—	—	—
V	2.28	—	—	—	—	—	—	—
Te	1.26	0.4	—	—	—	—	—	—
Sb	0.19	0.64	—	—	—	—	—	—
As	9.54	8.40	1.37	—	4.13	0.87	4.95	4.72
S	30.65	29.2	31.27	31.61	30.65	31.51	30.48	31.28
Ge	—	—	10.19	10.96	8.70	7.75	5.46	6.00
Ga	—	—	1.85	1.99	.76	—	0.52	0.55
Zn	—	—	3.95	4.25	2.58	3.53	0.00	0.00
Pb	—	—	0.96	1.03	0.66	—	2.15	0.00
Rem.		0.9			2.12		1.96	
	99.71	95.84	99.49	99.80	99.55	99.02	99.50	99.50

1. Colusite, Butte, Montana, Gonyer in Berman and Gonyer (1).
2. Colusite, Mountain View Mine, Butte, Montana. Anaconda Copper Mining Co. Spectroscopic analysis [J. M.] of colusite from this locality shows important V, undoubtedly accounting for the low summation.
3. Germanite, Tsumeb, Moritz (9). He states that there was an estimated 20% tennantite in the analyzed material, but this is impossible, as the As present, even if all assigned to tennantite, would allow only 6.75% of this mineral. His analysis recalculated to remove this tennantite, is not notably different, as shown in Column 3*a* above.
4. Germanite, Tsumeb, Kriesel (4). Rem. shows 1.282 Mo, 0.226 SiO_2, with lesser amounts of WO_3, MnO, Ni, Co, Cd, CaO, MgO, C, Au, Ag. This analysis was made on 50 gm. lots, and almost certainly was on contaminated material.
5. Reniérite, Kipushi. Vaes (17).

6*a*. W. Reiner, Tsumeb, on material 90% pure. Rem. Mo, MgO, CaO, SiO_2.

6*b*. W. Reiner, Tsumeb, calculated to 99.5% pure, with Pb as galena, Zn as sphalerite.

in the corresponding sets of lines for the other two. Third, a doublet for germanite appears at 3.42 Å and 3.34 Å, of which only one member can be indexed, but for reniérite and colusite definitely only one line appears in each case, under exactly parallel conditions of exposure. Fourth, reniérite and colusite each show a good doublet, 2.135 Å and 2.075 Å, but the line of spacing 2.13 Å is absent in germanite. In the patterns of reniérite and colusite both these lines of the doublet can be indexed. Fifth, reniérite shows well separated doublets at 1.444 Å and 1.435 Å [not indexable], 1.327 Å and 1.317 Å [not indexable], and 1.083 Å and 1.080 Å, [only one of which can be indexed] none of which appear as doublets in colusite or germanite.

Physical and Chemical Properties

The comparative physical and chemical properties of the three minerals are shown in Table 2.

Conclusions

X-ray powder photographs of germanite and reniérite show conclusively that they are isostructural with colusite, and have practically the same size unit cell. Lines on *x*-ray powder photographs of all three minerals that cannot be accounted for by any reasonable isometric unit cell, suggest that they are really pseudo-isometric, notwithstanding that colusite and germanite are optically isotropic, at least within range of visual observation. Reniérite, on the other hand, besides having a considerable number of lines in the pattern that cannot be properly indexed on the basis of any reasonable isometric unit cell, is definitely anisotropic, so that it may be considered as certainly pseudo-isometric. In comparison with germanite, the difference in amount of iron, with somewhat less germanium, the difference in color, in magnetism (germanite is entirely nonmagnetic), and the few but important variations in spacings of reflecting planes, as shown in the powder photographs, indicate strongly that reniérite should be considered as an independent species, rather than as ferroan germanite (Fleischer (2)).

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