THE CHEMICAL CONSTITUTION OF THE TETRAHEDRITE-TENNANTITE SYSTEM

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The application of the theory of atomic isomorphism to the problems of the constitution of the silicates has led to such favorable results that it seems reasonable to test the possibility of applying the same theory to the ore-minerals. The following study of the constitution of the tetrahedrite-tennantite system may be considered as part of this work.

Most of the standard text-books[1] of mineralogy now give the formula of tetrahedrite as $Cu_8Sb_2S_7$ with the comment that Ag, Zn, Fe, etc., may "replace" part of the Cu under valence control. That is, $Ag_8Sb_2S_7$, $Zn_4Sb_2S_7$ and $Fe_4Sb_2S_7$ are supposed to be possible constituents of tetrahedrite crystals to some extent. It is too early as yet to claim that the constitution of tetrahedrite can be expressed in any form which is correct beyond question, but it is at least possible to show conclusively that the current formula is incorrect, if the best analyses now available can be trusted.

Doelter[2] has recently summarized the literature dealing with the composition of tetrahedrite; he has also given tables of atomic ratios based on many of the analyses collected by Henglein[3]. Any further discussion may seem untimely, but Doelter makes no attempt to reach any conclusion except that it is impossible at present to give an uncontested formula for tetrahedrite. Therefor it is hoped that something can be gained by a study of the best analyses. Many tetrahedrite analyses are too old to have been made by the best modern methods; some are obviously incomplete, others were made on material not carefully selected; and not a few give unsatisfactory results when the calculated sulphur (to satisfy the bases) is compared with the reported sulphur[4]. It is unfortunately true that practically all analyses

[1]Dana: System and Textbook; Brush-Penfield: Determ. Mineral.; Moses and Parsons: Mineral. Cryst. Blowp. Anal.; and Kraus & Hunt: Mineralogy.

[2]Doelter: Handb. Mineralch. IV pp. 203–218, (1925).

[3]Doelter: Handb. Mineralch. IV pp. 173–203, (1925).

[4]The sulphur has been calculated according to the ordinary views regarding the valence of the bases and also according to the theory of Wherry and Foshag. No analysis has been rejected on account of unsatisfactory sulphur unless the reported sulphur would not check the sulphur *calculated either way*. However, this double calculation has had very little effect on the selection of analyses; if the sulphur were calculated only the first way analysis 19 would be rejected and analysis 1 would be in doubt.

now available were made on samples whose purity was not tested by microscopic methods; therefore it is all the more important to scrutinize the analyses carefully and eliminate all those which are not satisfactory according to the tests enumerated. By the methods outlined the 33 analyses of Table I were selected from the 136 on record; they are believed to be the best analyses of the tetrahedrite-tennantite system of minerals now available. In Table 1 the selected analyses have been recalculated[5] into atomic percentage composition.

A brief study of Table I is sufficient to show that the formula $Cu_8Sb_2S_7$ is incorrect. That formula requires for Cu 47.06 per cent, for Sb 11.77, and for S 41.18. As a matter of fact S ranges from 42.27 to 45.3, averaging about 44.5; Sb(+ As + Bi) ranges from 12.56 to 14.4, averaging about 13.6; and Cu(+ Ag + Zn + Fe, etc.) ranges from 39.26 to 44.81, averaging about 41.7.

Wherry and Foshag[6] have recently proposed a new formula for the tetrahedrite-tennantite system which represents the averages of the analytical data much better than the old one. They believe that Zn and Fe do not proxy for Cu but are always present in definite amount except when there is some divalent Cu. According to them the formula is $Cu_{10}(Zn, Fe, Cu)_2Sb_4S_{13}$. This requires 41.4 percent of Cu + Ag + Zn + Fe, divided into 34.4 of monovalent Cu + Ag and 6.6 of divalent Zn + Fe + Cu; it also requires 13.8 percent of Sb + As and 44.8 percent of S. If tetrahedrite has a fixed tenor of S it is probable that this formula is correct, but in a few cases analyses made with the greatest care on excellent material show an important deviation from the average value.

As early as 1899 Prior and Spencer[7] offered a different explanation of the constitution of tetrahedrite. According to them it consists of $Cu_6Sb_2S_6$ with or without minor amounts of $(Zn, Fe)_6$ Sb_2S_9. This explanation may be considered to be inconsistent with the atomic theory of isomorphism, but that theory, at least as understood by the writer, rests fundamentally on the proposition that a crystal atomic space-lattice can vary in constitution in

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[5] In the computations necessary to prepare Table I the writer has had the helpful cooperation of R. C. Emmons, Emilie Hahn, R. H. B. Jones, C. H. Stockwell, and T. B. Williams.

[6] *Jour. Wash. Acad. Sci.* XI. p. 1, (1921).

[7] *Mineral. Mag.* XII, 183, (1899).

TABLE I. ATOMIC PERCENTAGE COMPOSITION OF MINERALS OF THE TETRAHEDRITE-TENNANTITE SYSTEM FROM "SUPERIOR" ANALYSES

	Analyst	Date	S	As	Sb	Cu	Ag	Zn	Fe	Others	G	Doelter No.	Page
1	Prior	1899	43.8	...	13.8	41.0	...	...	1.35	Pb=0.03	4.921	15	175
2	Prior	1899	44.3	...	13.75	38.1	...	2.35	1.06	Pb=0.18, Bi=0.23	4.969	16	175
3	Kretschmer	1911	44.5	...	13.8	34.4	.06	5.76	1.14	Pb=0.2, Bi=0.14	5.079	17	175
4	Pilipenko	1909	44.1	1.3	12.36	35.6	...	4.3	2.07	Se=0.1, Co=0.2	4.781	19	175
5	Kretschmer	1911	44.8	1.4	12.4	34.0	0.24	6.6	0.9		4.780	21	175
6	Kretschmer	1911	44.6	2.0	11.9	34.37	...	6.1	0.9		4.736	22	175
7	Kretschmer	1911	45.07	1.7	11.85	34.6	0.36	5.36	1.08		4.794	23	175
8	Hidegh	1880	44.75	2.2	11.4	33.7	0.7	6.3	0.95		4.910	32	178
9	Loczka	1901	45.2	0.3	12.75	33.7	0.8	5.55	0.8	Pb=0.1, Mn=0.7	4.968	38	179
10	Prior	1899	44.1	...	14.1	29.34	8.64	4.25	3.8		5.047	39	179
11	Ungemach	1906	45.0	0.9	12.0	30.75	3.15	5.7	3.9	Pb=0.8, Mn=0.3	...	42	179
12	Kretschmer	1911	45.1	2.1	11.56	30.86	0.8		0.8	Pb=5.17	4.870	43	179
13	Clarke-Owens	1880	44.7	...	13.6	34.8	1.1		0.67	Ni=0.2	4.350	4	183
14	Manasse	1906	45.0	...	13.76	32.94		1.48	6.6	Ni=0.14		5	184
15	Hidegh	1880	44.93	...	13.9	33.3		1.7	6.06		4.926	6	184
16	Hidegh	1880	42.27	13.3	0.04	44.0	0.03		0.37		4.746	7	185
17	Kretschmer	1911	42.64	12.56		43.15			1.46		4.692	9	185
18	Kretschmer	1911	43.7	12.96	1.05	39.54	0.1	0.2	2.57		4.620	4	186
19	Prior	1899	44.4	13.2	...	40.46	0.9		1.0	Pb=0.08	4.610	8	187
20	Prior	1910	44.7	13.6	.5	34.1	0.6	6.1	0.6		4.610	18	187
21	Hidegh	1880	44.7	8.7	5.1	33.8	0.2	4.6	1.7	Mn=1.2	4.885	20	189
22	Genth	1885	45.3	2.4	11.9	33.16	0.3	6.1	0.64	Mn=0.1	4.738	22	190
23	Kretschmer	1911	44.7	6.54	7.06	34.9	0.1	4.0	2.5	Hg=0.2	4.740	23	190
24	Kretschmer	1911	44.6	7.4	6.54	36.1	0.04	1.2	4.17		4.597	24	190
25	Kretschmer	1911	44.85	8.9	4.8	35.1	0.02	4.95	1.4		4.776	6	191
26	De Benneville	1891	44.9	9.65	3.15	31.94	3.25	4.7	2.0	Mn=0.43		7	191
27	Steiger	1910	44.6	4.1	9.9	33.2	0.77	6.47	0.95		4.576	8	191
28	Kretschmer	1911	44.6	11.5	2.0	34.2	0.6	2.1	5.0		4.800	10	191
29	Pilipenko	1915	44.9	4.16	9.5	31.5	3.2	2.8	3.9	Bi=0.24, Co=0.26	4.870	7	192
30	Petersen	1881	44.07	14.16	...	37.77	...	0.68	2.78	Pb=0.1	4.82	9	192
31	Ungemach	1906	44.6	5.0	8.15	33.6	...	4.3	3.7	Pb=0.2, Bi=0.14	5.10	10	192
32	Ungemach	1906	44.47	...	13.8	34.4	0.06	5.8	1.1	Pb=0.08	4.897	...	...
33	Zsivny	1915	45.2	...	13.7	33.25	0.37	2.6	4.8				

No. 33 is from *Ann. Hist. Nat. Mus. Hungar.*, XIII, 577, (1915); *Mineral. Abst.*, I, 336, (1921).

only two ways, one of which may lead to a complete and continuous series, while the other can only lead to a partial series. The first way is by a "replacement" of certain of its atoms by others of similar size, and the second is by acquiring *small* atoms which are not essential to the stability of the structure as a whole, but can find place in it *between* (and not "replacing") the larger essential atoms. The first case is illustrated by the complete series: $NaAlSi_2O_8 - CaAlAlSi_2O_8$, $MgCO_3 - FeCO_3$, Fe_2SiO_4, etc. The second case is illustrated by the partial series: $FeS(+S), Fe_3O_4(+O)$, $- Mn_2SiO_4$, $NaAlSiO_4(+SiO_2)$ etc. All of these cases are known to exist and it is demonstrated in each case of the second kind that the first term is essential and the second term is not essential to the existence of the space lattice, but that a limited amount of the second term can be added to the lattice without destroying or materially changing it.

It seems possible that the tetrahedrite-tennantite system is an example of a condition which may be considered to be intermediate between the two cases just described, or to illustrate both cases simultaneously. That is to say if $Cu_6Sb_2S_6$ be accepted as the fundamental molecule of tetrahedrite, then it is probable that in its space lattice Zn atoms may proxy for Cu atoms; these atoms are of similar size and a complete and continuous series might be expected to result. However, the Zn atoms belong to a molecule $(Zn_6Sb_2S_9)$ which contains more S atoms than the fundamental tetrahedrite molecule so that one extra S atom is present for each pair of Zn atoms. The extra S atoms are small and not essential to the stability of the crystal space lattice, but they are essential to satisfy the valences of the Zn atoms. Accordingly, the number of Zn atoms which can proxy for Cu atoms in the tetrahedrite crystal space lattice is limited by the capacity of the lattice to accommodate extra S atoms.

Since tetrahedrite may therefore illustrate a new and complicated type of isomorphism it is important to study its constitution as fully as possible. X-ray patterns have been obtained from several tetrahedrite samples, but they are not very useful because they have not been made on analyzed material. The writer is eager to obtain samples of analyzed tetrahedrites in order to carry this part of the study further.

The analytical data of Table I may be used to test in various ways the two theories of the constitution of the tetrahedrite-

tennantite system. The most significant test which the writer has been able to develop is shown in the graph (Fig. 1); in which each numbered point represents the corresponding analysis of Table I, the point at the intersection of the two lines represents the position which all analyses should occupy if the theory of Wherry and Foshag is correct and if divalent Cu, assumed to be present in some cases, is added to $Zn + Fe$; further, the horizontal dashed
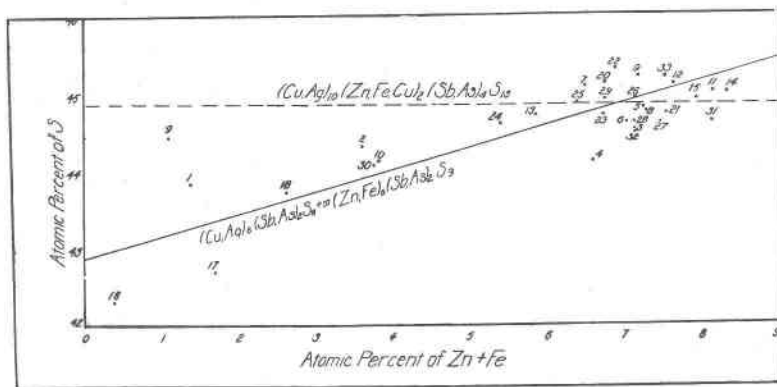

Fig. 1.   Relation between $Zn + Fe$ and S in the tetrahedrite-tennantite system.

line represents the position all analyses should take if the same theory is correct and divalent Cu is included with monovalent Cu; and the inclined line represents the position all analyses should take if the theory of Prior and Spencer is correct. A simple inspection of the diagram is sufficient to show that the best anaytical data now available strongly support the theory of Prior and Spencer as opposed to that of Wherry and Foshag. However, no final decision in the matter is possible until sufficient anaylses have been made on material of microscopically demonstrated purity.