Chemical Examinations of the Minerals of the Tetrahedrite Group.
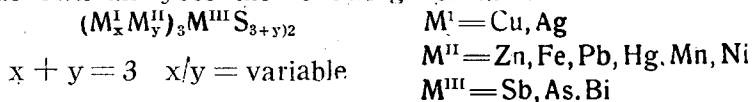
By Veronika Pákozdy.

Tetrahedrite is the sulpho salt of copper-antimony. Its composition varies to a great extent and it is widely distributed in hydrothermal lodes. In spite of its widespread occurrence there are relatively few deposites quoted in the literature where the tetrahedrite has been examined in detail. On the base of numerous greatly diverging analytical data its composition seems to vary greatly. This communication deals with the tetrahedrite occurring in 10 mines in Hungary and in the neighbouring countries. In this area it is found in numerous places, many of them are also mentioned in the literature (1—25.). Of the examined mines *Csiklova (Ciclova, Bánát), Dobsina, Alsósajó (Nisna Slana), Krasznahorkaváralja (Krasna Horka) Csecho-Slovakia, Felsőbánya (Baia Sprie), Kisbánya (Chiuzbaia) Roumania, Rudabánya, Hungary* have never been chemically examined. From the mines of *Ötösbánya (Kotrbach), Porács (Porac)* and *Rozsnyó (Rosnava) Csecho-Slovakia,* there are only earlier analytical data, which will be completed in this paper.

Composition, formula.

The generally used empirical formula of tetrahedrite is: Cu_3SbS_{3-4}. It belongs to the crystal class of the regular tetrakishexaedral. Its space group is T_d^3-143 m. $Z = 8$. The length of the edge of the unit cell varies between 10.19 and 10.32 Å. Its chemical formula has not yet been definitely established. All investigators believe it to be a complex isomorphous mixture of its components. All hitherto made analyses show widely varying results, which are, however, certainly not in accordance with the composition, the analytical data of the author also suggest the existence of a new component.

For a long time formula $(Cu_2Ag_2ZnFe)_4(SbAs)_2S_7$ was accepted, which was expressed by *Rose* in his study on the natural sulpho salts, (8), (1828). *Petersen* supplemented this formula, with more recent analytical data based on his examinations, writing formula $(Cu_2Zn)_3(SbAs)_2S_6$ (26.) *Kenngott* (27) 1881 expresses the tetrahedrite formula as follows $(Cu_2Ag_2)_4(SbAs)_2S_7$ and $x(FeZn)_3(SbAs)_2S_6$. *Rammelsberg* dissolves it into the components of $(Cu_2Ag_2FeZn)_4(SbAs)_2S_7$ and $(Cu_2Ag_2FeZn)_3(SbAs)_2S_6$ (28). *Hampe* introduces the empirical formula $(Cu_2Ag_2FeZn)_7(SbAs)_4S_{13}$ or assuming Cu and Ag to be monosulfids: $(Cu_2Ag_2FeZn)_{12}Sb_4S_{13}$. (29/a). The formula of *Luedecke* is: $3(Cu_2Ag_2FeZn)_3SbS_3 + (Cu_2Ag_2FeZn)_3SbS_4$, corrected:

(Cu$_2$Zn)$_3$Sb$_2$S$_6$ and 3 (Cu$_2$Zn)$_3$Sb$_2$S$_5$. *Tschermák* assumes Cu$_{10}$Zn$_2$Sb$_4$S$_{13}$ to be the empirical formula and 3 Cu$_3$SbS$_3$ + CuZn$_2$SbS$_4$ to be the components of the isomorphous mixture. (29) 1894. *Prior* and *Spencer* assume Cu$_6$Sb$_2$S$_6$ + xZn$_6$Sb$_2$S$_9$ to be the components of the tetrahedrite. x is a small fraction, frequently 1/5 and 1/10, but it can increase to ½ in cooperite which contains iron in abudance. (30) *Kretschmer* writes on the base of numeros earlier data and on those of his own analyses the following formula:

$$(M_x^I M_y^{II})_3 M^{III} S_{3+y)2} \qquad M^I = Cu, Ag$$

$$x + y = 3 \quad x/y = \text{variable} \qquad \begin{array}{l} M^{II} = Zn, Fe, Pb, Hg, Mn, Ni \\ M^{III} = Sb, As, Bi \end{array}$$

The sum of the Cu and Zn atoms (M^I and M^{II})) is constant and proportional to Sb as 3:1. The metals occur in bonds like those of sulpho salts. It must be mentioned here that the molecule of tetrahedrite does not contain lead, the presence of lead exhibited by the analyses is exclusively due to mechanical impurities. (31).

The specific formule of *Prior-Spencer, Tschermák* and *Kretschmer* corresponds to the general formula of Kretschmer. *Kretschmer* expresses his specific formula, assuming „isomorphous components having identical valence sums, but not identical numbers of atoms". According to him the tetrahedrite formula is: x(CuAg)$_9$Sb$_3$S$_7$ + Fe$_6$Sb$_2$S$_9$. The value of x ranges between 2—10, mostly between 3—4. In this case Cu$_9$Sb$_3$ and Zn$_6$Sb$_2$ are isomorphus atom groups, in which Cu and Zn respectively, can be replaced in the aforementioned way by metals having one and two valences respectively. Actually *Prior* and *Spencer's* assumption is also based on this conception, but the components of the tetrahedrite are differently summarized in their formula.

The examinations concerning the internal structure of the tetrahedrite resulted in great progess being achieved in the elucidation of the formula of the tetrahedrite. According to *Machatschki* (32) the unit cells contain 8 molecules of M$_3^I$M^{III} S$_3$, and metals having two valences may also enter the lattice in an isomorphous manner. Of course, in such cases the lattice must contain more S. He accepts the specific formula of *Tschermak* although it can only be applied with certain supplementations to the results of the analyses quoted as examples by him. According to the calculations of *W. F. de Jong* the unit cell of tetrahedrite contains Cu$_{20}$Zn$_{3.4}$Sb$_{6.8}$S$_{27}$, thus the formula is: Cu$_3$SbS$_{3-4}$. However, the results of the analyses seem rather to support the assumptions of *Machatschki*.

The lattice of the tetrahedrite belongs to the lattice type of the sphalerites and consequently it is also related to the lattice of the chalcopyrite which may be considered to be a distorted sphalerite lattice. This affords an explanation for the overgrowth of sphalerite and tetrahedrite and for that of chalcopyrite and tetrahedrite respectively. These two minerals are polimerically isomorphous, therefore the formation of a crystal mixture may also occur, but their structural relationship can also be illustrated by parallel growth. Among tetrahedrite crystals at Kisbánya the author found sphalerite-tetrahedrite overgrowths, which were however, not suitable for

crystallographic studies, thus it could not be established if we are really dealing in this case with parallel overgrowths. Among the tetrahedrites of Felsőbánya the author found chalcopyrite-tetrahedrite overgrowths which were already termed by Döll as pseudomorphis and described in detail by *Tokody*. This also proves that tetrahedrite and sphalerite have simular types of lattices. Even il chalcopyrite and tetrahedrite are not polimerically isomorphous yet it must at least be assumed that they are isotypical (16). On investigating the tetrahedrite samples of the aforementioned ten mines the author envisaged a double aim: to establish to which group of the tetrahedrite family they belong and thus to check earlier assumptions dealing with their origin, and to constribute new data to the contested formula of tetrahedrite.

Decomposition and Analysis.

The substance was first carefully cleaned under the microscope and then decomposed with chlorine by the method described by *H. Biltz* and *W. Biltz* (33) applying the modifications advocated by *Zsivny* (19). The advantage of this procedure is that it also separates the substance, thus facilating the determination of the insoluble residue of Cu, Ag, Fe, Zn, Hg, Pb, Sb, As, S the presence of which was shown by qualitative examination. The finely powdered ore decomposes completely on the action of chlorine gas. The volatile chlorides sublime already during the decomposition, nevertheless, they can only be entirely expelled into the receiver after the operation is completed. The absorbing part of the apparatus consists of a Peligottube and an absorbing tube with seven balls. The absorbing liquid is hydrochloric acid diluted in the ratio of 1:4 containing 5% nitric acid and 2,7% tartaric acid.

After removing the free chlorine the sulphur content, in form of $BaSO_4$, was directly determined from the solution of the volatile chlorides which had been collected in the receiver. (If the decomposition is carried out carefully it can be avoided that Fe and Zn pass over into the receiver). The Sb-As and Hg separated out from the mixture as sulphides and the As was dissolved in ammonium carbonate and determined according to *Reich Bennet, Eschweiler* and *Röhrs* (34, 35). The Sb was dissolved in ammonium polysulphide and separated out from a hot medium and strongly acidified with hydrochloric acid according to the method of *Vortmann* and *Metzel* (36), it was weighed at 280° C in a current of H_2S. The mercury sulphide remaining on the filter was determined in form of HgS (37). The remainder in the boat was dissolved in hydrochloric acid; there remained an insoluble residue AgCl, and in one case also a very slight amount of $PbCl_2$ which was dissolved in hot water. After having been dissolved in ammoniumhydroxide the Ag was determined as AgCl. The content of the filtrate was repeatedly precipitated and weighed as Fe_2O_3. The Cu content of the filtrate was determined by the method of *Rivot-Sarudi* (37) as CuSCN. The Zn content of the filtrate was determined according to the method of *Lundell* and *Naikim Bee* (38).

On the base of the result of the analyses the constituents were summarized in a formula according to the principles established by

Kretschmer. However, in the case of the investigated tetrahedrites it was only possible to apply the particular formula if a new constituent was introduced into the formula. In the case of several analyses CuS represented the remainder after the writing of the formula. It seems therefore justified to assume that this covellite is a decay product of tetrahedrite which can always be found in chalcographic studies of the polished surface and cannot even with the aid of most careful purification be removed from the substance.

On the basis of their occurrence the author has divided the examined tetrahedrites into following groups:

Postpneumatolitic hydrothermal: Csiklova (Ciclova, Bánát).

Hydrothermal: Dobsina (Dobsina), Rozsnyó (Rosnava), Alsósajó (Nisna Slana), Krasznahorkaváralja (Krasna Horka), Ötösbánya (Kotrbach), Porács (Porac) Csecho-Slovakia.

Rudabánya Hungary.

Felsőbánya (Baia Sprie), Kisbánya (Herja) Roumania.

Csiklovabánya.

At this deposite in the Bánát the postpneumatolitic hydrothermal sulphide ores are already predominating. Amongs these *pyrite* and *bornite* are the most frequent, but *arsenopyrite* also occurs in a significant amount. Whereas *chalcopyrite, sphalerite* and *chalcocite* are rarer. *Tetrahedrite* cannot either be ranged among the frequently occurring ores. Csiklova is the only deposite in the Carpathians where one of the sparingly occurring *bismuth tellurides tetradymite* is very abundant.

The author's sample consist of tetrahedrite crystals (2—5 mm) which are strongly etched, round and associated with sphalerite, the base of which is composed of *quartz* containing pyrite inclusions on which well developed and distinguishable quartz crystals are deposited, on which in turn the aforementioned tetrahedrites are deposited. The tetrahedrite is encrusted with pyrite. Sphalerite is the older of the two ores. The examined tetrahedrite crystals are + tetrahedrons. Owing to the corrosion of the surface and its pyrite coating it was not possible to identify other crystals shapes on magnification, they are also not suitable for crystallographic investigations. For the chemical investigations several smaller carefully purified crystals were used. They have a dark-gray colour with a dark-reddish tinge. The streak also shows a reddish shade and if the substance is finely powdered it is distinctly red too indicating that it contains Ag and As.
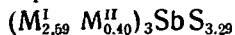
The result of the chemical analyses is:

Sp. gr: 4.623   Sample: 0,3085 gram.

Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 37.18 %	5849)		2.59	39
Ag 3.61	335) 6184			
Fe 2.94	527)		0.40	6
Zn 2.90	444) 971			
Sb 26.02	2137)		1.00	15
As 1.84	246) 2383			
S 25.15	7845		3.29	48
99.64 %				

The empirical formula of tetrahedrite of Csiklova is:

$$(M^I_{2.59} M^{II}_{0.40})_3 Sb S_{3.29}$$

Dissolved into its components:

$$4 (CuAg)_2Sb_3S_9 + (FeZn)_3Sb_2 S_9 + Cu_3SbS_3$$
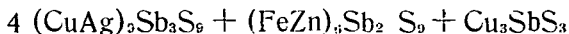
Dobsina.

Its predominant ore is coarsely granular, light coloured *siderite,* which is associated — mainly in the upper layers — with sulphidic ores. Among these *tetrahedrite* plays a significant part. The examined tetrahedrite is massive and always embedded in *chalcopyrite,* each sample exhibiting signs of an initial stage of oxidation. The minerals characterizing the belt of oxidations *limonite, azurite, malachite* can always be found associated with it.

On performing chalcographical investigations it can be observed that *pyrite* belongs to the earliest sulphides. Its crystals are idiomorphous. It has been replaced by the younger sulphid ores, by chalcopyrite and tetrahedrite. All these ores exhibit signs of oxidation. *Quartz* is the earliest formation. Its crystals are idiomorphous and have a hexagonal transection which can be well observed in the polished sections. After quartz pyrite forms. It is usually strongly corroded. The difference of its hardness as compared with the softer ores surrounding it can be particularly well observed on applying the illumination sidewise. Chalcopyrite ranges next in age, which in turn is replaced by tetrahedrite. Chalcopyrite is also replaced by *chalcocite,* which is represented by its *blue isotrop modification,* or occasionally in association with another of its modifications. Chalcocite occurs in considerably large amounts and may be well observed as it consumes the chalcopyrite, some small remainders of which can still be detected in the center of the chalcocite grain. Under high power magnification a few grains of isotrop chalcocite are also clearly visible in the tetrahedrite. The replacing solution penetrated along the fissures of the brittle tetrahedrite and owing to the oxidation process tile ore formed, the edge of which, in the vicinaty of the tetrahedrite, is bordered by chalcosine. The veins of the tile ore contain siderite of younger origin bordered by limonite granules. In some places along the fissures remainders of chalcopyrite can be detected. It is surrounded by *covellite, chalcosine, azurite, malachite* and *limonite.* The most recent member of the primary ore series is arsenopyrite. It is easily detected by the characteristic rhomboid form of its transection, its hardness which is similar to that of pyrite and its colour, which is, however, far lighter than that of the latter. Its light reflectivity is perfect, between $+$ N it is strongly anisotrope. As mentioned by *Rahmdohr* (40) another characteristic is its replacementlike overgrowth with tetrahedrite probably on its formation owing to the decomposition of tetrahedrite.
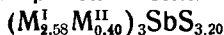
The author did not find any data in the literature referring to the composition of the tetrahedrites of Dobsina. The results of her own analyses are as follows:
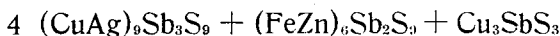
Sp. gr.: 4.839.

Sampie: 0.5122 gram.

Weight%		Mol. Quot.		Atomic relations:	
Cu . . . . 39.46 %	.	6507	} 6216	2.58	39
Ag 0.10		9			
Fe 3.77		575	} 969	0.40	6
Zn 1.92		294.			
Sb 29.35		2411	} 2419	1.00	15
As 0.06		8			
S 24.88	.	7761		3.20	48
insol . . . 0.24					

99.78 %

The empirical formula of tetrahedrite is:

$$(M^I_{2.58} M^{II}_{0.40})_3 SbS_{3.20}$$

And dissolved into its components:

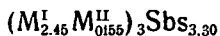$$4\ (CuAg)_9 Sb_3 S_9 + (FeZn)_6 Sb_2 S_9 + Cu_3 SbS_3$$

Rozsnyó.

Siderite is the dominating mineral, *tetrahedrite* is one of the sulphide minerals occurring fairly frequently in its upper layers. The tetrahedrite of Rozsnyó has already been described in our literature. Its occurrence and crystallographic conditions have been reported by *Károly Zimányi* (15). The chemical analyses of crystallized, as well as that of massive tetrahedrite, have been carried out by *Zsivnyi* (14) (1915). The author will report his analytical data, comparing them with her own.

The author investigated well developed crystals, owing to their simple forms and scanty faces it did not seem to be of interest to apply crystallographic measurements. The surface of these crystals are smooth, lustrous and have a dark gray colour. The examined massive pieces occur in the lodes of Bernard. The ore occurs in that region in association with medium sized, coarse, siderite grains and *chalcopyrite.* This tetrahedrite shows, mainly on its fractured surface, a bright metallic lustre with a light gray slightly brownish shade. A piece deriving from the belt of oxidation is almost spongy and its hollows contain the oxidation products of tetrahedrite and siderite: *azurite, limonite* and *malachite.* On the polished section the rejuvenation, a characteristic feature of the ore formation of that area, can be detected very distinctly. The tetrahedrite has displaced siderite which can be found in some places in idiomorphous, rhombohedral transections. Along the fissures the younger siderite can already be detected. The tetrahedrite contains in several places *bournonite* in polygonal grains varying in size. It has no reflectional pleochroism, between + N it is anisotrope, it has a yellow colour with a greenish, bluish-greenish shade, respectively. In the case of parallel N it is a shade harder than tetrahedrite and its colour is lighter, with a bluish tint. The piece which underwent oxidation contains residual chalcopyrite bordered by *covellite.* The tetrahedrite is also delicately interwoven by covellite in all directions. The siderite has decomposed into limonite. From these parts the covellite veins disperse into branches indicating the paths of the fissures where

on the action of the solution the decomposition of the tetrahedrite started. The middle sections of the covellite veins contain thin striates of limonite. The siderite in turn contains the regular pentagonal dodecahedral transection of the *pyrite* which is the earliest ore and is displaced by the younger chalcopyrite and tetrahedrite.

The empirical formula of crystallized tetrahedrite is according to *Zsivny:*

$$(M_{2.45}^I M_{0.155}^{II})_3 Sbs_{3,30}$$

and dissolved into its components: $3\ (CuAg)_9 Sb_3 S_9 + (FeZn)_6 Sb_2 S_9$

On the base of his second analysis he could not establish a formula which would have corresponded to the empirical formula. According to the analysis carried out by the author the empirical formula of tetrahedrite is: $(M_{2.55}^I M_{0.39}^{II}) Sbs_{3,20}$ dissolved into its components:

$$4\ (CuAg)_9 Sb_3 S_9 + (FeZn)_6 Sb_2 S_9 + Cu_3 SbS_3.$$
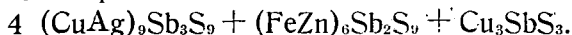
Residual: 2 CuS, covellite.

The results of the chemical analisis are:

Sp. gr.: 4.832.　　　　　　　　　　　　　　Sample: 0.4052 gram.

Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 39.96 %	6365 ⎫	6411	2.55	41
Ag 0.50	46 ⎭			
Fe 3.13	556 ⎫	938	0.39	6
Zn 2.50	382 ⎭			
Mn . . . . trace				
Sb 28.30	2324		1.00	15
S 25.05	7935		3.20	50
insol . . . 0.04				
99.48 %				

Alsósajó.

In the upper layer of the lodes of the mines of Szentháromság the *schwatzite (Hg-tetrahedrite)* was the main ore besides it secondary *cinnabar* was mined. The zone containing the thin veins extends in a talc schist. Its lodes consist of the massive *quartz* and *dolomite* and to a lesser extent of granular *barite, chalcocite* and *siderite*. On the sample, particularly on examining under the microscope, it can be most accurately observed how the cinnabar surrounds the *tetrahedrite* from all sides and replaces it. Although this schwatzite was mined and utilised commercially and is also a well known ore, yet the literature does not contain any data relating its analyses.
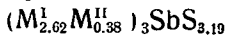
The analytical data are as follows:

Sp. gr.: 4.962.　　　　　　　　　　　　　Sample: 0.3935 gram.

Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 35.12 %	5525		2.62	41
Fe 1.14	204 ⎫	809	0.38	6
Hg 12.15	605 ⎭		1.00	15
Sb 25.65	2107		3.19	50
S 21.61	6741			
insol . . . 3.92				
99.59 %				

The empirical formula of tetrahedrite of Alsósajó is:
$$(M^I_{2.62}M^{II}_{0.38})_3SbS_{3.19}$$
and dissolved into its components:
$$4 \quad Cu_9Sb_3S_9 + (FeHg)_6Sb_2S_9 + Cu_3SbS_3$$
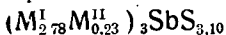(Residual 2 CuS, covellite.)
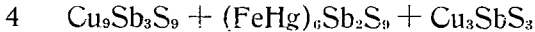
Krasznahorkaváralja.

Massive *tetrahedrite* occurs here in the *Málhegy* in pure white spatic *barite* in association with a small quantity of other sulphidic ores. Its colour is light gray with a sightly bluish tinge. With the aid of chalcography the order of its formation can readily be established: *quartz* is the primary formation which is followed by baryte, or the ores *pyrite* was the first, its small cubes can still be found. It was displaced by *chalcopyrite* which has, however, entirely been absorbed by the tetrahedrite only containing sparingly some chalcopyrite granules.

Hitherto this occurrences has not been mentioned in the literature

The results of the chemical analysis are:

Sp. gr.: 4.880.   Sample: 0.3190 gram.

Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 40.99 %	6275	⎫ 6448	2.78	75
Ag 1.18	102	⎭		
Fe 2.45	439	⎫ 530	0.23	6
Mn 0.50	91	⎭		
Sb 28.63	2351		1.00	27
S 23.12	7212		3.10	84
insol . . . 2.74				
99.61 %				

The empirical formula of tetrahedrite is:
$$(M^I_{2.78}M^{II}_{0.23})_3SbS_{3.10}$$
and dissolved into its components:
$$8 \quad (CuAg)_9Sb_3S_9 + (FeMn)_6Sb_2S_9 + Cu_3SbS_3.$$
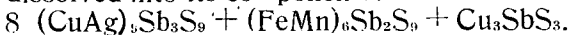
Ötösbánya.

The spatic *siderite* vein extends in the talcic green schist in which the *tetrahedrite* containing Hg occurs, it is termed by the literature as schwatzite. It is mentioned a few times, and some analyses are also quoted. Up to data mercury is still produced from tetrahedrite obtained as the associated by-product of siderite. The examined sample is a massive, compact tetrahedrite and has a dark grey colour a weak luster and a black streak. It is associated vith white crystal *barite* and interwoven with thin veins of *chalcopyrite*. It contains everywhere the small idiomorphous cubes of the earlier formed *pyrite*. On the polished section the order of formation of the sulphid ores can be established as follows: pyrite, chalcopyrite, tetrahedrite.

Although it is termed in the literature as schwatzite the only analysis establishing that it contains 17% of Hg was made by *Rath* in 1855. Among the more recent investigators Kretschmer established the lowest Hg content (1911). It is, however, possible that the layers

containing abundant amounts of Hg have already been removed. The authors analytical data approach very closely those of *Kretschmer*. Before Kreschmer, Ag is not exhibited by any analysis. In the analyses of the author it could not either be detected.

Kretschmer: Author:

Sp. gr.: 4.651   Sp. gr.: 4.632.   Sample: 0.2880 gram.

	Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 40.57 %	39.19 %	6151		2.59	30
Ag 0.03	—				
Fe 4.53	5.33	955 ⎫			
Zn 1.61	1.22	187 ⎬ 1217		0.49	6
Hg 1.52	1.50	75 ⎭			
Sb 20.60	22.30	1882 ⎫ 2465		1.00	12
As 5.07	4.82	643 ⎭			
S 25.21	25.42	7929		3.20	39
insol . . . 0.75	0.16				
99.89 %	99.78 %				

The empirical formula *of Kretschmer is:* $(M_{2.66}^{I} M_{0.40}^{II})_3 SbS_{3.15}$
The empirical formula *of the author:* $(M_{2.49}^{I} M_{0.49}^{II})_3 SbS_{3.20}$
Dissolved into its components:

$3\ Cu_9 Sb_3 S_9 + (FeZnHg)_6 Sb_2 S_9 + Cu_3 SbS_3.$
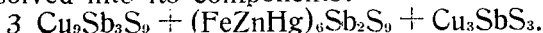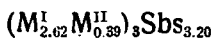
Porács.

The investigated *tetrahedrite* occurs associated with *chalcopyrite* in lodes of coarse grained *siderite*. There also occur fairly large well developed crystals ranging between 2 mm — 1 cm in size, however, owing to the minute tetrahedrite crystals deposited on their surfaces the crystals were not suitable for crystallographic studies. The luster of the fresh fractural surface has a brilliant, metallic luster and a dark gray colour with a slightly bluish tint, its streak is dark gray with a reddish shade. C. v. Hauer carried out chemical analyses of tetrahedrite occurring in the area of Porács in 1852. According to him the tetrahedrite is schwatzite, containing Hg. On the base of the analytical data of the author on the other hand, it seems to contain only small quantities of Hg pointig to the fact that the investigated tetrahedrite is not schwatzite.
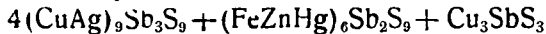
The analytical data are as follows:

Sp. gr.: 4.651.   Sample: 0.4056 gram.

Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 38.94 %	6126 ⎫	6191	2.62	39
Ag 0.78	65 ⎭			
Fe 4.82	864 ⎫			
Zn 0.06	9 ⎬	931	0.39	6
Hg 1.17	58 ⎭			
Sb 28.46	2337		1.00	15
S 24.02	7492		3.20	48
insol . . . 1.25				
99.50 %				

The empirical formula is:

$$(M_{2.62}^{I} M_{0.39}^{II})_3 SbS_{3.20}$$

dissolved into its components:

$$4(CuAg)_9Sb_3S_9 + (FeZnHg)_6Sb_2S_9 + Cu_3SbS_3$$

Rudabánya.

In the tenth layer of the second part of the Andrássy mine the following sulfide minerals occur in the christalline white *barite pyrite, chalcopyrite* and *tetrahedrite.* The remainders of the pyrite and chalcopyrite, but particularly those of barite can always be found in the tetrahedrite replacing them. This selection is very difficult, so that the specific gravity could not be established, as a suitable homogenous substance for this purpose was not available.

The tetrahedrite of Rudabánya has been described in our literature by *Koch* (24). These minute, grains were detected in the polished sections among the other sulphide ores by him. Based on the genetical data *Kertai* (25) assumes that Hg tetrahedrite must occur in this place as the belt of oxidation contains Hg and secondary cinnabar. *Koch* describes in detail (24) the native Hg occurring there which he found associated with dark gray tile ore and coarse granular crystalline *cuprite.* The cavities of the tile ore are encrusted with crystallized *azurite, malachite,* and as the youngest mineral with earthy *cinnabar.* On the delicate needles of the malachite minute — generally smaller than 1 mm — droplets of native mercury were found by him. The associated occurrence of native mercury and cinnabar with cuprite suggests that probably the described piece fomed on the decomposition of a large tetrahedrite inclusion (24)
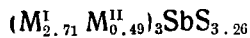
The author succeeded in demonstrating on the basis of her analysis that the assumption was correct and that no mercury tetrahedrite really occurs at Rudabánya.

The results of the analysis are:

Sample: 0.3261 gram.

Weight%		Mol. Quot.		Atomic relations:	
Cu	39.01 %	5665		*2.71*	31
Fe	5.78	1035		0.49	6
Hg	1.22	60	1095		
Sb	27.49	2258		1.00	12
S	23.60	7361		3.26	40
insol...	2.30				

99.40 %

The empirical formula of the tetrahedrite of Rudabánya is:

$$(M^I_{2.71} M^{II}_{0.49})_3 SbS_{3.26}$$

and dissolved into its components:

$$3(Cu_9Sb_3S_9) + (FeHg)_6Sb_2S_9 + Cu_3SbS_3$$

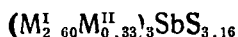(Residual CuS, covellite.)

Felsőbánya.

Tetrahedrite can be ranged into the ores occurring fairly rarely in the lodes of Felsőbánya. The cystallized tetrahedrite found here is described by *Tokody* (16). The dominating form of these crystals is the dodecahedron this type is rare and usually occurs in the tetrahedrites containing As. The examined sample was found in a massive quartz lode also containing *sphalerite* and *chalcopyrite.* Minute, co-

lumnar *quartz* crystals are deposited on the massive quartz, among them tetrahedrite crystals can be detected 3—5 mm in diameter. Most crystals are tarnished to a nice red, lilacish, steelblue and bright green colour. The author also found the chalcopyrite tetrahedrite ovegrowths described by Tokody. *Machatschki* (32) calls it common antimony tetrahedrite without applying any analytical examination. So far, there is no knowledge of anybody having carried out a chemical analysis of the tetrahedrite occurring at Felsőbánya
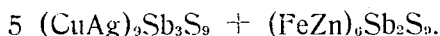
The analytical data are:

Sp. gr.: 4.641.   Sample: 0.4080 grom.

Weight%		Mol. Quot.		Atomic relations:	
Cu . . . . 39.30 %	6182		6293	2.60	45
Ag 1.20	111				
Fe 2.40	430		807	0.33	6
Zn 2.40	377				
Sb 28.13	2310		2417	1.00	17
As 0.80	107				
S 24.49	7639				
insol. . . 0.90				3.16	54
99.62 %					

The empirical formula of tetrahedrite of Felsőbánya is:

$$(M_2^I{}_{.60}M_0^{II}{}_{.33})_3SbS_{3.16}$$

and dissolved into its components:
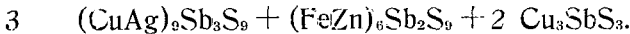
$$5\ (CuAg)_9Sb_3S_9 + (FeZn)_6Sb_2S_9.$$

Kisbánya.

The *tetrahedrite* crystals (2—5 mm) are found as· overgrowths on *sphalerite* which is abundant in iron, or as intergrowths in its· hollows. The crystal faces are uneven, the surface is corroded and not suitable for crystallographic studies. Its polished sections are also found associated with *galena,* the latter having consumed it to a great extent, both ores are replaced by *jamesonite (parajamesonite).* According to *Petrulián* (24) the different paragenetic phases of the minerals at Kisbánya commence with that of the Fe-Zn sulphides, which is introduced by *pyrite* and then followed by sphalerite, *pyrrhotine* and *arsenopyrite.* The second phase involves the formation of the Cu-Pb sulphides, in this case chalcopyrite and galenite form. The third phase comprises the formation of the various sulpho salts commencing with antimony, tetrahedrite is also formed in this phase. *Marcasite* and the associated *carbonates* are formed from ascending solutions. The analysis was carried out with 11 minute crystals (1—2 mm). Among these regular parallel grouping of sphalerite and ttrahedrite occurred.

The results of the chemical analysis are:

Sp. gr.: 4.693.   Sample: 0.1523 gram.

Weight%	Mol. Quot.		Atomic relations:	
Cu . . . . 37.02 %	5824 ⎫	6095	2.54	33
Ag 2.92	271 ⎭			
Fe 2.34	419 ⎫	847		
Zn 2.80	528 ⎭		0.35	6
Pb . . . . trace				
Sb 29.22	2400		1.00	13
S 24.88	7761		3.23	42
99.18 %				

The empirical formula is: $(M^I_{2\cdot54}M^{II}_{0\cdot35})_3SbS_{3\cdot23}$
and dissolved into its components:

$$3 \quad (CuAg)_9Sb_3S_9 + (FeZn)_6Sb_2S_9 + 2\ Cu_3SbS_3.$$

Summary.

1. Of the examined tetrahedrites only that occurring at Alsó-sajó proved to be schwatzite containing 12,91% Hg. The one occurring at Ötöshánya and Porács also contains Hg it is, however, not, as was generally assumed, schwatzite. A recently described tetrahedrite containing Hg is that found at Rudabánya it contains 1,22 % of Hg. This is a proof of the correctness of the conclusion, based on the genetical data, that such an ore really exists.

2. All other samples of tetrahedrite occurring at Csiklova, Rozsnyó, Dobsina, Krasznahorkaváralja, Felsőbánya, Kisbánya which were examined contained silver. Most of them, however, only contained it in subordinate amounts (less than 1 % or about 1 %). Only the tetrahedrite accurring at Kisbánya contained 2,92 % of silver. Thus none of these occurrences are freibergites as was hitherto supposed.

3. Several contain As, but none can be considered to be an As tetrahedrite.

4. According to the results of the analyses the composition of the investigated tetrahedrites corresponds to the empirical formula of Krtschmer.

5. On dissolving the formula into its components a new component had to be added. This is in fact ground molecule of tetrahedrite which is mixed in slighter or greater extent — in the examinations of the author the ratio is usually 4:1 — with the two isomorphous mixture components. The ratio of these components determines the place of the tetrahedrite among the tetrahedrite groups and their quantity also exerts an influence on the value of the specific gravity. According to Machtschki this is du to the modification of the edge of the lenght of the unit cell.

6. On analysing the tetrahedrite occuring at Rozsnyó, Alsó-sajó and Rudabánya, after the expressig of the formula, an excess of CuS remained. The chalcographic investigations actually showed the presence of the finely dispersed covellite in all places.

According to the opinion of the author the formula of tetrahedrite, which is always completely homogenous under the microscope and is crystallographically an identical isomorphous mixture, cannot

be accurately determined chemically. It will only be possible to establish its final formula, corresponding exactly to its composition, after having determined accurately the fine structure of its lattice and the exact valence and isomorphous conditions.

Contribution from the Mineralogical and Petrographical Institute of the University of Szeged.

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Kémiai vizsgálatok a tetraedrit család tagjain.

Írta: Dr. Pákozdy Veronika.

1. A vizsgált tetraedritek közül schwatzitnak bizonyult az alsósajói, 12.51% higanytartalommal. Higanytartalmú az ötösbányai és porácsi is, de nem schwatzit, mint ezt általánosan feltételezték. Ujonnan leírt Hg-tartalmú fakóérc a rudabányai. Hg tartalma 1.22%. Evvel beigazolódott a genetikai következtetés, mely létét feltételezte.

2. A többi elemzett tetraedrit: Csiklova, Rozsnyó, Dobsina, Krasznahorkaváralja, Felsőbánya, Kisbányáról mind tartalmaz ezüstöt. Az ezüst tartalom a legtöbbnél kevés, 1%-nál kevesebb, illetve 1% körüli. Egyedül a kisbányai tetraedritben éri el a 2.92% Ag tartalmat. Tehát ezen előfordulások egyike sem freibergit, mint ahogy eddig tartották.

3. As tartalom többnél előfordul, de arséntetraedritnek egyik sem mondható.

4. Analisis eredményeim szerint a vizsgált tetraedritek összetétele kielégíti a Kretschmer féle általános tapasztalati képletet.

5. A komponensekre bontott formulázásnál egy új komponensrészt kellett felvennem. Ez tulajdonképpen a tetraedrit alapmolekulája, melyhez több-kevesebb mennyiségben — nálam az arány legtöbbször 4:1, keveredik a két isomorf elegyrész. Ezeknek a komponenseknek aránya szabja meg a tetraedrit helyét a fakóérccsoportban és ezeknek a mennyisége befolyásolja a fajsuly értékét is.

6. Három esetben: Rozsnyó, Alsósajó és Rudabánya tetraedritjének analisisénél, a képletbe foglalás után CuS felesleg maradt. Az ércmikroszkópi vizsgálat a finom eloszlásban jelenlevő covellint valóban mindenütt kimutatta.

A tetraedritnek, mely ércmikroszkóp alatt mindig teljesen homogén, kristálytanilag azonos megjelenésű isomorf elegy, képlete kémiai úton nem formulázható nézetem szerint pontosan. Végleges, általános, összetételének pontosan megfelelő képlet csak rácsa finomszerkezetének, a valencia és isomorfia viszonyoknak pontos megállapításával lesz lehetséges.