The Identity of Kilbrickenite with Geocronite: and Analyses of Miersite, Marshite, and Copper-pyrites.

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(1) The Identity of Kilbrickenite with Geocronite.

THE mineral kilbrickenite was analysed, described and named by Dr. James Apjohn in 1840[1]. The specimens which he examined were sent to him by Mr. P. M. Taylor, who conducted the mining operations at the Kilbricken mine in County Clare, where the mineral was discovered. Apjohn's analysis showed the presence of lead, antimony and sulphur in proportions corresponding fairly closely with the formula $6PbS.Sb_2S_3$. It was only in the preceding year that L. F. Svanberg had described a new mineral, geocronite[2], to which he assigned the formula $5PbS.(Sb,As)_2S_3$. The announcement of this new mineral appears to have escaped Apjohn's notice, since geocronite is not included in the list of sulphantimonites of lead with which he concludes his paper. Had he been aware of the existence of geocronite, he would probably not have ventured to found a new species on the result of an analysis of a massive mineral differing so little in composition from geocronite, for the numbers in his analysis really correspond to a formula intermediate between $5PbS.Sb_2S_3$ and $6PbS.Sb_2S_3$.

A priori therefore the identity of the two minerals seems highly probable, and in fact, in the earlier editions of Dana's 'System of Mineralogy,' kilbrickenite appears as a variety of geocronite. In later editions, however, and in other text-books the mineral is elevated to the dignity of a separate species.

Recently, through the kindness of Mr. J. J. Beringer, there has been placed at my disposal for analysis material from specimens of kilbrickenite contained in the Museum of the Mining School at Camborne, Cornwall. The genuineness of these specimens is guaranteed by the fact that they form part of the Taylor Collection and are accompanied by two letters, one from Dr. Apjohn to Mr. P. M. Taylor giving the results of his

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[1] Proc. Roy. Irish Acad., 1841, vol. i, pp. 469–73.

[2] Kongl. Vetenskaps-Acad. Handl. (for 1839), Stockholm, 1841, p. 184; Ann. Phys. Chem. (Poggendorff), 1840, vol. li, p. 535.

analysis of kilbrickenite, and the other from Mr. P. M. Taylor to Mr. John Taylor stating that he was sending him 'two good pieces of kilbrickenite together with Dr. Apjohn's letter and analysis.'

Physical Characters.—The two specimens of kilbrickenite belonging to the Camborne Mining School are precisely similar in appearance to specimens of massive geocronite in the British Museum from the original locality, Sala, Sweden. They show the same lead-grey colour with metallic lustre, and indications here and there of an imperfect cleavage on which can be seen faint striations in two rectangular directions. The hardness is 3, and the mineral is only slightly brittle. The specific gravity (weight of 1 cc. at 21° C.) of the material used in the analysis is 6·45, practically the same as that of geocronite from Tuscany analysed by Kerndt.

Chemical Composition.—Of the two specimens, one showed some galena in association with the kilbrickenite, but the other appeared to be homogeneous and free from galena. The material used in the analysis was therefore taken from the latter specimen.

The mineral was decomposed in chlorine, the lead was determined as chloride, the arsenic as pyroarsenate of magnesia, and the antimony as sulphide after heating to 260° in carbonic acid. The sulphur was determined in a separate portion by fusion with sodium carbonate and nitre.

Under I is given the result of the present analysis of geocronite ('kilbrickenite') from Kilbricken mine, Co. Clare; under II that of a recent analysis by G. D'Achiardi[1] of crystals of geocronite from Val di Castello, Tuscany; and under III the theoretical composition required by the formula $5PbS.Sb_2S_3 + 5PbS.As_2S_3$.

	I.			II.	III.
	(Kilbricken).	(Atomic ratios).		(Val di Castello).	(Theoretical).
Pb . . .	68·49	·3318		70·02	69·62
Sb . . .	9·13	·0758	·1370	7·78	8·07
As . . .	4·59	·0612		4·47	5·05
S . . .	17·20	·5376		17·57	17·26
	99·41			99·84	100·00

Weight of material used in analysis = 0·8236. $PbCl_2 = 0·7620$; $Sb_2S_3 = 0·1051$; $Mg_2As_2O_7 = 0·0780$. Weight of material used in sulphur determination = 0·5020. $BaSO_4 = 0·6279$ gram.

The numbers obtained correspond fairly closely with the formula $5PbS.(Sb,As)_2S_3$.

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[1] Atti Soc. Toscana Sci. Nat., 1901, Mem. vol. xviii.

The result of the analysis therefore, combined with the correspondence in physical characters, leaves no room for doubt that kilbrickenite is identical with geocronite.

The most important difference between the present analysis and that of Apjohn is the presence of arsenic. In his paper, Apjohn makes no mention of having tested qualitatively for arsenic, nor would his method of quantitative analysis have led to its detection, since he simply precipitated the antimony by sulphuretted hydrogen and weighed the precipitated sulphide after drying at 100°.

The percentage of arsenic (4·59) found in the Kilbricken mineral is very close to that found by Svanberg in the original geocronite from Sala (4·70), and that by Kerndt (4·72) and more recently by D'Achiardi (4·47) in the mineral from Tuscany. This fact that the mineral from three widely different localities contains approximately the same percentage of arsenic lends considerable support to D'Achiardi's suggestion that geocronite is the double salt $5PbS.Sb_2S_3 + 5PbS.As_2S_3$.

It must be pointed out, however, that the acceptation of this idea would necessitate the reference to another species of the 'schulzite' from Meredo, Spain, analysed by Sauvage[1], and the mineral from Björkskogsnäs, Sweden, analysed by Nauckhoff[2], both of which contain no arsenic.

(2) Analysis of Miersite.

Miersite, the new iodide of silver and copper, has been described by Mr. L. J. Spencer in this volume (p. 41). The material, on which the following analysis was made, was collected by him from one specimen (No. 83466) in the British Museum, and was very carefully picked out under the lens and microscope until it showed no trace of impurities.

On this specimen, from Broken Hill, New South Wales, the yellow crystals and crystalline aggregates of miersite rest on a matrix of granular quartz containing copper-glance and a few brown garnets. A little limonite is dusted over the matrix and the miersite, and to remove this the material used in the analysis was digested in warm, dilute nitric acid.

The mineral was decomposed by means of zinc and sulphuric acid. The precipitated silver and copper were dissolved in nitric acid, and the silver determined as chloride and the copper as sulphide. A double precipitation of the copper with sulphuretted hydrogen in fairly acid solution was necessary in order to obtain the sulphide of copper free from zinc. The iodine in solution as zinc iodide in the filtrate from the silver

[1] Ann. des Mines, 1840, ser. 3, vol. xvii, p. 525.

[2] Geol. För. Förh. Stockholm, 1872, vol. i, p. 88.

and copper was liberated by nitrous acid, dissolved in carbon bisulphide, and determined by titration with sodium thiosulphate in the usual way. The following are the results obtained :—

		Atomic ratios.
Ag . . .	38·17	·353 or 4
Cu . . .	5·64	·090 „ 1
I. . . .	56·58	·446 „ 5
	100·39	

Weight of mineral used in the analysis = 0·4328; I = 0·2449; AgCl = 0·2195; Cu_2S = 0·0306 gram.

Specific gravity (weight of 1 cc. at 23° C.) = 5·640.

The numbers agree very closely with the formula 4AgI.CuI, to which Mr. Spencer had been led by means of fusion experiments (see this volume, p. 44).

(3) ANALYSIS OF MARSHITE.

Material for the following analysis, free from impurities, was collected from one specimen (No. 84520) in the British Museum by Mr. L. J. Spencer, who has described the physical characters of the mineral in this volume (p. 38).

The marshite on this specimen, from Broken Hill, New South Wales, occurs as numerous fairly large flesh-red tetrahedra (crystals of 'type B,' *loc. cit.* p. 40), encrusting platy psilomelane, which in its turn rests upon an incoherent mixture of cerussite, limonite and garnet with a few bright octahedra of cuprite.

The mineral was decomposed by digestion (several times repeated) with a strong solution of caustic soda. In the residue after filtration the silver was determined as chloride and the copper as sulphide, while the iodine in the soda solution was liberated with nitrous acid and determined by titration with sodium thiosulphate. In the filtrate from the iodine a little copper was precipitated by sulphuretted hydrogen. The following are the results obtained :—

		Atomic ratios.
Cu . . .	32·35	·513
Ag . . .	1·19	·011
I . . .	65·85	·520
	99·39	

Weight of mineral used in the analysis = 0·4808; I = 0·3166; AgCl = 0·0076; Cu_2S = 0·1949 gram.

Specific gravity (weight of 1 cc. at 23° C.) = 5·590[1].

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[1] Recently W. Spring (Zeit. f. Anorg. Chem. 1901, vol. xxvii, p. 308) has given

The numbers correspond closely to the formula CuI. The silver is probably due to a slight isomorphous admixture of miersite.

(4) ANALYSIS OF COPPER-PYRITES.

The specimen (No. 63230) of copper-pyrites, the result of the analysis of which is given below, is from Wheal Towan, St. Agnes, Cornwall. It was selected for analysis owing to the peculiarities of its crystals. These, although in other physical respects like copper-pyrites, are in habit apparently cubic and show what seem to be dodecahedral faces. The crystals (measuring about 3 cm. across, and associated with small crystals of quartz and mispickel on a matrix of quartz and chlorite) are so rough and striated that only measurements with the contact goniometer are possible: the angles between the faces intersecting in apparently dodecahedral edges were mostly about 60°. The striations are parallel to the longer diagonal of the rhombic faces, and in the opinion of Mr. L. J. Spencer these crystals are similar to the complex twins of stannite recently described by him in this volume (pp. 54–65) and figured in plate II, fig. 3, i. e. they are probably interpenetrant symmetric twins composed of three individuals with *e* (101) as twin-plane. The appearance of the fractured surface of the crystals, which exhibits a very delicate rippling, is also suggestive of repeated twinning.

In the analysis the copper was determined as sulphide, the iron as oxide, and the sulphur in a separate portion as barium sulphate. The results obtained are:—

		Atomic ratios.	
Cu . . .	33·60	·5442 or	1
Fe . . .	30·92	·5533 „	1·02
S . . .	34·90	1·0912 „	2·04
	99·42		

Weight of mineral used in analysis = 0·8170; Cu_2S = 0·3520; Fe_2O_3 = 0·3608. Weight used for sulphur determination = 0·4092; $BaSO_4$ = 1·0390 gram.

Specific gravity (weight of 1 cc. at 22° C.) = 4·17.

The result of the analysis shows that the mineral is perfectly pure copper-pyrites, the numbers agreeing very closely with the usual formula $CuFeS_2$. The peculiarities in crystal structure have therefore no connexion with anomalies in chemical composition, nor with any admixture of impurities such as iron-pyrites.

for the specific gravity of precipitated cuprous iodide the value 5·631, as the mean of four determinations, varying from 5·563 to 5·677, made on air-dried, on fused, and also on compressed material.