XIII.—*On some Minerals from Chile.*

By FREDERICK FIELD.

A SHORT paper published in the Journal of this Society (Vol. xii, p. 8) on some minerals containing arsenic, sulphur, and copper from Chile, was concluded by the observation that I was then engaged in the investigation of a mineral containing sulphur, antimony, copper, and iron, with small quantities of silver, the ore being thickly sprinkled with bisulphide of iron: no specimen could

* If the atomic weight of silicic acid be taken, according to Berzelius, as 30·8, that of silicon, upon the above hypothesis, would be 7·2; or, if that given by Pelouze (30·2) be employed, the atom of silicon would be 7·1, almost exactly double that of boron.

be obtained pure enough for analysis. After much time had been bestowed upon this substance, no formula could be deduced, as the iron pyrites seemed to be intimately blended with the mineral itself. The discovery of the compound $\text{Cu}_2\text{S}, \text{AsS}_3$ analogous to the beautiful silver mineral AgS, AsS_3 rendered it very interesting to find a corresponding $\text{Cu}_2\text{S}, \text{SbS}_3$ to the dark antimonial silver ore AgS, SbS_3 . All endeavours, however, as just observed, were unsuccessful. The pentasulphide of antimony in combination with 3 equivalents of disulphide of copper, corresponding to *Guayacanite* (the new mineral I described in the paper above referred to) which consists of pentasulphide of arsenic, with 3 equivalents of disulphide of copper, is also unknown at present.

Further investigations, however, led to the discovery of many singular specimens, some of which, though not altogether new to mineralogical science, may prove interesting to the Society.

Protoxide of Copper.—The combination of one equivalent of copper with one of oxygen, as a mineral production, is rather rare. The suboxide of copper so frequently encountered where the native metal prevails, appears, upon exposure to the atmosphere, or from other causes more difficult to explain to pass at once to the dicarbonate, assuming at the same time both oxygen and carbonic acid. The black earthy looking belt, which so frequently surrounds masses of ruby copper, and which is described in some works as the protoxide, contains, as far as my own experience extends, a very large proportion of sulphur, and although, not perhaps, a true definite oxysulphide, can by no means be regarded as a protoxide; in fact it contains no protoxide whatever, but is a mixture of disulphide and suboxide of copper. The black oxide of copper had only been known as existing in the Vesuvian lavas, until the great discoveries in North America, both in the valley of the Mississippi and on the borders of lake Superior, revealed this mineral in comparatively large quantities. Quite recently extensive veins of copper ore have been discovered in the extreme north of Chile (at longitude 25° S.), consisting essentially of protoxide of copper associated with carbonate of lime and a dark lustrous mineral, apparently a variety of hornblende. The ore, which has a dark brown earthy aspect, effervesces strongly upon addition of hydrochloric acid, so that at first it might be supposed to be a combination of the metal with carbonic acid; but that this is not the case is evident, upon a closer investigation of

the mineral, as well as from the fact that it can be ignited to low redness, and maintained at that temperature for some little time, without suffering much diminution in weight, whereas the carbonates of copper are deprived of their carbonic acid almost instantaneously when exposed to high degrees of heat. A qualitative examination showed the presence of oxide of copper, sesquioxide of iron, carbonic acid, lime, chlorine, water, and a substance insoluble in acids. A quantitative analysis gave the following numbers :—

Copper	36·34
Lime	11·61
Peroxide of iron . .	7·87
Carbonic acid . .	9·32
Chlorine	0·25
Water	0·28
Residue	25·23
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	90·90

The chlorine in the mineral was associated with copper, oxide of copper, and water, forming the oxychloride of the metal, and the carbonic acid with the lime, as 11·61 of that earth requires 9·12 of carbonic acid to form a carbonate, and analysis shews 9·32. The greater part of the copper evidently exists as protoxide, and the constitution of the mineral may be thus expressed:—

Oxide of copper	42·92
Oxychloride of copper (3CuO, CuCl, 4HO) .	2·89
Carbonate of lime	20·73
Peroxide of iron	7·87
Residue	25·23
Loss	0·36
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	100·00

If the impurities be removed, viz., the residue insoluble in acids, peroxide of iron and carbonate of lime, we obtain

Oxide of copper . .	93·69
Oxychloride of copper .	6·31
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	100·00

Black Amorphous Sulphate of Lead.—An exceedingly curious form of sulphate of lead was found in a mine a few leagues N.W. of Coquimbo. It occurred in large black masses, in the centre of which a small vein of finely grained galena was running. The sulphate, having a black earthy appearance, with no trace of metallic lustre was rejected by the miners as worthless. Its high specific gravity proved however that it consisted essentially of a compound of one of the heavier metals, and analysis shewed that it was sulphate of lead coloured with a small percentage of protoxide of iron. Hydrochloric acid at the boiling temperature decomposed it entirely, forming a pale green solution, due to protochloride of iron, or rather perhaps protosulphate, as free sulphuric acid existed in the liquid, and on cooling the greater part of the lead was deposited as chloride. Sp. gr. of the mineral 6·20 100 grs. yielded

Sulphate of lead . . .	96·74
Protoxide of iron . . .	3·16
Silver	traces
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	99·90

The galena, which formed as it were the nucleus of the mass contained (as is generally the case with the fine-grained sulphide of lead) appreciable quantities of silver, far more so than the exterior sulphate.

Basic Persulphate of Iron.—This beautiful mineral has been described in mineralogical treatises as *fibroferrite*. As however numerous sulphates appear to exist, among which may be mentioned, Fe_2O_3 , SO_3 , generally cited in chemical works as the one found native in South America, an account of the true fibroferrite may not perhaps be out of place.

This mineral is found in botryoidal masses, each rounded nodule being built up of innumerable silky fibres diverging from the centre, and of a pale golden green colour. It consists of two equivalents of sulphuric acid in combination with one of sesquioxide of iron (Fe_2O_3 , 2SO_3), and 10 of water.

	Calculated.	Found.
Sulphuric acid . . .	32·0	31·94
Peroxide of iron . . .	32·0	31·89
Water	36·0	35·90
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	100·0	99·73

After exposure to the air for a few weeks, it loses two equivalents of water and becomes $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 8\text{HO}$, and does not decrease further in weight even after many months. Heated in a water bath at 212°F ., it loses 7 atoms of water, the residue consisting of $\text{Fe}_2\text{O}_3, 2\text{SO}_3, 3\text{HO}$, and it requires a very high temperature for the expulsion of the last 3 equivalents. When subjected to a temperature of between 500° to 600°F . for some hours, the whole of the water is expelled and a pure bisulphate of peroxide of iron, perfectly anhydrous, remains.

	Calculated.	Found.
Peroxide of iron .	50.00	49.87
Sulphuric acid .	50.00	49.98
	<hr/> 100.00	<hr/> 99.85

When fibroferrite is digested in cold water, it is partially dissolved, the solution containing both iron and sulphuric acid, and having a slightly acid reaction to test paper. The phenomena produced by the action of boiling water are interesting. The mineral becomes decomposed at a temperature of about 120°F ., into an ochreish yellow amorphous substance, and a soluble salt, the solution of which is strongly acid. 10.00 grains of fibroferrite were digested in boiling water for an hour, and the residue dried on a water bath at 212. This insoluble portion weighed exactly 3.00 grains, and yielded on analysis 2.100 peroxide of iron, .528 sulphuric acid, and .368 water, being evidently a combination of 2 equivalents of peroxide of iron, with 1 of sulphuric acid, and 3 of water.

	Calculated.	Found.
2 Fe_2O_3 . . .	70.49	70.00
1 SO_3 . . .	17.61	17.60
3 HO . . .	11.90	12.26
	<hr/> 100.00	<hr/> 99.86

or $2\text{Fe}_2\text{O}_3, \text{SO}_3, 3\text{HO}$.

The sulphuric acid in the filtrate was found to weigh 2.640, and the peroxide of iron 1.06, the loss agreeing very closely with the 7 equivalents of water which separated at 212° .

Sulphuric acid evidently exists in a free state, as well as in combination with peroxide of iron, as the persulphate. Thus it

appears that 3 equivalents of fibroferrite have split up into 1 equivalent of a very basic sulphate, 1 of ordinary sesquisulphate, 2 of free sulphuric acid and water.

The insoluble compound described above is found native, and very often associated with fibroferrite. Should the sesquisulphate of iron and free sulphuric acid come in contact with sesquioxide of iron and water, fibroferrite might be reproduced.

It is somewhat singular that from $\text{Fe}_2\text{O}_3, 2\text{SO}_3$, in which two atoms of acid are united with one of base, a compound with two of base with one of acid should be derived.

Bournonite.—Bournonite was unknown in South America, and I believe in the New World, until the year 1858, when I met with it in a mine near Huasco, in the northern part of Chile. The specimen was crystallized. Hardness 2·5; specific gravity 5·80. It resembled in every respect the samples found in Cornwall and some parts of Germany. 100 grains yielded—

Sulphur	.	.	.	.	.	20·45
Antimony	.	.	.	.	.	26·21
Lead	.	.	.	.	.	40·76
Copper	.	.	.	.	.	12·52
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						99·94

A specimen from Cornwall gave—

Sulphur	.	.	.	.	.	20·30
Antimony	.	.	.	.	.	26·30
Lead	.	.	.	.	.	40·80
Copper	.	.	.	.	.	12·70
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						100·10

This mineral is mentioned in the present memoir not only as being the first of the kind found in America, but also for the purpose of introducing a few remarks, relative to the separation of arsenic and antimony, from lead, copper, and other metals of that group. In 1854 MM. Rivot, Beudant, and Daguin, published a very interesting paper in the *Comptes Rendus*, wherein it was pro-

posed to separate antimony, arsenic, and sulphur from many other elements, by digesting the mineral in a warm solution of potash, which after a time dissolved the arsenical and antimonial sulphides, and passing a stream of chlorine through the potash solution, by which were formed sulphuric, arsenic, and antimonious acid. By adopting this means, the authors remark, the whole of the antimony, arsenic, and sulphur, may be removed from lead, copper, &c. I have repeatedly tried this process, and although in my experiments, the minerals were in a very finely divided condition, complete decomposition, especially when antimony was present, could not be effected. In most instances, much of that element and nearly all the arsenic were dissolved, but even after many days digestion, antimony was invariably found in the residue. Hypochlorites of the alkalies or alkaline earths do not answer better. Dr. Aug. Streng (Ann. Ch. Pham., xcii, 411, and Chem. Gaz., xii, p. 269), endeavoured in his volumetrical determination of lead, to decompose galena with hypochlorite of lime, but without success. I also have tried hypochlorite of soda upon that and many other minerals with equally unsuccessful results. Streng, however, acted upon the galena with strong nitric acid, thus converting it into sulphate of lead, and then, after neutralizing the fluid with potash, digested, at a temperature a little below 212°F ., with chloride of lime, when after some time, decomposition was complete, the whole of the sulphate of lead having passed into the state of peroxide. When bournonite is treated in the same way, chloride of soda being employed, instead of the lime-salt, a considerable quantity of antimony passes into solution, but 2 or 3 per cent. always remains in the residue.

The process answers admirably in the analysis of copper or lead minerals containing arsenic and sulphur. For *guayacanite*, $(3\text{Cu}_2\text{S}, \text{AsS}_3)$ for example, the mineral is finely pulverized, digested in fuming nitric acid, and evaporated nearly to dryness; hypochlorite of soda is then added in considerable excess, and the whole boiled for about 20 minutes. All the arsenic and sulphur pass into the filtrate, pure oxide of copper remaining undissolved.

The same is the case with the sulpho-arsenides of cobalt and nickel. The stronger solutions of potash and soda in very great excess, and after violent ebullition, fail to decompose the arseniates of these metals completely; but if a stream of chlorine be passed through the alkaline liquid previous to boiling, or which is simpler,

a hypochlorite be at one employed, no trace of arsenic can be detected in the residual oxides.

Double Sulphide of Copper and Lead.—This very rare mineral, which I discovered in a mine near the silver district of Arqueros, consists of three equivalents of disulphide of copper and one of sulphide of lead, differing entirely from *Cuproplumbite* Cu_2S , 2PbS , also from Chile, which was analysed by Plattner, many years ago. 100 grs. of the new double sulphide yielded—

Copper	.	.	.	.	.	53·28
Sulphur	.	.	.	.	.	17·69
Lead	.	.	.	.	.	28·81
						<hr/>
						99·78

or $3\text{Cu}_2\text{S}, \text{PbS}$

	Calculated.	Found.
3Cu_2	53·34	53·28
4S	17·78	17·69
1Pb	28·88	28·81
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	100·00	99·78

It may be mentioned that this mineral has received the name *Alisonite*, in honour of Mr. Robert E. Alison, a gentleman who from his extensive smelting operations in no less than five different points in the Republic of Chile, has effected very much in the development of the mineral riches of South America. I observe that the great American Minerologist Dana, to whom I sent a short note upon the mineral in question, has published it under the name *Alisonite* in his supplement to the last edition of his work.

This mineral adds another to the list of the tribasic sulphides which have been already discussed in the two papers I have had the honour of transmitting to the Society.

Arsenical Rosicler	.	.	.	.	$3\text{AgS}, \text{AsS}_3$
Antimonial do	.	.	.	.	$3\text{AgS}, \text{SbS}_3$
Sulphide of copper and arsenic	.	.	.	.	$3\text{Cu}_2\text{S}, \text{AsS}_3$
Guayacanite	.	.	.	.	$3\text{Cu}_2\text{S}, \text{AsS}_5$
Alisonite	.	.	.	.	$3\text{Cu}_2\text{S}, \text{PbS}$

Mr. David Forbes, on his return from Chile, published an

account of a new arsenide of copper in the Philosophical Magazine for last December, and has named it *Darwinite*. This adds another to the list of arsenides, the first of which is *Domeykite*, and the second *Algodonite*, of which I published an account in the Journal of this Society in 1857.

Domeykite	.	.	.	.	Cu_6As
Algodonite	.	.	.	.	Cu_{12}As
Darwinite	.	.	.	.	Cu_{18}As .