Mineralogical Notes from Torreon, State of Chihuahua, Mexico.

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1.—On a new locality for Aurichalcite.

IN the early part of 1890 I noticed in some of the workings of the Torreon Mines, and chiefly on a decomposed chalcopyrite or in close connection therewith, a greenish-blue to sky-blue lamellar coating about $\frac{1}{8}$ inch in thickness, with sometimes isolated plumose groups of scaly crystals having a pearly lustre. Both appearance and mode of occurrence of the mineral led me to think it a basic sulphate of copper, probably cyanotrichite, or possibly a new species. Soon afterwards however, it was noticed that when the ore, as sorted for smelting, contained any quantity of the pale blue incrustation the cyanide assay failed to give accurate results in the estimation of copper, and on testing such ore qualitatively for zinc quite an appreciable quantity was found. Want of leisure prevented a more extended examination, but a good many specimens were selected and carefully preserved.

A few months ago some of the crusts were broken up, and with the help of lens and forceps carefully separated from gangue till some 6 grams of almost absolutely pure crystals were obtained for analysis. Preliminary examination proved the presence of CO_2 and absence of Fe and SO_3 . Material weighing 3.089 grams was therefore taken for estimation of CO_2 in a Schrodter's apparatus with dilute H_2SO_4 , and after solution the insoluble residue weighed .049 gram, consisting of minute grains of hæmatite and quartz. The quantity of clean mineral taken was therefore 3.040 grams, while the percentage of CO_2 indicated was $16.22 \,^{\circ}/_{O_2}$. The solution was treated with H_2S after addition of HCl to separate the copper, while the zinc was precipitated in the filtrate also with H_2S after alkalising with ammonia, the absence of iron having been already ascertained. After separating the zine the filtrate was concentrated by evaporation and the lime precipitated as oxalate. The bulky copper and zine sulphide precipitates were each dissolved and made up to 250 c.c., of which 50 c.c. were taken in each case for assay in duplicate, the copper being precipitated with caustic potash and weighed as CuO, while the zine was precipitated with Na₂CO₃ and calcined to ZnO. Very concordant results were obtained, the duplicates for copper yielding 19.87 and 19.96 p.c. CuO, while those for zine gave 54.85 and 54.69 p.c. ZnO.

For water a quantity weighing 2.432 grams was heated gradually over a good spirit lamp in iron crucible jacket till constant, the loss being 0.591, equivalent to 24.32 p.c. of carbonic acid and water. The residue still contained carbonic acid equivalent to 0.40 p.c., so that only 15.82 p.c. had been driven off together with 8.50 water.

The results were :---

H_2O		•••	•••	•••	8.50
CO_2	•••	•••	•••	•••	16.22
CuO	(mean)	•-•	•••	•••	1 9·91
ZnO	(mean)	•••	•••		54 ·77
CaO	•••	•••	•••	•••	0.46
SO_3	•••				trace
					99.86

The lime may probably be regarded as extraneous, being due to the inclusion of minute granules of calcite. It is plain that the minoral is aurichalcite, resembling the variety analysed by Risse, from Santander, as given in Dana. The percentage of water is, however, less than would be required to satisfy any of the formulæ given by Dana, and is in fact insufficient to form the ordinary hydrates of the metallic oxides. We may therefore suppose either that the original hydrates were somewhat more basic than the theoretical composition, or that in the long exposure to this very dry atmosphere they have lost some of their originally combined water; and this latter does not seem an unreasonable supposition when we remember how comparatively unstable are the hydrates of copper and zinc.

The original source of the zinc was at first matter for curious speculation, since no other zinc mineral has ever been noticed in the mines nor indeed within at least a couple of miles. On analysing the decomposed chalcopyrite, which is the prevailing ore of copper, the source of the zinc became at once evident, since even after an oxidation and decomposition which has removed practically all the sulphur no less than G-84 p.c. of zinc remains in the residue,

MINERALOGICAL NOTES FROM TORREON, STATE OF CHIHUAHUA, MEXICO. 17

2.-- On a peculiar decomposed Chalcopyrite.

The original source of all the copper minerals occurring in the Torreon Mines, among which may be mentioned chalcocite, malachite, azurite, chrysocolla, was undoubtedly the chalcopyrite brought up in the great igneous masses of garnet rock which form so prominent a feature of the locality; but curiously enough the occurrence of this mineral in an unaltered condition is extremely rare. The characteristic tetrahedral form is frequently recognisable in somewhat confused aggregations of fair-sized crystals, but the colour has mostly disappeared, the crystals on fracture are found to have a general dull blackish appearance, and are often covered with a drusy coating of malachite. There are, however, always to be seen in the fracture specks and patches showing a metallic lustre and usually retaining their original yellow colour, while from the manner in which these are disposed, being most concentrated towards the centre, it is evident that the decomposition proceeded inwards from the outer surface along innumerable cracks forming an intricate network, which is most distinctly visible where the oxidation is incomplete, and in which no trace of system or regularity is discoverable.

For analysis those specimens were selected in which the decomposition had proceeded as far as possible, but even in the dullest and blackest small specks of undecomposed chalcopyrite could be easily distinguished. Together with the chalcopyrite itself —often indeed absolutely enclosed in the large crystals—were found cubes of iron pyrites completely converted into oxide, and in addition minute crystals of quartz and calcite, which it was impossible to completely separate with the aid of a lens. A large quantity was coarsely broken and picked out as clean as possible, yielding on analysis the following results :—

SiO ₂ (adventitious)			5.52	
CuO			83·34	=(26·62 p.c. Cu)
$Fe_{2}O_{3}$			41.97	(=29·38 p.c. Fe)
ZnO	•••		1.26	
CaO		•••	0.81	
CO_2			6.86	
S			1.53	
Combined water			8.22	
			99.51	

The perfection of the oxidation is remarkable, for the amount of yellow unaltered chalcopyrite in the sample taken for analysis was certainly very nearly sufficient to account for 1.5 p.c. of sulphur out of some 33 p.c. originally present: it follows therefore that the perfectly clean dull black portions must be almost absolutely free from sulphur, probably containing less than 0.5 p.c.

The carbonic acid is probably derived from minute veinlets and cavities filled with malachite, which run through most of the crystals and could not be separated, and from portions of the malachite coating not completely scraped off.

The proportion of iron is somewhat in excess of that which would correspond to a typical chalcopyrite, and if the zinc replaces copper the difference is still more marked, since taking the mean of the analyses quoted by Dana a typical chalcopyrite should contain for 30.79 p.c. Fe no less than 32.23 p.c. Cu. It is most probable that the missing copper went to form the coating of little drusy crystals of malachite covering the large tetrahedra, which was scraped off as completely as possible before breaking them up for analysis; and if the crystals had been analysed as a whole, coating included, probably the proportions of iron and copper would have been about normal.

We might also suppose that a portion of the copper had been leached out while the iron remained, but such leaching could only be effected by acid solutions removing the copper as sulphate, which hypothesis seems to me quite incompatible with the constant presence of malachite in connection with this chalcopyrite, and the *entire absence of the sulphates of iron and copper, both neutral and basic*, not a single specimen of any of which has been observed in the whole locality.

This remarkable fact has led me to the conclusion that acid solutions played no part in the decomposition, neither was this due to ordinary atmospheric oxidation, such as may be constantly noted in connection with large pyritous masses containing copper. It seems to me that the decomposition most probably took place quite apart from the influence of atmospheric oxygen—i.e. at considerable depths from the surface, and that the decomposing agent was simply heated water containing more or less carbonic acid and bi-carbonate of lime in solution. The monosulphides of iron and copper are, as is well known, acted upon by steam with the production of H_2S : and we might expect the more powerful agent, superheated water under pressure, to be fully capable of attacking chalcopyrite, which is half a monosulphide (CuFeS₂ being probably Cu₂S FeS FeS₂). The constant occurrence of calcite in these ore-deposits, together with the malachite, lends additional confirmation to this hypothesis, since it is d flicult to see how this mineral can have existed or have been formed in the presence of soluble sulphates or acid solutions. The reactions which took place may perhaps be explained by the following equations :---

$$2\text{CuFeS}_{9} + 5\text{H}_{2}\text{O} = 2\text{CuO} + \text{Fe}_{2}\text{O}_{3} + 4\text{H}_{2}\text{S} + \text{H}_{2}$$
$$2\text{CuFeS}_{9} + \text{CO}_{2} + 6\text{H}_{2}\text{O} = \underbrace{\text{CuCO}_{3}\text{.CuH}_{2}\text{O}_{2}}_{\text{Malachite}} + \text{Fe}_{3}\text{O}_{3} + 4\text{H}_{2}\text{S} + \text{H}_{3}$$

Occasionally are found in the malachite spots, "eyes" or kernels of chalcocite, and it seems to me that such an occurrence of this mineral affords additional support to my theory, since the very gases liberated by the former reaction may have reacted upon some of the oxide of copper previously formed, in places where there occurred an accumulation of the gases together with more or less deficiency of water, and probably at a lower temperature, so re-forming a sulphide of copper; but in this case the subsulphide, according to the equation

$$2CuO + H_2S + H_2 = Cu_2S + 2H_2O$$
.

The subsulphide once formed would not be likely to be again decomposed, being much more stable and less likely to oxidise than the CuS originally existing in the chalcopyrite.

I am not aware that this theory of the decomposition of chalcopyrite has ever been suggested before. The peculiar circumstances of this locality have forced it upon my attention as the only one which succeeds in explaining the observed facts, but it seems probable that further investigation will prove its applicability to many other localities where chalcopyrite, malachite, and chalcocite occur together, or where the two latter alone remain. It will probably be found in the majority of cases that the former mineral was the original source of the copper, both malachite and chalcocite being of secondary origin, and in not a few cases it will be found that the decomposition proceeded in the manner above described.