### Remarks on Professor Prime's Paper.

# BY PERSIFOR FRAZER, JR.

# (Read before the American Philosophical Society, December 21, 1877.)

The paper of Professor Prime is exceptionally interesting to me because similar, though (as I apprehend him) not identical and perhaps not coeval, deposits of limonite occur in many parts of the district which I have been studying for four years, and which includes Franklin, Adams, Cumberland, York and Lancaster Counties. The two lines of limonite banks to which Professor Prime refers are also found there, and apparently in analogous position, viz: at the upper and under surfaces of the calciferous formation (but not usually in the latter position when there is no representation of the slates). Besides these two horizons of ore (if the term horizon may be applied to local deposits, in many cases principally produced long after the strata on the borders of which they lie) there are at least several others which cannot be referred either to the top or the bottom of the formation, but at various positions between the two. On the general maps accompanying my report of progress for 1874, there appear to be four or five such lines besides two principal ones nearly converging near Hanover, York County.

This rough conformity of the limonite to the limits of the limestone rock indicates a connection between the two more close than can be attributed to accident.

It has been often repeated before that the greatest exhibitions of iron ore of this character are almost invariably found directly in contact with the limestone, and one would naturally suppose that the cause was to be sought either in the action of one upon the other or in conditions which resulted in evolving both of them. It is true that the position of the clays in all these banks (including the larger ones just referred to), forbids the supposition that the deposits have been entirely produced by infiltration from other points, for, as Dr. Hunt has long ago conclusively shown, there are strings and lenticular masses of iron hydrates, &c., which lie within, and, conformably to the edges of the kaolinized slates, repeating all the convolutions of the latter, and showing other unmistakable signs of contemporaneous history.

Nevertheless, the alteration of the ferriferous minerals which were the origin of these limonite nests has apparently gone forward more rapidly when there was an abundance of carbonate of lime present, than when this rock was represented by the argillaceous and schistose members of the series to which it gives its name.

As to the amount of material necessary to produce all these beds, it might have been much more than furnished by the Pyrite alone, of which we know the former existence by the countless pits and casts which completely permeate the strata; as I endeavored to show several years ago.

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In opposition to the chemical hypothesis of the origin of these limonites, it is only just to cite the occurrence at Bull's Run (five miles south of Wrightsville, York County), amongst the calciferous slate, and even the limestone itself, of unusually large Pyrite crystals still in a perfect state of preservation, though under conditions very favorable to metamorphosis. Perhaps the generally gentler dip of the strata at that point protected the pyritiferous layers from the percolation; or perhaps some other cause may account for it; or perhaps the whole idea of the chemical production of limonite is erroneous, though in its support may be mentioned the results of the following experiments:

About 20 grams of crystallized ferrous sulphate were dissolved in 100 c c. of water.

About 50 grams of crystalline limestone were then ground up into fine powder, and placed in a glass stoppered bottle, into which 50 c c. of water was poured.

Ten c c. of sulphuric acid of density about 1.7 were then added, and the contents agitated. After the effervescence had subsided, the iron solution was poured into the same beaker, and the contents again strongly agitated.

After the subsidence of the powdered carbonate of lime, and upon it the light precipitate of calcium sulphate, the liquid was left undisturbed. It gave at first a feeble acid reaction, but later became quite neutral.

From time to time in the course of 24 hours the bottle was shaken, and the sediment again allowed to subside.

A light film of iron hydrate began to be perceptible in a few moments after the first shaking, and was quite perceptible both as a layer above the calcium sulphate, and as a ring which formed around the interior of the flask at the surface of the contained liquid.

This can be observed in the flask which I have brought here, the yellowish brown ring occurring at about the height of the upper surface of 150 c c in this bottle.

It suggested itself that possibly this action might result from the oxidation of the iron solution and precipitation at the surface. To test this the bottle containing the substances above described, was placed in a beaker of about 1.5 liter capacity, and water was carefully poured into the latter so as to overflow and finally submerge the lip of the bottle about 3 cm below its surface, the solution from this time being left undisturbed.

In the course of 24 hours or less there was a very copious flocculent precipitate of iron hydrate in the bottom of the beaker, and on the sloping neck of the bottle while the surface of the fluid was covered with an iridescent film like that on many natural chalybeate waters.

This experiment seemed to show that in presence of limestone the neutral sulphate of iron is readily decomposed in contact with atmospheric air, and the sediment precipitated as a flocculent mass from the upper surface of the fluid.

The reaction of the solution was entirely neutral.

Very little of the precipitate was observed upon the surface of the powder, the rapidity of the chemical change being proportional to the extent of surface in contact with air, and probably to the strength of the solution. The fact that the fluid exhibited no signs of acid reaction is sufficient proof that for every molecule of iron hydrate thus set free one atom of calcium took its place as a sulphate.

To test whether this exchange was effected by the intermediate production of iron bicarbonate, and the decomposition of this at its contact with air, the fluid was examined for carbonates in solution, but none were detected.

It seems probable then that in presence of bodies of limestone and free oxygen, iron sulphate is decomposed and its base precipitated at the expense of the calcium in the limestone.

Another experiment was tried to ascertain the amount of diffusibility of this solution of iron sulphate.

Another beaker of about 1 liter capacity was placed by the side of the first, and filled with water. A piece of large French filtering paper having been rolled up, the ends were immersed in the respective beakers. After standing for 24 hours with the fluid in the beakers at about the same level, the contents of the beaker last employed were tested without finding a trace of iron in it.

A gum tube of about 30 mm. internal cross-sections was then bent, filled with water, the ends stopped by the thumbs, and placed beneath the surface of liquid in the respective beakers.

After two hours of this syphon connection, the contents of the second beaker were again tested without finding any traces of iron.\*

In connection with this subject several years ago I sought to explain the chemical reactions involved in the production of limonite by means of limestone in the following four chemical equations from pyrite (though I never have considered it necessary to assume that pyrite was the only ferriferous mineral concerned in this production).

	$\mathrm{Fe}~\mathrm{S_2} + \mathrm{O_7} + \mathrm{H_2O}$	$\begin{bmatrix} \text{in presence of oxygen, water and} \\ \text{limestone.} & \text{O} + \text{H}_2\text{O} + \text{CaCO}_3 \end{bmatrix}$
a.	D , 1 · 1	$FeSO_4 + H_2SO_4[Ox, Aq. limestone.]$
b.	$By decomposing 1 molecule of \\CaCO_3 $ =	$FeSO_4 + CaSO_4 + CO_2 + H_2O$ [Ox, Aq. limestone.]
c.	$ \left. \begin{array}{c} \text{By decomposing one molecule} \\ \text{of CaCO}_3 \text{ and absorbing 1} \\ \text{molecule of } H_2\text{O} \\ \text{By oxidation in air (twice} \\ \text{the previous)} \end{array} \right\} = $	
d.	By oxidation in air (twice }=	$(CaSO_4)_4 + H_xFe_2O_y + (CO_2)_2$ [Ox, Aq. limestone.]

It now appears however, that the intermediate stage of iron bicarbonate is not necessary, but that the oxide may be directly produced after the hy-

\*The same experiment was tried, after the beakers had been connected by a column of water for over a week, with he same result.

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droxidation of the pyrite by reaction with limestone in presence of air thus :

 $(H_2O)_3 + O + (FeSO_4)_2 + (CaCO_3)_2 = (CaSO_4)_2 + H_6Fe_2O_6 + (CO_2)_2.$ 

In the region which I have studied, it seems to be as difficult to define any horizon or horizons of hydromica slate as to define an horizon of moisture, or of hard and soft rock. Hydromica slate in the counties before named occurs at any horizon, and in all possible relative positions to the limestone. So far as I have been able to judge the relations of these strata to the limonite, they are twofold: 1st, as a carrier of the pyrites, and perhaps other iron bearing minerals, which by their separation from the other constituents have been washed down and collected in the impervious strata *actually* beneath them. 2d, as the material out of which the impervious clays themselves have been produced.

As to the age of these hydromicas, they appear to be represented in the rocks of several ages. There are some which seem to be intercalated with, and therefore of the same age as the limestone itself.

Some are found geologically beneath the limestone and intercalated among the chlorites, quartzites, and orthofelsites of the South Mountain group.

# Crystallography in Sculpture.

### BY PERSIFOR FRAZER, JR.

### (Read before the American Philosophical Society, January 4, 1878.)

Mr. Spring an artist and a modeler in clay has conceived the ingenious idea of making the human head out of a number of plane surfaces of different area, and he designs these models, less to aid in teaching anatomy than to aid in teaching sculpture.

There are some fifty planes more or less represented on the small models such as this here shown, and of course it is of value to be able to designate each of them by some succinct and comprehensive notation.

It was suggested to Mr. Spring to apply to crystallography for this purpose.

The head here represented is of a high Caucasian type, unless I am deceived, and the symmetry of the features is as striking as their representation by planes is novel.

Of course since a plane represents a certain portion of such variable parts as the flesh, lips, ear, &c., no crystallographic formula would represent the same feature on each of two twins, nor would it represent the same individual in different frames of mind, and states of physical condition, viz.: angry; sentimental; after dinner; after sleep, &c.; nevertheless, a sort of rough approximation to his mean condition will enable if



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