The alteration of Pyrite by underground water.

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IT has for many years been proposed to form a reservoir with an area of some 36 square kilometres for irrigation purposes near Hiriyur in Northern Mysore, by erecting a dam at Marikanave, where the River Vedavati or Hagari crosses a rocky ridge running north-north-west and south-south-east.

Doubts were raised as to whether the rock would form a sufficiently firm foundation, but Mr. Robert Bruce Foote, late Superintendent of the Geological Survey of India, and my predecessor as State Geologist in Mysore, reported that it was in every way suitable for the purpose. The engineers, however, were apprehensive that the water from the tank would penetrate into the rock below the dam, and disintegrate it in the same manner as the rock of the ridge, which has suffered considerable decomposition from the continued action of surface water during long periods of time. A committee was accordingly formed consisting of two engineers and two geologists, Mr. T. H. Holland, of the Geological Survey of India, and myself, to report on the subject.

An excavation had been made on the northern bank of the river, where it passes through the ridge. The unaltered rock was found at a depth of four or five metres below the level of the river in ordinary flood. The strata exposed appear to belong to the Dharwar formation, the earliest of the non-fossiliferous systems of southern India that shows evidence of a sedimentary origin. The beds at Marikanave consist of ferruginous schistose slates and chlorite schists striking parallel with the direction of the ridge. The cleavage and stratification, which are indistinguishable, are nearly vertical. The slate is the predominant rock, but chloritic bands are repeatedly interstratified with it. Both, but more especially the slate, contain a large amount of iron pyrite. Not only are laminæ of pyrite intercalated parallel to the stratification, but the joint planes are occupied by films of the same material. This is also widely disseminated through the substance of the rock, which was, however, found, when tested in its unaltered condition, to possess more than the strength required by the engineers.

But in the ridge, and wherever the surface water had penetrated, the pyrite has been oxidised and removed. That in the joint planes was apparently first attacked, most of the iron was dissolved out, and only a little powdery ferric hydrate remained, which was soon washed away, and the rock became a mass of loose tile-like fragments. These, too, suffered decomposition, partly by the removal of the contained pyritic material, and partly as a result of the action of the sulphuric acid produced by the decomposition of the pyrite, sulphates of the bases in the rock being formed[1] and removed in solution, leaving only a certain amount of incoherent earthy material. The question for decision was whether underground water derived from the tank would ultimately have the same effect on the rocks below the dam.

Pyrite is of very frequent occurrence in the older rocks of the south of India. In many cases where they have been exposed to the action of surface weathering it has disappeared, the empty cavities which it once filled being the only indication of its former presence. Elsewhere, though the rock is quite unaltered in general character and apparently as strong as ever, the pyrite has been replaced by exact pseudomorphs in limonite, with or without cores of the original material.

It is at once obvious that the retention of the iron and the unaltered character of the rock must be due to the presence in the water, that effected the oxidation of the pyrite, of some substance that reacts with the sulphate of iron and sulphuric acid formed, so as to precipitate the iron and prevent the acid from corroding other parts of the rock. The only compounds likely to be present in any quantity that can produce this result are the carbonates of the alkaline earths and alkalis. As a general rule carbonate of lime must be the principal agent in the reaction.[2]

The changes that occur may be expressed by the equation :—

$$4FeS_2+15O_2+3H_2O+8CaCO_3=(Fe_2O_3)_2(H_2O)_3+8CaSO_4+8CO_2.$$

A simple calculation will show that the occurrence of complete pseudomorphs of limonite after pyrite implies the retention of the whole of the iron. The density of pyrite varies from 5·2 to 4·83. Four

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[1] $FeS_2+H_2O+4O_2=FeSO_4+H_2SO_4$. A slight incrustation of hydrous aluminium sulphate was detected at one point by Mr. Holland. It is probable that sulphurous acid is at first formed, but is at once oxidised to sulphuric acid.

[2] The action of carbonates in promoting the formation of limonite from pyrite has been recognised by Dr. Justus Roth, *Allgemeine und Chemische Geologie*, I, pp. 101-5, 236.

gramme molecules (each of 119·24 grammes) of pyrite will therefore occupy a space of $\frac{477}{5\cdot2}$ to $\frac{477}{4\cdot83}$—that is 92 to 99 cubic centimetres. Limonite has a density of from 4 to 3·6, so that one gramme molecule of the complex limonite combination, containing the same amount of iron as the four gramme molecules of pyrite, will occupy a space of 93 to 103 cubic centimetres, which is practically identical with the volume of the pyrite.[1]

If all the iron is to be retained in the pseudomorph, it is obviously necessary that the carbonates required to react with the iron and hydrogen sulphates formed by the oxidation of the pyrite should be present in the same water that provides the oxygen. The amount of oxygen soluble in water at 15° C. is about 30 litres per cubic metre. At normal pressure this will amount to 1·27 gramme molecules or 40·4 grammes of oxygen in a cubic metre, and will be enough to fully oxidise both the iron and the sulphur, as in the above equation, of ·339 gramme molecules of pyrite, and it will require twice that number of gramme molecules of carbonates (considered as normal carbonates and excluding carbonic anhydride in a free state or combined only with water), that is 40·4 grammes of the CO_3 group to react with the sulphates resulting from such oxidation.

The highest amount of oxygen in ordinary spring or river water among the analyses given in the 1877 edition of Watts's *Dictionary of Chemistry* under the article "Water" is only 11 litres per cubic metre.[2] The average is 7 litres.

The following table gives the details of the oxidising power of these quantities of dissolved oxygen and the carbonates required to react with the oxidised products[3] :—

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[1] If the iron had been converted into hæmatite the volume would have been 60 to 65 cc.; if into magnetite 61 cc.; if into turgite 75 to 78; if into göthite 80 to 88; while if it had passed into xanthosiderite it would have exceeded in volume the limonite. Accordingly, if all the iron be retained and none added, limonite is the only oxide or hydrate of iron that can form exact pseudomorphs after pyrite. It seems possible that the amount of space available may sometimes determine the quantity of water which enters into combination with the ferric oxide.

[2] Among mineral waters one analysis gives 13 litres. The highest in Thorpe's *Dictionary of Applied Chemistry* is 7·26 litres (III, p. 964).

[3] The identity of the figures in the 4th and 7th columns is of course accidental.

	Oxygen in cubic metre.			Pyrite oxidised.	Sulphates formed and carbonates required.	CO_3 (as normal carbonate) required.
	litres.	gramme molecules.	grammes.	gramme molecules.	gramme molecules.	grammes.
Maximum oxygen soluble at 15° C. and 760 mm.	30	1·27	40·4	·34	·68	40·4
Maximum oxygen recorded in ordinary spring or river water	11	·47	14·8	·12	·25	14·8
Average oxygen in river and spring water	7	·30	9·4	·08	·16	9·4

Among the 89 analyses of spring and river water (excluding mineral waters) given in the same edition of Watts's *Dictionary of Chemistry*, 76 have more than 9·4 grammes of the CO_3 group (combined as above) per cubic metre, 74 more than 14·8 grammes, and 68 more than 40·4 grammes; the average being 127 grammes. There is therefore in most cases far more than the amount of carbonates required.

The percentage of oxygen in the water of the proposed reservoir would probably be rather less than the above average, both on account of the higher temperature and because of the lower pressure at a height of about 700 metres above sea level. The presence of limestone in the drainage area and the occurrence of calcareous concretions in the recent alluvium of the river leave no doubt that the reservoir would contain an ample amount of carbonates to ensure that any pyrite it might oxidise in its incipient penetration of the rock would be at once converted into compact limonite completely filling the same space, thereby preventing to a great extent the further extension of the action of the water and preserving the strength of the rock. It would at the same time neutralise any sulphuric acid formed which would otherwise have attacked and dissolved the bases present.

As a general rule none of the calcium sulphate formed will be deposited; for the amount resulting from the reaction above described would be insufficient to saturate the water even though it had been saturated with oxygen which was all employed in oxidising pyrite, and the whole of the carbonate reacting with the sulphate formed were calcium carbonate. In that case the calcium sulphate produced would amount to ·68 gramme molecules, or 92 grammes in a cubic metre of water—which is capable of dissolving as much as 2,591 grammes at 18°C. Gypsum is, however, occasionally found in pseudomorphs after pyrite with or without a kernel of limonite. This is probably attributable to the slow evaporation of the water *in situ*.[1]

I have made a few simple experiments on the subject of this paper. I placed 1·060 grammes of powdered pyrite in a low beaker within a larger vessel containing distilled water which was frequently changed, mainly by means of a syphon which allowed the water to fall into the vessel, drop by drop, at intervals of a few seconds. After about four months of this treatment the pyrite was still bright, there being scarcely a trace of iron oxide present. There was however a loss of weight of ·0136 grammes—representing pyrite which had passed into solution as ferrous sulphate and sulphuric acid, the former being no doubt afterwards converted into ferric sulphate.

At the same time a practically identical amount (1·062 grammes) of similar powdered pyrite was placed in a beaker of the same shape, in a vessel containing New River water, which was renewed in the same manner as the distilled water. The former was, on titration, found to contain 161 grammes per cubic metre of the CO_3 group (combined with alkalis or alkaline earths, and estimated as normal carbonate). After the same period of treatment a considerable amount of hydrated ferric oxide, resembling limonite in appearance, was visible amongst the pyrite and on the sides of the beaker. As the liquid remaining was allowed to evaporate a little gypsum was also seen, but was easily dissolved out with distilled water. The total loss in weight, after the removal of the gypsum, was only ·0033 grammes, which represented the difference in weight between the pyrite decomposed and the ferric hydrate formed. If the whole of the iron in the pyrite which was decomposed were converted into a ferric hydrate having the composition of limonite, the loss in weight would theoretically amount to 22 per cent. of the pyrite decomposed. As the water was in both cases added drop by drop, and the vessels in which the experiments were conducted exposed to the air an equal amount of surface, which was large in proportion to the volume of the liquid, it is reasonable to suppose that the actual amount of oxygen present in solution was practically the same in the two experiments (being in excess of that usually found in spring or river water), and we may infer that the amount of pyrite oxidised was the same in each case. On the supposition that this was so, and that in the New River water all the iron of the decomposed pyrite remained as limonite, the theoretical loss in weight that might have been expected would work out as ·0030, which is closer to the figures

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[1] Roth, *loc. cit.* p. 236.

actually obtained than would have been expected, taking into account the conditions under which the experiment was performed and the probably indefinite character of the hydrate produced.

In another series of experiments small fragments of marcasite were placed in a vessel of distilled water. At the end of two months they were only slightly tarnished, but had diminished in weight from 7·453 to 7·430 grammes. A slight film of ferric hydrate was visible on the surrounding glass. Similar fragments were placed in another vessel filled with water, in which lumps of calcium carbonate were also placed. In less than twenty-four hours ferric hydrate was visible on the glass in the immediate neighbourhood, and in two months a considerable amount had accumulated both on the fragments and round them. Similar results were obtained with almost equal facility when such fragments were placed in a vessel in which New River water was allowed to fall drop by drop.

Similar experiments were conducted with zinc blende, which received a brown coating in calcareous water, but was unaltered in distilled water. Copper pyrites in calcareous water was coated by a similar brown ferruginous film, which was however slightly iridescent. In distilled water it was unaltered, though traces of iron could be detected in the solution. Further action would no doubt have resulted in the formation of appreciable quantities of copper sulphate. In old copper workings near Shimoga, in the north of Mysore, the action of surface water has resulted in the formation of fine stalactites of copper sulphates.

No effect was observable in the case of galena in the brief space of two months during which the experiments lasted.

Kupfernickel, smaltite and mispickel were unaltered in water containing carbonate of lime.

In distilled water kupfernickel was coated with a green film, indicating the formation of annabergite. In the case of smaltite, a white powder, probably arsenic trioxide, was deposited round the specimen, which showed scarcely any perceptible traces of erythrine being formed. No change was perceptible in the case of mispickel. This was contrary to expectation; the mineral is extensively disseminated through the crystalline schists in Mysore, and under the action of surface water all the sulphur is oxidised, the iron is dissolved out as sulphate, and the sulphuric acid attacks and removes a large proportion of the bases of the rock, the final result being a soft earthy material strongly impregnated with yellowish and greenish arsenates of iron, which sometimes extends over a distance of hundreds of metres.

Conclusions.

Where sulphides are exposed to the action of water free from carbonates, they will usually be slowly removed in solution as sulphates. When sufficient carbonates are present, as is the case with nearly all spring and river water, we may expect metallic carbonates, hydrates and oxides to be formed. In the case of iron it is the hydrate which is normally the first product. Free carbonic anhydride plays apparently no part in the formation of oxides, hydrates and carbonates from sulphides. When carbonates are not present in the water acting on the rock, the sulphides will usually be oxidised and removed as sulphates. The action of distilled water on metallic arsenides results in the formation of arsenates, which are in most cases insoluble. The presence of carbonate of lime seems in this case to retard the action.