ART. XXV.—*Replacement of Quartz by Pyrite and Corrosion of Quartz Pebbles*; by C. H. SMYTH, JR. (With Plate II.)

I. *Replacement of Quartz by Pyrite.*

THE lowest beds of the Oneida conglomerate, in Central New York, are characterized by the presence of considerable pyrite, serving as a cement to bind together the quartz grains and pebbles of which the rock is mainly composed. The relations between the two minerals are worthy of note.

The quartz is, of course, elastic, while the pyrite has been deposited from solution, and would naturally be expected simply to fill the interstices between the more or less perfectly rounded grains of the former mineral, as is the case with the secondary quartz cement of the upper beds of conglomerate.

The pyrite, however, behaves quite differently. Instead of being molded upon the quartz grains and taking its shape from them, the reverse relation holds good, and the form of the pyrite is deeply impressed upon the quartz grains, giving them angular, jagged and pitted contours, totally unlike their original elastic forms. That these contours are secondary and conditioned by the pyrite, admits of no doubt; for not only is the shape of the grains wholly incompatible with water transportation, but, when sections are examined in detail, it is evident that the outlines of the quartz grains are commonly determined by crystal faces of the pyrite, the latter mineral occurring with its own forms, pyritohedron and cube, to which the older quartz has been forced to accommodate itself. In other words, the surfaces of the quartz are such as would have resulted had it been deposited from solution upon the already crystallized pyrite, which is just the reverse of the actual relation. The pyrite seems to have crystallized as readily as though filling open spaces or pushing aside some soft medium, like clay, instead of forcing its way into so refractory a substance as quartz; and, in consequence, the quartz grains are bounded, not by their normal, water-worn surfaces, but by variously oriented minute planes, conforming to the crystal faces of pyrite. Between such grains and those showing their original contour there is a complete gradation, and some of the latter are surrounded by pyrite. But this is decidedly exceptional, the pyrite nearly always eating its way to a greater or less distance into the quartz, while in the absence of pyrite the quartz retains its original form.

Some idea of these various features may be gathered from the accompanying photomicrographs (Plate II). Although

affording a very unsatisfactory substitute for actual sections under the microscope, they suffice to show that the relation between the two minerals is quite different from that ordinarily subsisting between clastic quartz grains and their cement, and can be explained only as resulting from the simultaneous solution of quartz and deposition of pyrite, or, in other words, the metasomatic replacement of quartz by pyrite.

The amount of replacement varies considerably, even within the limits of an ordinary thin section, and sometimes a grain of quartz is considerably replaced on one side, showing the jagged contour impressed by the pyrite, while the other side retains the clearly defined original outline. Figures 1, 5 and 6 (Plate II) show cases of this kind, where the replacement is in early stages and the grains retain their original outlines to some extent, although the pyrite has eaten into them considerably. In figures 2 and 4, on the other hand, few traces of the original margins of the grains are left.

Thus far, in spite of the variation in the amount of replacement, no section has been seen which contains pyrite and does not show replacement. Even where there are but a few scattered crystals of pyrite, they have eaten into the adjacent quartz just as in parts of the rock that are strongly pyritiferous (fig. 1). Sometimes such isolated crystals, and even larger masses of pyrite occur entirely within quartz grains, having, doubtless, been deposited from solutions entering cracks. It is evident, however, that, as a rule, the replacement started at the surfaces of the grains.

This is a matter of interest in its bearing upon the history of the replacement, as it shows plainly that the solutions effecting the change circulated through the beds of sand and gravel before they were cemented. For, had these beds been indurated, as the upper beds are now, by secondary quartz, filling the interstices between the grains, any replacement that might have followed would have been controlled by secondary surfaces, resulting from fractures subsequent to cementation, and would show no such dependence upon the original surfaces of the quartz grains.

Such openings as escaped complete filling by pyrite were subsequently closed by secondary quartz. It is evident that when this happened the quartz would take the form of the pyrite, and thus give a texture identical in appearance with that described above. This relation is shown in figures 3, 5 and 6, and may be seen frequently in the sections, but it is always a minor feature; and while, in photographs with low powers, it might be confused with replacement, when seen under the microscope, the results of the two processes are easily distinguished, as they are in figures 5 and 6. There might be some

doubt in the case of very small grains, but with reference to the general relation of quartz and pyrite in the rock, secondary quartz is an entirely negligible factor.

As to the relative amounts of interstitial filling and of replacement, the evidence is quite clear. In the non-pyritiferous rock, the quartz grains are very closely packed and the interstitial filling correspondingly slight, but in the pyritiferous beds the quantity of pyrite between the grains is often considerable. The amount of replacement is greater or less according as the original interstitial space was large or small. While sometimes well-rounded grains are widely separated by pyrite, much the commoner case is the occurrence of jagged contours, and when parts of the original surfaces remain, it is evident that their complete restoration would largely take up the space now filled by pyrite (figs. 5 and 6).

This is repeated so often that it is deemed excellent evidence for believing that the original sand was closely packed, like that of the overlying beds, with small interstitial cavities, and that the considerable space now occupied by pyrite is due chiefly to replacement. According to this view, figures 2, 3 and 4 represent later stages in a process whose earlier stages are represented by figures 1 and 5.

If the space now filled by pyrite were regarded as original, it might be concluded, as there is no reason for assuming the former presence of any other cement, that the sand and pyrite were deposited simultaneously, the pyrite coating the grains and thus keeping them from being closely packed. Primary deposition of pyrite in sediments is common, an instance described by Rensch* being of particular interest in this connection; and this explanation is favored by the apparently fixed stratigraphic position of the pyrite, and the fact that it was deposited before the secondary quartz. But if the foregoing interpretation of the texture of the rock is correct, a later introduction of the pyrite is indicated; although, so far as the evidence goes, it may have followed closely upon the deposition of the sand and gravel, while they were still exposed upon the sea bottom. This latter view, which is but a slight modification of the preceding, would account equally well for the position of the pyrite and for its deposition before the secondary quartz.

While it is a general rule that the primary pyrite of sediments is deposited in the presence of abundant organic matter, which is lacking in the conglomerate, the underlying Lorraine formation would be a possible source of hydrogen sulphide and other reducing agents.

* Neues Jahrbuch f. Mineralogie, etc., 1879, p. 255.

Thus, so far as the pyrite itself is concerned, there is reason for thinking that it was deposited in the gravel and sand lying uncovered on the sea bottom. But, on the other hand, it is difficult to believe that, had the pyrite been so deposited, there would have been any replacement of quartz. Such metasomatic processes usually take place after rocks are deeply buried, and subjected to the action of underground waters; and while, in the case of a readily soluble mineral, such as calcite, sedimentation and replacement are often practically simultaneous, with our present limited knowledge of the chemical reactions on the sea bottom, it seems unlikely, in spite of the evidence given later as to the solubility of quartz under surface conditions, that this would be true of quartz. Thus, it appears probable that the replacement of quartz by pyrite was effected by ground waters, rather than by chemical reactions coincident with, or directly following, the deposition of the sand and gravel. But as this conclusion is based upon general considerations rather than upon direct and positive evidence, it may be modified by future investigation.

As to the bearing of the stratigraphic position of the pyrite upon the above conclusions, it should be said that, owing to the unsatisfactory exposures of the formation, there is much to be learned with reference to the precise distribution of the pyrite, and it is certain that the higher beds often contain enough of the mineral to weather yellow, brown and black. It seems, therefore, unwise to lay great stress upon the stratigraphic position until it is more accurately determined.

However, even if the pyrite is largely confined to a definite horizon, at the bottom of the conglomerate, it is possible to reconcile the fact with the above conclusion as to its secondary origin. Before cementation, the conglomerate must have been a permeable formation, permitting a free circulation of water. Immediately beneath it, on the other hand, the fine-grained Lorraine formation would be relatively impervious, and thus, along the contact, or in the bottom beds of the conglomerate, the conditions would be favorable for deposition. These beds might be quite uniformly impregnated with such a mineral as pyrite, which, in consequence, would have a definite stratigraphic position, in spite of its secondary origin.

With so much that is uncertain, it is not worth while to make any attempt to explain in detail the chemistry of the deposition of pyrite and replacement of quartz, but it is natural to suppose that hydrogen sulphide and iron and alkaline carbonates were active agents in the process. These compounds are sufficiently common in ground-waters to warrant the assumption of their former presence where effects are observed of which they would be a probable cause, although there are

difficulties as regards concentration. In the present case, while there is no obvious source for any unusual quantity of alkaline carbonates, a sufficient supply might, perhaps, be furnished by overlying shales, while the Lorraine formation might be a source of hydrogen sulphide. Iron may have been original in the conglomerate, or derived from overlying rocks. In this connection, Doelter's* production of artificial pyrite by the action of hydrogen sulphide and sodium sulphide on iron carbonate is very suggestive, and may represent some approximation to the conditions involved in the case under consideration.†

If this is true, it is evident that the replacement of quartz by pyrite is caused by common, rather than peculiar, agents, and therefore might be expected to occur with some frequency. As a matter of fact, judging from the literature of ore deposits, it is by no means rare. Lindgren‡ in particular has described several instances within very recent years.

But in all the cases that the writer has thus far found mentioned, the process is connected with some type of mineral vein formation, where, with the hot alkaline solutions and mineralizers, and resultant powerful chemical action, it is not surprising to find even so resistant a mineral as quartz yielding to the agents of alteration. In some of these cases it is, as in the present instance, the quartz of sedimentary rocks that is replaced, but always under the conditions involved in the filling of mineral veins.

These conditions are so unlike those controlling the deposition and subsequent existence of the Oneida conglomerate that the occurrence of pyrite replacing quartz in veins would hardly suggest the probability of the same thing taking place in the conglomerate, and explanations of the former process would, doubtless, require modification before being applied to the latter.

The reagents suggested above are similar to those filling veins, but in the case of the conglomerate their action would, probably, be less intense, owing to lower temperatures and pressures, greater dilution, and the absence of some of the more powerful reagents. Compensation might be afforded by the ready permeability of the formation and the large surface of quartz exposed to attack, while, of course, the time factor

* *Allgemeine Chemische Mineralogie*, p. 148.

† See a theoretical discussion of the chemistry of pyrite-quartz replacement by C. S. Palmer, *Eng. and Min. Jour.*, lxxix. p. 169.

‡ *Metasomatic Processes in Fissure Veins*, *Trans. Am. Inst. Min. Eng.*, xxx, p. 615, et seq.

Gold and Silver Veins in Idaho, 20th Ann. Report, U. S. Geol. Survey, iii, p. 219 et seq.

Geological Reconnaissance across the Bitterroot Range, etc. U. S. Geol. Survey, Professional Paper No. 27, pp. 109-110.

would be most important in determining the amount of replacement.

How frequently all the conditions necessary for the replacement of quartz by pyrite are fulfilled in formations similar to the Oneida conglomerate, it is at present impossible to say. Judging from the literature, the matter has never been investigated, which doubtless explains the fact that, so far as the writer can learn, no case similar to the present one has been described.

Whatever sheds light upon the geological relations of so important a mineral as quartz is worth recording, but it is evident that this case of the replacement of quartz by pyrite is of particular significance in its bearing upon ore deposits. In the present instance, the total amount of replacement is comparatively small, but there seems to be no reason why, under more favorable conditions, there should not be a more extensive, or even complete, replacement of quartz by pyrite, and, perhaps, by other sulphides. Although this may be going too far, it is, at least, evident that the phenomena described suggest interesting possibilities.

II. *Corrosion of Quartz Pebbles.*

While the replacement of the quartz is clearly a process which was accomplished early in the history of the conglomerate, the same mineral occasionally shows evidence of another change, going on under very different conditions at the present time. Several specimens have been found with projecting pebbles of quartz deeply corroded in a manner indicating the action of some solvent, working, not throughout the mass of the rock, but upon surfaces of bedding planes, or, rarely, of joints and boulders—in other words, where there is exposure to weathering conditions.

The pebbles show most irregular surfaces, often pitted, with sharp jagged projections, and in extreme cases, appear to have lost a considerable fraction of the original mass. As a rule, solution has been most rapid on the tops of the pebbles, and as the cement and sand work out beneath, there is also rapid solution here, the result being the reduction of pebbles to thin plates, with very jagged edges and rough surfaces. Such a marked effect is, however, exceptional, the pebbles more commonly showing a less pronounced change of form, but having the characteristic etched surfaces. The accompanying illustration from a photograph (fig. 1), showing a portion of the surface of a typical specimen (natural size), gives a fairly clear representation of corroded pebbles. While the sand grains are similarly affected, the phenomena are, naturally, much less easily observed.

Unlike the replacement by pyrite, this corrosion of the quartz seems to be a rather exceptional feature of the rock, as but few good examples have been found.

The character of the corroded pebbles is essentially the same as that described by Hayes* and by Fuller,† but in both of these latter cases the pebbles appear to have suffered greater loss, while there is a stronger tendency towards a rapid solu-

tion of the center of the pebble, leaving the margin as a projecting rim. This form is seldom even approximated in the Oneida specimens, but the resemblance to wind-faceted pebbles, noted by Hayes, is sometimes quite pronounced.

Hayes explains the corrosion as due to the action of the azo-humic acids of decaying organic matter, combined with potash derived from forest fires, and regards the process as taking place at the surface.

Fuller concludes that the quartz is dissolved by organic acids supplied by plants buried in the rock when it was deposited,

* Bull. Geol. Soc. Am., viii, pp. 213-226.

† Jour. Geol., x, pp. 815-821.

and holds that the process has taken place at moderate depth beneath the surface.

Long ago, Newberry* regarded the impressions of plant stems upon the quartz pebbles of conglomerate as due to organic acids, and, as quoted by Bolton,† explained in the same way the corrosion of quartz pebbles occurring in carbonaceous clay.

As the present instances of corrosion show no connection with unusual supplies of decomposing organic matter and alkalis, at the surface; and as the conglomerate contains little, if any, original organic matter, none of these explanations seems applicable; but, unfortunately, no satisfactory substitute is forthcoming.

As already stated, the corrosion appears to be a superficial process—a peculiar phase of weathering. To this may be added the striking fact that, thus far, corroded pebbles have been found only in the pyritiferous beds, though carefully sought for in the overlying pure quartz conglomerate.

Thus, corrosion seems to be dependent upon two conditions,—presence of pyrite and weathering,—which suggests the conclusion that the products of the weathering of pyrite act as solvents of quartz. But, so far as the writer is aware, such a conclusion finds no support in the results of laboratory study; and an explanation of the phenomena must await further investigation.

It might be suggested that the corrosion is merely apparent, not real, resulting from the weathering out of pyrite from partly replaced quartz, thus leaving, as would evidently be the case, a rough pitted surface. This simple explanation is not, however, in harmony with the facts. The replacement though greatly modifying the shape of small sand grains, perhaps even completely destroying them in some cases, does not go deep enough to materially change the shape of the larger pebbles, upon which corrosion is conspicuous. So, while mere weathering out of pyrite would give a rough surface, it would not yield the deeply corroded pebbles. Furthermore, a surface left by the removal of pyrite would be marked by depressions corresponding in shape with the pyrite, and, thus, often bounded by small plane faces, which is distinctly not the case with the corroded pebbles.

The rough surface left by the removal of pyrite would, of course, favor solution of the quartz by any agent present, and to this extent, surely, replacement is a factor in the subsequent corrosion.

The Oneida conglomerate, then, presents two types of solu-

* Geol. of Ohio, vol. ii, pt. I, p. 111.

† Ann. N. Y. Acad. Sci., i, 1877, pp. 35-36.

tion of quartz, one accompanied by simultaneous replacement by pyrite, and thus metasomatic, the other purely destructive in its nature, and in harmony with the general tendency of weathering. While neither of these processes is of great moment in the history of the formation as a whole, they are interesting in that, as they seem to represent no very unusual conditions, they suggest the possibility that quartz, though unquestionably an exceedingly resistant mineral, may yield rather more readily to the attack of natural solvents than has generally been supposed.

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DESCRIPTION OF PLATE II.

- FIGURE 1.—Early stage of replacement, with crystals and irregular masses of pyrite growing between, and into, the quartz grains. Magnified 26 diameters.
- FIGURE 2.—Original margins of quartz grains almost entirely removed, giving jagged contours determined by the forms of pyrite. Magnified 26 diameters.
- FIGURE 3.—Pyrite with unusually irregular forms. Some secondary quartz in upper half of section. Magnified 26 diameters.
- FIGURE 4.—A typical example of replacement in a fine-grained specimen. Nearly all the quartz grains are affected, and show the characteristic contours resulting. It is quite possible that some small grains have entirely disappeared. Magnified 23 diameters.
- FIGURE 5.—Pyrite filling interstitial spaces, and projecting slightly into quartz grains, whose original margins are partly preserved. Some secondary quartz. Magnified 67 diameters.
- FIGURE 6.—Shows very clearly the contrast between original and secondary contours of quartz grains, together with the dependance of the latter upon the forms of pyrite. Some secondary quartz. Magnified 67 diameters.

Fig. 1, $\times 26$ diam.

Fig. 2, $\times 26$ diam.

Fig. 3, $\times 26$ diam.

Fig. 4, $\times 23$ diam.

Fig. 5, $\times 67$ diam.

Fig. 6, $\times 67$ diam.