ART. XVII.—*On the Serpentine (Peridotite) occurring in the Onondaga Salt-group at Syracuse, N. Y.*; by GEORGE H. WILLIAMS.

(Paper read before the National Academy at Washington, April 20, 1887.)

ABOUT the year 1837 there was discovered on the side of the hill just east of what was then the town of Syracuse, N. Y., a narrow and apparently horizontal bed of a dark colored rock, which presented a striking contrast to the lighter colored shales and porous limestones both above and below it. The late Professor Oren Root of Hamilton College, was at that time the principal of the Syracuse academy, and the unusual, massive rock interested him so much that he used often to take his students with him to the locality to collect specimens. He readily recognized the rock as a typical serpentine and first brought it to the attention of Professor Vanuxem, who was then engaged upon the geological survey of this part of the State.

The exact locality where this serpentine appeared is now occupied by the lawn of Mr. Howard G. White. The band extended from what is now the center of James street, nearly across the lawn to where the house stands. It was for the most part a disintegrated, dark-green, earthy mass, through which large nodular blocks of the less altered rock were scattered.*

Vanuxem described this serpentine in his Third Annual Report in 1839, and in his final volume on the Geology of the Third District of New York in 1842. Dr. Lewis Beck also mentions it in his report on the Mineralogy of New York in

* For these and some other details the writer is indebted to the kindness of Mr. J. Forman Wilkinson, of Syracuse, who was one of Professor Root's pupils in the old academy. A large portion of his letter on the subject has been published in "Science" for March 11th, 1887. The localities given by Vanuxem and Beck are both different, but neither of them are so accurate as that above mentioned.

1842. The geological position of the serpentine, as defined by Vanuxem, has been so well summarized by Dr. T. Sterry Hunt in his recently published volume of essays,* that no further account of it need here be given, but Vanuxem's descriptions of the rocks themselves are so true that I cannot forbear quoting some of them. In a supplement to his Third Annual Report of 1839 he says: "The green and trap-like rocks observed near the top of the hill to the east of Syracuse have been examined so far as time would admit. They are all serpentines, more or less impure, and of various shades of bottle-green, black, gray, etc. . . . Some have a peculiar appearance, like bronze, owing to small gold-like particles, with a lamellar structure, resembling bronzite or metalloidal diallage; also other particles, highly translucent, like precious serpentine, with frequently small nuclei, resembling devitrifications or porcellanites, colored white, yellow, blood-red, variegated, etc." In his final report (p. 109) he mentions the occurrence of both black and white mica and "accretions resembling granite." In one case hornblende replaced the mica producing an apparent "syenite." He also speaks of "calcareous accretions enveloped in the serpentine."

In 1858 Dr. T. Sterry Hunt published an analysis of a specimen of the Syracuse serpentine which he had obtained from Professor James Hall, of Albany.† This contained 34.77 per cent carbonate of lime, 2.73 per cent carbonate of magnesia and 62.5 per cent serpentine. This latter was found to have the following composition:

SiO ₂	40.67
Al ₂ O ₃	5.13
FeO.....	8.12
MgO.....	32.61
H ₂ O.....	12.77
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	99.30

No traces of nickel or chrome were detected.

The Syracuse serpentine was also mentioned by the Hon. Geo. Geddes in his Report on the Agricultural Industry of Onondaga County,‡ and Prof. James D. Dana, in his Manual of Geology.§ It has recently acquired an additional interest on account of the argument for the origin of serpentine by chemical precipitation based upon it by Dr. Hunt.|| Vanuxem

* Mineral Physiology and Physiography, 1886, pp. 443-447.

† This Journal, II, xxvi, p. 237, Sept. 1858.

‡ Transactions of the N. Y. State Agricultural Society for 1859.

§ Third Edition, 1880, p. 233.

|| "The Geological History of Serpentine." Transactions of the Royal Society of Canada, vol. i, p. 174, 1883, and Mineral Physiology and Physiography, 1886, p. 443.

says of the Syracuse serpentine, (Final Report, p. 110): "The great interest of all these metamorphic products is that they have not been caused by a dry heat or fire, no evidence of the kind existing; nor is any needed to effect the change there observed, though it can and has and does produce the same result. All that is required is the presence of the elements of the products observed at Syracuse and in a state admitting of solution and of moisture, to which every degree of heat added would greatly aid their mutual action upon each other; and from solution crystallization would take place, and thus metamorphic products or rocks would be formed, no igneous action, commonly so called, being requisite, but a thermal one only." Dr. Hunt also says after discussing this occurrence (l. c., § 34, pp. 447 and 448): "From a study of the facts before us, it is apparent that we have here evidence of the formation by aqueous deposition of a bed of concretionary silicate of magnesia, taking the form of serpentine, with a little associated bastite or bronzite, and probably some other crystalline silicates."

It is therefore plain that the main point of interest connected with this now inaccessible occurrence of a typical serpentine relates to its mode of origin.

Through the liberality of Professor Albert H. Chester of Hamilton College, the original collections of the Syracuse rock, made by Professor Root while he was principal of the Syracuse Academy, have been placed in the writer's hands for study. This abundant and representative material, from which, however, the micaceous (granitic) and hornblendic (syenitic) accretions mentioned by Prof. Vanuxem are unfortunately absent, has been subjected to a thorough microscopical examination and it is the aim of the present paper to show that all the facts heretofore observed and stated by former investigators are perfectly in accord with the igneous origin of this rock; while certain other facts, here mentioned for the first time, place it almost beyond doubt that the serpentine was, in its original state, an intrusive mass, and *not* an aqueous deposit.

A macroscopical examination shows that the serpentine itself is represented by two quite distinct types. One of these is a very dark-green, almost black, rock, filled with minute glistening specks which the lens at once reveals as mica. Occasional larger plates of a brass-yellow color are also seen (4×6 mm.), and a more careful search discovers a few small masses of a lighter green, more compact serpentine with a sharp crystal-form.

The second type has a lighter color than the last. It is composed of a dense compact base which incloses numerous lighter spots with a sharp crystal outline, thus producing a decidedly

porphyritic structure. The irregular blood-red patches spoken of by Vanuxem are scattered through this rock. The porphyritic crystals here mentioned produce what Dr. Hunt has called the "concretionary structure" of the serpentine.

Under the microscope the rock of the *first type* appears as a medium-grained aggregate of brown mica, octahedral crystals of both a yellow transparent, and of an opaque black mineral, green or colorless serpentine and carbonates. Occasional larger crystal-forms are scattered through this matrix. It is remarkable that, in spite of nearly all the substance of this rock being secondary, the original structure is almost perfectly preserved. Sharply defined crystal-forms show by their shape that they must have once been *olivine* or *enstatite*, although none of the original substance now remains except rarely in the case of enstatite. The *mica* is that peculiar brown biotite which is well known to be characteristic of the eruptive peridotites.* It is without crystal-form, and often shows a peripheral zone of a lighter color due to bleaching. The minute octahedral crystals mentioned above are from .05 to .005mm. in diameter. The opaque black ones are for the most part *chromite*, although some of them may be *magnetite*, as the magnet shows that there is a little of this substance in the rock. If the serpentine powder be treated with hydrofluoric or with concentrated sulphuric acid, everything is dissolved except these small black octahedrons, which give a strong chromium reaction in both the phosphorous and borax beads. There is therefore little doubt that they are mostly chromite.

The little transparent yellow crystals entirely disappeared when the rock was treated with either of the above mentioned acids, and the solution in each case gave a strong titanium reaction with H_2O_2 . This, together with the fact that they showed an isotropic character when examined in polarized light, suggested the possibility of their being *perovskite*, and such upon further investigation proved to be the case. In spite of the frequently repeated assertion in mineralogies that perovskite is not attacked by acids, it is well-known that it is dissolved by concentrated sulphuric acid, as stated by Dana† and Rosenbusch.‡ That it must also be attacked by hydrofluoric acid is shown by the fact that both Baumhauer§ and Ben Saude|| used this reagent in a dilute form to produce etched figures on the planes of perovskite crystals. Stelzner¶ also found that it was impossible to isolate the minute octahedrons of perovskite from

* Vid. Rosenbusch: Die massigen Gesteine, 2d ed., 1886, p. 259.

† System of Mineralogy, 5th ed., p. 146.

‡ Die petrographisch wichtigen Mineralien, 2d ed., p. 295.

§ Zeitschrift für Krystallographie, Bd. iv, p. 187, 1880.

|| Ueber den Perowskit, Göttingen, 1882, p. 22.

¶ Neues Jahrbuch für Mineralogie, etc., II Beilage Bd., p. 332.

the melilite basalt of Hochbohl by hydrofluoric acid. The method proposed by this latter investigator was therefore made use of in the present case with complete success. The finely powdered rock was digested for a long time in concentrated hydrochloric acid under pressure, and all the components dissolved except the octahedral crystals and the mica. These were separated by washing until finally a powder was secured which the microscope showed was composed of the black and yellow crystals in about equal proportions along with a small amount of the brown magnesia mica. This powder, which was found to weigh .0442 gr., was then treated with strong sulphuric acid, in which .0277 gr., of the chromite remained undissolved. A quantitative analysis of the filtrate, containing only .0165 gr., was kindly made for me by Mr. J. H. Kastle, of the chemical laboratory of the University with the following result:

TiO ₂	34.54
CaO	12.12
FeO	54.54
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	101.20

This analysis can only be regarded as an approximation on account of the extremely small amount of material at command. Mr. Kastle says that the iron is undoubtedly too high. What of this substance is present is partly contained in the perovskite, isomorphous with CaO; partly derived from the mica which is dissolved by sulphuric acid. The above proportion of CaO puts the nature of the mineral as perovskite beyond a doubt, as no other mineral is present which contains a trace of lime. Moreover any other titanium mineral, as for instance anatase,* would not have been completely dissolved by sulphuric and hydrofluoric acids.

Perovskite was first recognized as a rock constituent in 1876 by Boricky† in the nepheline basalt of Wartenberg in Bohemia. In 1878, Hussak‡ discovered it in the basalt lava of Scharteberg in the Eifel, and in 1883, it was isolated and analyzed from the melilite basalt of Hochbohl by Stelzner.§ In all of these cases the crystals were simple octahedrons, and Hussak describes them as doubly refracting, like most of the larger crystals of this species. Sauer|| has recently described large crystals showing the cube and octahedron in the coarse veins of the nepheline-basalt from Wiesenthal in Saxony.

* The suggestion was ventured in the preliminary description of the Syracuse serpentine, published in "Science" of March 11th, that these crystals might be anatase.

† Sitzungsber. d. böhm. Ak. d. Wiss., 1876.

‡ Sitzungsber. d. Ak. der Wiss. in Wien., April, 1878.

§ Neues Jahrbuch für Mineralogie, etc., II Beilage Bd., p. 390.

|| Zeitschrift d. deutsch. geol. Gesellschaft, xxxviii, 1885, p. 441.

The occurrence of perovskite in the Syracuse serpentine is in all respects identical with that in the rocks described by Boricky, Hussak and Stelzner, specimens of which have been carefully examined for comparison. It is interesting as being the first instance on record of perovskite as a constituent of any American rock, and also as the first discovery of perovskite in a peridotite or serpentine from any locality.

The *porphyritic type* of the Syracuse serpentine is essentially identical with that above described in all points except its structure. The groundmass is finer grained, which throws the characteristic crystal-forms of the olivine and enstatite into a sharp relief. The structure of this rock is represented

in the accompanying figure. The octahedral crystals are much smaller than in the other rock and are confined wholly to the groundmass. The brown mica is here much less abundant. The porphyritic olivines especially are most representative examples of the well-known serpentine pseudomorphs, so often described and figured by Tschermak and others in eruptive rocks. They are sometimes stained deep red by iron oxide, which occasions the above mentioned blood-red spots.

The persistence of structure in this rock, in spite of the profoundest chemical changes, is remarkable. In one porphyritic specimen the groundmass is almost all carbonate, the mica has become quite colorless, and the olivine crystals are changed to a perfectly isotropic, colorless substance, enclosing the sharpest possible rhombohedra of dolomite; in fact none of the original components remain except the chromite, and yet the structure is just as sharp and characteristic as in the specimen above figured.

The geological occurrence of the Syracuse serpentine can unfortunately no longer be studied, as the exposure has been inaccessible for over forty years; still some evidence of its character may be derived from the testimony of observers and from a study of specimens. Mr. Wilkinson, in his letter above alluded to, says that an opening made only 50 feet away, *on the strike of this serpentine, passed entirely through gypsum*. The deposit is described as a horizontal bed between layers of porous dolomite, but it may have been intruded in this form between them as along the line of least resistance.

It is particularly mentioned by Vanuxem that the Syracuse serpentine has nowhere modified the surrounding limestone in a manner that would indicate that it was once in a molten state. Now, as is well-known, among all the igneous rocks, peridotite is the particular one which is *least* liable to produce contact metamorphism in the adjoining beds. Rosenbusch, in his most recent work, omits all mention of this subject in connection with peridotite, although he lays much weight upon it in connection with all the other plutonic rocks. Nevertheless, Mr. Diller has lately shown that the eruptive peridotites of Elliott Co., Ky., have altered to a slight degree, the shales through which they break; and I think that there is undoubted evidence that the Syracuse rock did the same. This alteration could not, however, be detected without the aid of the microscope. It is now impossible to examine the action of the mass as a whole, but certain specimens in my possession show plainly the effect of heat upon fragments of limestone which have been included in the serpentine mass.

If the serpentine of Syracuse were eruptive we should naturally expect to find the more granular variety near the center, and the porphyritic variety near the edge of the mass. No notes relating to such a distribution exist on any of Prof. Root's labels, but that such was the relative arrangement, is shown by inclusions of a very fine-grained, compact, gray limestone which are abundant in the porphyritic variety. Some specimens are mere limestone breccias with a serpentine cement. These inclusions are the "calcareous accretions"* of Vanuxem; and, though the line of contact between them and the serpentine is very sharp, they show an important modification consisting of the development in them of a greenish substance. This is most pronounced near the serpentine and fades away gradually as we go from it. The band is sometimes only a few millimeters wide and often has a zonal structure. One polished specimen shows the line of contact with the adjacent limestone (probably not an inclusion) and in this there are irregular

* His granitic and syenitic accretions may have been foreign inclusions brought up with the rock from far below the surface.

green bands running perpendicular to the line of contact across the entire surface. This green color is seen under the microscope to be due to the secondary development of a green mineral in a very finely divided state, which, to judge from its color, extinction angle and pleochroism, is amphibole, although it possesses no crystal form. More rarely there is some brownish substance resembling mica, but not in a well characterized form. Both of these are common contact minerals in limestones and have here undoubtedly been secondarily developed by heat.

The main points of evidence, therefore, that the serpentine at Syracuse was originally an igneous and intrusive rock, belonging to the family of peridotites, are as follows:

1st. The structure of the rock, which is such as is only known to be produced by crystallization from a molten magma.

2d. The existence of a more granular and a porphyritic modification, as is so often the case in eruptive dykes.

3d. The inclusion in the rock of fragments of the adjacent limestone and possibly of other rocks brought up from below.

4th. The indication that these limestone fragments have been modified by the action of heat.

5th. The fact, stated by Mr. Wilkinson, that 50 feet away from the exposure, on the strike of the rocks, only gypsum was encountered.

This evidence has been developed at such length, because aside from its bearing upon Dr. Hunt's theory of the origin of serpentine, this rock is interesting as being the only known instance of an igneous intrusion in the unaltered and undisturbed palæozoic strata of New York.

In conclusion it is worth while to notice the extremely close resemblance between the Syracuse rock and the peridotites of Carboniferous age which Mr. J. S. Diller of the U. S. Geological Survey, has recently described from Elliott Co., Ky.* These rocks are intrusive through Carboniferous strata and hence must be of as late origin as these, although they may be considerably younger. They contain fragments of the adjoining shale, which they have metamorphosed in a manner similar to that in which the dolomite inclusions have been changed by the Syracuse peridotite. Fragments of syenite and granulite were also found analogous to those granitic and syenitic aggregates mentioned by Vanuxem. In structure the two rocks present the closest possible similarity. The size and form of the large porphyritic olivine crystals appear to be identical in both; the groundmass of both also has the same appearance, containing

* "Science" for January 23, 1885, p. 65; this Journal, xxxii, p. 121, August 1886, and Bulletin of the U. S. Geological Survey, No. 38, the proof-sheets of which were kindly placed at the writer's disposal by Mr. Diller.

in each case, an abundance of opaque and transparent octahedral crystals. Nevertheless certain mineralogical differences are apparent. The pyrope with its alteration rim, described by Mr. Diller, is wanting in the Syracuse rock; ilmenite too, estimated to compose 2.2 per cent of the Kentucky peridotite, was not detected in the Syracuse occurrence. On the other hand, biotite and enstatite are much more important constituents in the latter than in the former. The little transparent crystals in the Kentucky peridotite are considered by Mr. Diller, as anatase (octahedrite) which has resulted from the alteration of the ilmenite. For reasons above stated, those in the Syracuse rock must, however, be regarded as perovskite, although their resemblance is so great as to suggest that they are the same mineral in both cases.

Petrographical Laboratory of Johns Hopkins University, Baltimore, April, 1887.