ART. LVII. — *A Study of the Cherts of Missouri;** by EDMUND OTIS HOVEY.

THE investigations herein reported were carried forward on material collected by the officers of the State Geological Survey of Missouri and kindly furnished me by Mr. Arthur Winslow, when State Geologist, together with a long list of references to the literature on the subjects of flint and chert. The chemical analyses which will be quoted were made, unless otherwise stated, at the office of the survey, by Mr. J. D. Robertson. Thirty-eight specimens from different parts of the State, and fifty thin sections made from them, were examined.

The material falls naturally into two groups according to geological age. About half of the specimens came from the Lower Magnesian Series† (Cambrian?), and the rest from the

* Read before the Geol. Soc. Am., August, 1894.

† The Missouri strata which have long gone by the name of the "Magnesian Limestone Series" have been designated the "Ozark Series" by Prof. G. C. Broadhead (Amer. Geol., vol. viii, 33, 1891) and the term has been adopted by the Missouri Geological Survey.

Lower Carboniferous. It is aside from the purpose of the writer to discuss the geologic relations of the cherts, but the Lower Magnesian cherts present some features which separate them more or less sharply, lithologically, from the Lower Carboniferous ones. The former contain few fossils or moulds of fossils, while the latter are usually crowded with stems and plates of crinoids and other fossils, or the cavities left by their removal, though occasionally a Lower Carboniferous chert is found which shows no indication of organic remains. In both groups the color varies very much from pure white to gray, while very many of the cherts are stained brown or black by iron, and one Lower Magnesian specimen is a decided pink. The texture, likewise, is very various, some specimens being very dense, aphanitic to the naked eye, and without fossils or cavities, while others are vesicular from the solution of pebbles or are full of cavities from the removal of fossils. There is great difference, also, in the state of preservation of the chert, much of it being almost perfectly fresh except for an outer shell of decomposition, while other has suffered alteration throughout its mass, as is shown in several Lower Magnesian specimens and in the heavy beds of "tripoli" in the Lower Carboniferous at Seneca and elsewhere.

Petrography.—These cherts consist almost entirely of chalcedony or silica in the chalcedonic state, but quartz and opal are present to some extent in some of the specimens. The slides are almost colorless and featureless under the microscope in ordinary light, but in polarized light the structure of the rock is very clearly indicated and is shown to be a very fine grained mosaic, mottled by reason of variation in fineness of grain. In several of the specimens from the Lower Magnesian series, notably one from Morgan County, the material is aggregated into small spherules. These are optically negative, which proves that they are made of chalcedony. Chalcedony has a higher index of double refraction than quartz, but the polarization colors in these sections rarely rise above gray of the first order, because the grains, whether in mosaic or in concentric spherule, are too small to give the thickness required for the higher colors. For photo-micrographs showing the mosaic and concretionary or oölitic structures of chert the reader is referred to Irving and Van Hise's treatise on "The Penokee Iron-Bearing Series of Michigan and Wisconsin," 10th Ann. Rep. U. S. G. S., 1890, Pt. 1, Pl. 24, fig. 2, and Pl. 28, fig. 2. The presence of opal silica is indicated in some of the slides by apparently amorphous areas, but possibly with more definiteness in other specimens by the solubility of a portion in KOH (caustic potash), though, as will be shown, even this is not a certain criterion. Quartz occurs in

the cherts as well terminated crystals of some size more or less completely filling cavities in the chalcedony, as drusy coatings to cavities, and as well rounded grains which may or may not form the nuclei of spherules. The crystallized quartz seems to be secondary to the chalcedony in its deposition, or to form the last phase in the aggregation of the cherts, the latter appearing to be the case where seams of coarsely granular chalcedony grade into lenses of finely granular or crystallized quartz. The strictly secondary quartz lines or fills cavities in the chert without having any apparent connection with the chalcedony. The rounded grains are evidently quartz sand which has been caught within the chalcedony as it was depositing or aggregating. From the frequent occurrence of inclusions in them they are probably granitic in their origin, and this view is strengthened by the rare presence of a grain showing the multiple twinning lamellæ of microcline. Dr. C. R. Keyes* describes cherts from the Lower Carboniferous (Burlington) of the northeastern part of the State which "upon exposure to the weather quickly slacken like quicklime to a fine, intensely white powder." This would indicate that the silica in them was amorphous, but specimens of this character were not sent the writer. Scattered through all the slides there are minute irregular scales and specks of a yellowish brown to black substance which may be referred to amorphous iron oxide (limonite) though some of them are more probably grains of magnetite. A noteworthy feature of most, if not all, of the thin sections, is a "dusty" appearance as seen in ordinary light. This dust disappears to a considerable extent when the light is cut off from the upper side of the section. The phenomenon may be due to clayey matter present in the rock. In view of the discovery by Professor H. A. Nicholson† and Dr. G. J. Hinde‡ of radiolaria in chert from the Lower Silurian (Ordovician) strata of Scotland, and by Professor W. J. Sollas§ and Dr. Hinde,‖ of sponge spicules in Carboniferous chert from Ireland, very careful search was made through these Missouri cherts for indications of anything of a similar nature. Nothing whatever of this kind was found, with the possible exception of some slender cylindrical rods in a specimen from the Lower Carboniferous at Webb City in Jasper County. The rods are noticeable in cavities in the rock, and the one which was measured was 2^{mm} long by $0{\cdot}12^{mm}$ in diameter, but it seemed to have been thickened by some

* This Journal, III, xliv, 451, 1892.
† Trans. Edinb. Geol. Soc., vol. vi, pt. 1, p. 56, 1890.
‡ Ann. and Mag. Nat. Hist., VI, vol. vi, p. 40, 1890.
§ Ann. and Mag. Nat. Hist., V, vol. vii, p. 141, 1881.
‖ Geol. Mag., N. S., Dec., III, vol. iv, p. 435, 1887.

extraneous deposit. What appear to be the cross-sections of these rods have nuclei of brown matter surrounded by clear chalcedony, but sometimes several exactly similar nuclei string themselves together within a common shell of chalcedony. Between crossed nicols there is no line of demarkation between these bodies and the matrix, all is granular chalcedony. I hesitate, therefore, to refer these rods to sponge spicules. Many of the Lower Carboniferous cherts are highly fossiliferous, being more or less crowded with the remains of crinoids, brachiopods and corals. These remains, however, are calcareous in nature and form a breccia with the chalcedony of the chert as the cement, though in the cherts described by Dr. Keyes* the fossils have been silicified. A specimen from this group at Grand Falls, Newton County, shows several sections of a branching form of *Stromatopora* and this genus also occurs in chert from Sulphur Springs, Arkansas. The chalcedony occasionally shows a tendency to form concretionary granules. In the specimen just cited there are true fibrous sphærocrystals which give a black cross in polarized light. The pronounced granular or oölitic character is confined to five of the Lower Magnesian specimens in the suite under discussion. In some of these the chalcedony has formed granules without any apparent foreign nucleus, while in others rounded grains of quartz were the nuclei of deposition. Siliceous oölite was noted by G. W. Featherstonhaugh† in Wayne County, Missouri (?), Tennessee and Kentucky and reported as "silicified oölite" of Carboniferous age, but his stratigraphy is not to be depended upon. Concretionary or granuliferous chert is one of the three divisions made by A. Renard‡ in his study of the Carboniferous cherts of Belgium. A preliminary microscopical and chemical investigation of siliceous oölite was made by E. H. Barbour and J. Torrey§ on specimens sent them from Center County, Pennsylvania. Since then the rock has been reported a second time from Tennessee‖ and it appears probable from an able discussion of the Pennsylvania oölite by Dr. W. Bergt,¶ which first came to the present writer's knowledge some months after his own article** on the same subject had been published, that several rocks from widely separated parts of the world and described under other names really belong in this category. Our specimens, therefore, add five localities for

* Loc. cit.

† Geol. Rept. of an examination of the elevated country between the Missouri and the Red Rivers, 1835, pp. 54, 55.

‡ Recherches lithologiques sur les phthanites du calcaire carbonifère de Belgique. Bull. de l'Acad. Roy. des Sciences, etc., de Belgique, II, xlvi, 1878, p. 494.

§ This Journal, III, xl, Sept. 1890, p. 246.

‖ G. R. Wieland in the Mineralogist's Monthly, vol. vi, Nov. 1890, p. 2.

¶ Abhandlung d. Isis in Dresden, 15, 1892.

** Bull. Geol. Soc. Am., vol. v, p. 627.

this interesting rock: Wright County, Camden County, Morgan County, Osage River, and Taney County, in Missouri. Mr. Winslow reports that the oölitic chert of the Missouri Lower Magnesian strata is of common occurrence and that frequently the beds are more than a foot thick. One of the Lower Magnesian localities furnishes a rock which is partly oölitic in structure and two others give rocks in which rounded grains of quartz have been cemented in an abundant matrix of chalcedony, without the formation of concretionary spherules about them. In one of the latter, however, the chalcedony shows that there was some tendency within it to form shells about the quartz grains, and an occasional small spherule of chalcedony may be seen in the matrix.

Chemistry.—As was to be expected from the microscopic characteristics, the cherts, when not fossiliferous, are almost pure silica. The analyses made by the Missouri Geological Survey show a much higher percentage of alumina and iron-oxide than is present in the cherts from the same strata and the same general region which were analyzed by the U. S. Geological Survey, but this difference is probably due to the fact that the specimens analyzed by the Missouri survey were selected more to illustrate the transitions between cherts and other rocks than to exemplify pure chert. Mr. Robertson reports that in making the analyses the $Al_2O_3+Fe_2O_3$ was redissolved after the first precipitation and precipitated again to make sure that no SiO_2 was included in the amount. The percentage of soluble silica was determined in only four of these analyses: Prof. Seamon, in his report on No. 11 for the Tripoli company, says that "7·28 per cent of the silica was soluble in a 10 per cent solution of caustic soda on boiling for three hours;" the U. S. Survey reported 4·52 per cent in No. 13, 3·99 per cent in No. 14 and 3 35 per cent in No. 18, and that the determination was made in the following manner: the solution used was made up of one part solid caustic potash to three parts water, and one gram of the finely powdered chert was heated in each case with fifty cubic centimeters of the solution for one hour on the water bath. No. 14 was somewhat porous, Nos. 13 and 18 were compact, the last showing occasional cavities filled with quartz crystals.* These percentages, however, cannot be taken as the measure of the amorphous silica present in these rocks, for undoubted quartz is noticeably soluble in caustic potash, Rammelsberg† finding from 5 to 7·75 per cent of vitreous massive quartz thus soluble, and quartz crystals and quartzite tested for the Arkansas Survey‡ gave from 2·59 to 6·28 per cent soluble in this medium.

* Ark. Geol. Surv., Ann. Rep., 1890, vol. iii, Novaculites, p. 161.
† Quoted in Dana's Syst. Mineralogy, 5th ed., p. 193.
‡ Op. cit, p. 164.

ANALYSES OF MISSOURI AND OTHER SIMILAR CHERTS.

Analyses of Missouri and other similar cherts.	1. Chert, Lebanon, La Clede Co., "decomposed."	2. Decomposed chert, Olden, Howell Co.	3. Chert, 72 ft. below surface, Roaring Spgs., Newton Co.	4. Chert, Henderson Mines, Barry Co.	5. Chert, Grand Falls, Newton Co., calcareous.	6. Calcareous chert, Sulphur Springs, Ark.	7. Calcareous chert, Aurora, Lawrence Co.	8. Ditto.	9. Decomposed chert, Webb City, Jasper County.	10. Decomposed chert, Joplin, Jasper Co.	11. Decomposed chert, ("tripoli") Seneca, Newton Co.	12. Ditto.	13 Chert, unaltered, Bellville, Jasper Co.	14. Chert, altered, Bellville, Jasper Co.	15. Ditto.	16. Chert, gray, unaltered, Joplin, Jasper County.	17. Chert, blue, unaltered, Galena, Kan.	18. Chert, white, altered, Galena, Kan.	
Silica (SiO_2)	96·88	89·45	94·91	98·33	63·67	71·29	91·25	88·92	97·03	96·14	98·100	98·28	98·17	98·71	98·92	99·46	99·23	99·13	SiO_2
Alumina (Al_2O_3)	2·48	0·94	2·85	2·18	2·20	2·43	1·28	1·25	2·32	1·44	0·240	0·17	0·83	0·43	0·48	0·29	0·22	0·16	Al_2O_3
Iron oxide (Fe_2O_3)											0·270	0·53							Fe_2O_3
Carb. lime ($CaCO_3$)	1·11	9·44	0·75	--	33·12	26·24	6·56	10·02	1·10	2·16									$CaCO_3$
" magnesia ($MgCO_3$)	*tr.*	0	*tr.*	--	0·57	*tr.*	0·17	*tr.*	*tr.*	*tr.*									$MgCO_3$
Lime (CaO)											0·184	*tr.*	0·05	0·03	0·03	0·04	0·02	*tr.*	CaO
Magnesia (MgO)												*tr.*	0·01	0·02	0·02	*tr.*	*tr.*	0·01	MgO
Potassa (K_2O)												0·17							K_2O
Soda (Na_2O)											0·230	0·27							Na_2O
Water (Ignition)											1·160	0·50	0·78	0·50	0·42	0·34	0·50	0·20	Ign.
Organic matter											0·008								Org.
Totals	100·47	99·83	98·51	100·51	99·56	99·96	99·26	100·19	100 45	99·74	100·192	99·92	99·84	99·69	99·87	100·13	99·97	99·50	Totals.

Notes on the analyses.—Nos. 1 and 2 were from the Lower Magnesian strata; Nos. 3 to 18, from the Lower Carboniferous. Nos. 1 to 10 were made at the laboratory of the Missouri Geological Survey by Mr. J. D. Robertson; No. 11, at the Mo. School of Mines, Rolla, by Prof. W. H. Seamon, for the American Tripoli Co., of Seneca, Mo.; No. 12, by the Arkansas Geol. Survey, and it is quoted from their Annual Report for 1890, vol. iii, p. 397; Nos. 13 to 18, by the U. S. Geological Survey, and they are quoted from the same volume of the Arkansas reports, p. 161.

The amounts given above for the Missouri cherts are below these maxima and, therefore, do not necessarily indicate the presence of opal (amorphous) silica, since chalcedony is held to have the same chemical characteristics as quartz. When a large percentage of the silica is soluble in caustic potash the presence of opal silica is indicated; e. g., the Arkansas Survey chemist found 30·72 per cent of a Silurian chert, 35·56 per cent of a Tertiary chert and 88·38 per cent of a geodized coral from Tampa, Florida, to be thus soluble. These geodized corals are known to be opal and the two cherts must contain large amounts of amorphous silica. Edward T. Hardman* analyzed a series of twelve specimens of chert from the Upper Carboniferous strata of Ireland. He tested the rocks in hydrochloric acid and found traces of soluble silica in several and 1 per cent, 1 22 per cent and 1·5 per cent in three cases. All the Cretaceous chalk flints contain much opal silica and show high percentages of silica soluble in caustic potash.†

It will be seen from the table that the chemical difference between "altered" and "unaltered" chert is so very slight that they can be distinguished only by physical characteristics. The most completely altered chert is that from Seneca, which is minutely porous, breaks to pieces readily between the fingers and may be ground to an impalpable powder in an ordinary mill. There is an extensive bed 18 ft. thick of this material at this locality and it is quarried for the manufacture of filtering disks and tubes and of a high grade of polishing powder. A similar rock occurs near Seneca in the Indian Territory, at Dayton, Newton Co., Mo., and in township 4 S., 26 W. in central Arkansas.‡ The Arkansas rock disintegrates to a fine powder on exposure to the atmosphere, but the Seneca rock does not. Another item of interest in the analyses is the very low percentage of water (by ignition) which was found, especially in the pure cherts, whether altered or unaltered. This would argue against the presence of more than a very small amount of opaline silica. Mr. Hardman's analyses of the Irish Carboniferous cherts brought out the same fact regarding the presence of water.

Origin of the chert.—There has been much speculation as to the origin of flint, hornstone and chert. The Cretaceous flints of the chalk formation in England and elsewhere contain so many remains of originally siliceous animal organisms (skeletons of siliceous sponges and polycystines) that some authors claim that all their substance has come from this source,

* Sci. Trans. Roy. Dub. Soc., I, vol. i, pp. 85, 1878.
† Vid. Geology, J. Prestwich, vol. ii, pp. 321 and 322.
‡ Ark. Geol. Surv., Ann. Rep., 1890, vol. iii, p. 384.

while others contend that the silica of the flints is entirely due to chemical precipitation. Other theories lie between these extremes. A concise summary of the various theories which have been proposed to account for the flints is given by Prof. Prestwich,* who gives as his own opinion the theory that silica in the colloid or soluble state was present as a chemical precipitate in the mud of the Chalk seas and that this colloid silica, having a strong affinity for other forms of silica, gelatinous substances (like the sarcode of sponges) and other foreign bodies, aggregated about sponge spicules, replacing the sarcode as that decayed, and about the tests of echinoderms and the shells of molluscs. The irregular masses thus produced continued to grow as long as there was any colloid silica within the range of attraction.

The Corniferous hornstone partakes so largely of the characteristics of the Chalk flints that it probably had its origin in the same way.†

The Upper Carboniferous cherts of Ireland were studied by Messrs. Hull and Hardman,‡ who came to the conclusion that the chert was "essentially a pseudomorphic rock consisting of gelatinous silica replacing limestone of organic origin chiefly foraminiferal, crinoidal and coralline," the silica being a chemical precipitate from the sea water of the period. M. A. Renard§ came to a similar conclusion for the cherts of Carboniferous age in Belgium. This view has been vigorously combatted by Dr. Geo. J. Hinde,‖ who, starting from the discovery made by Prof. Sollas that there were sponge spicules in the Irish cherts, had numerous thin sections of the rocks made for himself. From the study of these Dr. Hinde decided that the cherts were wholly organic in origin and that they were due to the aggregation and disintegration of the skeletons of siliceous sponges.

Pre-Cambrian cherts have been studied by Irving and Van Hise¶ in their work on the Penokee iron-bearing series of Michigan and Wisconsin. This series belongs to the Huronian subdivision of the Algonkian system and two of its four members contain much chert. The author's conclusion regarding the origin of the chert is, "First, that the chert was mainly deposited simultaneously with the iron carbonate with which it was so closely associated; and, second, that it is probable that the chert is of organic origin, although we have no posi-

* Op. cit., pp. 320–324. Vid. also, Ark. rep't cit., pp. 177–187, where an extended summary of theories is given.

† Cf. Manual of Geology, J. D. Dana, 3d edition, 1880, p. 257.

‡ Sci. Trans. Roy. Dub. Soc., II, vol. I, pp. 71 and 85, 1878.

§ Op. cit.

‖ Geol. Mag., N. S., Dec., III, vol. iv, p. 435, 1887.

¶ Tenth Ann. Rep. U. S. G. S., p. 347.

tive proof that it is not an original chemical sediment, while it may in part be from both sources." This statement is made to apply with equal force to the other chert-bearing member of the series.*

Regarding the Lower Magnesian and Lower Carboniferous cherts from southern and southwestern Missouri, the present writer's conclusion is, that they are due to chemical precipitation, probably at the time of the deposition of the strata in which they occur or before their consolidation.

Am. Mus. Nat. Hist., N. Y. City, July, 1894.