NOTES ON CATLINITE AND THE SIOUX QUARTZITE

Ernest L. Berg, *University of Minnesota, Minneapolis, Minnesota.*

Introduction

The Sioux quartzite, where it outcrops at Pipestone, Minnesota, contains a thin bed of red, metamorphosed shale of peculiar properties. The shale is soft and easily carved. It is commonly referred to as "pipestone" since it was formerly used by the Indians of that region in the manufacture of pipes.

The pipestone quarry was visited by white men as early as 1836 when George Catlin journeyed all the way from New York for the purpose of seeing the renowned quarry.[1] He noted[2] that

> the Indians procure the red stone for their pipes by digging through the soil and several slaty layers of the red stone to the depth of four or five feet. From the very numerous marks of ancient and modern digging, or excavations, it would appear that this place has been, for many centuries, resorted to for the red stone, and from the great number of graves and remains of ancient fortifications in the vicinity (as well as from their actual traditions) it would seem that the Indian tribes have long held this place in high superstitious estimation, and also that it has been the resort of different tribes, who have made their regular pilgrimages here to renew their pipes.

Catlin collected a sample of the red pipestone and sent it to Professor C. T. Jackson of Boston who made a chemical analysis and reported that it was not steatite but a new substance somewhat similar to agalmatolite, a stone used by the Chinese in carving. He named the pipestone *catlinite*[3] in honor of Mr. Catlin.

At this early date the Pipestone, Minnesota, quarry was the only known source of the red pipestone. Since that time, however, several reputedly similar beds have been reported in Algonkian quartzites near Devil's Lake,[4] Wisconsin; Rice Lake,[5] Wisconsin; Sioux Falls,[6] South Dakota; and elsewhere.

Of late years catlinite has not been recognized as a separate species, but has been variously classified as a silicified shale or as an indurated

[1] Winchell, N. H., Geology of Minnesota, vol. 1 of the Final Report: The Geology and Natural History Survey of Minnesota, p. 63, **1884.**

[2] Catlin, George, *Am. Jour. Sci.*, vol. **38,** p. 138.

[3] Jackson, C. T., Catlinite or Indian pipestone: *Am. Jour. Sci.*, First Series, vol. **35,** p. 388, 1839.

[4] Woodman, E. E., The pipestone of Devil's Lake, Wisconsin: *Wis. Acad. Sci. Trans.*, vol. **5,** pp. 251–254, 1882.

[5] Hotchkiss, W. O., Mineral Land Classification: Wisconsin Geology and Natural History Survey, pp. 37–38, **1915.**

[6] Winchell, N. H., *op. cit.*, p. 542.

clay. There is, however, no published study relating to the mineralogy and petrography of the catlinite bed. Its historical importance and the peculiar properties of the stone itself seem to warrant such a study. For this reason the writer visited the outcrop during the last summer and collected samples of the catlinite bed and the overlying quartzites for laboratory study.

Field Relations

The pipestone quarry lies about one half mile north of Pipestone, Minnesota, in the southwestern part of the state. The region is mostly overlain by glacial drift but a ridge of quartzite, a mile or more in length, rises out of the prairie at the quarry site. The ridge presents a west-facing escarpment 25 to 30 feet high (see Fig. 1). A modern rock quarry which started at the face of the escarpment has been worked back into the ridge. The quarry walls offer a fresh vertical section for study. The Indian quarry lies 700 to 800 feet west of the rock quarry (Fig. 1). It consists of a long north-south trench at the bottom of which is found the catlinite bed. Quarrying of the catlinite is accomplished by stripping the overlying quartzite from the eastern wall of the trench and throwing it back onto the quarry refuse heap. Between the modern rock quarry and

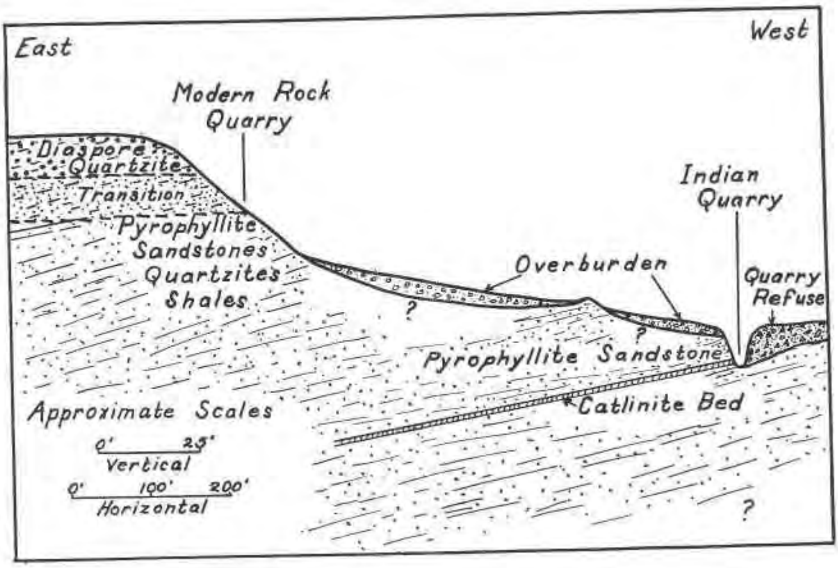


Fig. 1. Generalized cross-section through the Sioux quartzite at Pipestone, Minn. The quartzite at the top is cemented with diaspore. Below that, the cement is of diaspore and pyrophyllite (the transition zone). The lower portion of the outcrop is cemented with pyrophyllite. Quartz is an auxiliary cement throughout. See figures 2, 3 and 4.

the Indian quarry the quartzite is covered with glacial drift and slope wash, except for a distance of several feet where a quartzite bed outcrops.

The formation at this locality dips east at an angle of approximately 15°. Vertical joints are numerous and well developed. They belong to two main systems crossing each other at nearly right angles and striking N.E.–S.W. and N.W.–S.E.

Colors of the formation are variable, being predominantly shades of red and purple, but some of the thinner beds are nearly white. Along the joint planes the darker colored beds have often been bleached to a yellow or white color. So variable are the colors that in some instances it is impossible to trace an individual bed for more than a few feet horizontally.

The texture, excluding the fine-grained catlinite bed, varies from coarse sand to sandy shale. In the modern rock quarry the higher beds are the coarser while at lower horizons sandy shales are prevalent. Cross-bedding and ripple-marks may be seen in the sandy beds but they are not evident in the more shaly horizons. The sandy beds are of a somewhat uniform reddish purple color but greater variation occurs in the color of the shaly beds. All the beds are well cemented.

Samples were taken in the Indian quarry (a 6 foot section) and in the rock quarry (a 35 foot section). The vertical interval between samples was not uniform but averaged about 2 or 3 feet. The samples were numbered according to their relative stratigraphic position.

The Catlinite Bed

The catlinite bed is from 15 to 18 inches thick. It is massive but has partings parallel to the bedding which permit the stone to be broken into slabs 1 to 4 inches thick. No slaty cleavage is present. The pipestone is of a prevailing blood-red color but some of it has been replaced by a white or yellow-white mineral. The present study indicates that the catlinite, or red pipestone, is composed predominantly of sericite and that the light colored replacing mineral is pyrophyllite.

Pyrophyllite has replaced the top and bottom of the catlinite bed to a depth of 1 inch. Replacement has also taken place along the partings parallel to the bedding (see Fig. 6). Numerous lenses of pyrophyllite are found in the massive catlinite. These lie generally with their long axes parallel to the bedding. The lenses vary up to 4 inches in length. Pyrophyllite specks are scattered throughout the body of the catlinite and it would be difficult, on a polished surface, to find as much as a square inch of the red pipestone which did not contain these specks.

Minerals visible microscopically in the catlinite bed are sericite, pyrophyllite, diaspore, hematite (red), specularite and pyrite. Rutile is suspected because of the titanium present (see chemical analysis), but it is probably indistinguishable from the hematite dust. The bulk of the diaspore (see Fig. 7) is found in the pyrophyllite replacements. The same is true of all the specularite and pyrite. Nearly all of the red hematite, a few grains of diaspore and the rutile (?) are found in the sericite.

The sericite was identified by *x*-ray and chemical methods. In thin section the red pipestone is seen to be composed of exceedingly fine grains with no definite orientation. These are too small to permit identification by optical methods. An *x*-ray diffraction pattern identified the bulk of the material as sericite since it showed only sericite (muscovite) lines.[7] Previous chemical analyses[8] of the red pipestone (all older than 1880) showed no potash, however, and this could not be reconciled with the *x*-ray determination. Therefore a new and more complete analysis was made. The specimen selected for the chemical analysis was blood red in color and nearly free from pyrophyllite specks. The analysis is given in Table 1. (Dr. R. B. Ellestad, analyst, Laboratory for Rock Analysis, University of Minnesota.)

TABLE 1

SiO_2	49.01	H_2O+	5.63
Al_2O_3	35.17	H_2O-	.24
Fe_2O_3	3.06	TiO_2	.44
FeO	none	Li_2O	.16
MgO	.23	Ignition, less total	
CaO	.05	H_2O	.24
Na_2O	.06		
K_2O	5.62		99.91

The chemical analysis supports the *x*-ray data in showing that the bulk of the material is sericite. If we assume that nearly all of it is sericite, the composition would be approximately $R_2O \cdot 5Al_2O_3 \cdot 12SiO_2 \cdot 5\ H_2O$. Although the potash content is lower than that of most muscovites, several secondary micas or sericites with about these molecular ratios have been reported.[9]

A microscopic study of the analyzed catlinite showed the presence of hematite, rutile (?), diaspore and pyrophyllite. A small amount of quartz is conceivably present but it has not been identified. The above minerals

[7] The writer is indebted to Dr. J. W. Gruner for the *x*-ray diffraction patterns and their interpretation.

[8] Winchell, N. H., *op. cit.*, p. 542, **1884.**

[9] Sericite from Carroll Driscoll Mine, Idaho. Shannon, E. V., *Bull.* **131,** *U. S. Nat. Mus.*, p. 367, 1926.

Secondary mica, Etta Mine, S. Dakota. Schwartz, G. M., and Leonnard, R. J.: *Am. Jour. Sci.*, vol. **11,** p. 262, 1926.

Sericite associated with pyrophyllite. Standard Mineral Co. Mine, N. Carolina. Stuckey, J. L., analyst: *Econ. Geol.*, vol. **20,** p. 457, 1925.

may make up as much as 10 per cent of the red stone, but if they were present in much larger amounts the diaspore would have increased the water content and the pyrophyllite and quartz (?) would have increased the silica content of the rock to figures larger than those given in the above chemical analysis.

The hematite, and probably the rutile, occur in the red pipestone as exceedingly fine grains or dust. While a thin section of catlinite is gray to tan in color, a section slightly thicker is dark red and nearly opaque because of the numerous hematite inclusions. Near the pyrophyllite replacements some of the catlinite is banded (see Fig. 6). This is undoubtedly due to the leaching of the hematite. The diaspore is present in small blades, up to .2 mm. in length, resembling those shown in figure 7 but not nearly as abundant as there shown. The pyrophyllite specks in the red pipestone may be seen in the dark band in figure 6.

The pyrophyllite was identified by *x*-ray and optical methods. The indices of refraction are: $\alpha=1.553$, $\beta=1.587$, $\gamma=1.598$; all $\pm.003$. The replacements consist of a number of small grains oriented in all directions. Because of its high birefringence these differently oriented pyrophyllite grains are outlined even in plain light (Fig. 7). In most instances the pyrophyllite replacements are light in color and are composed of pyrophyllite with a few diaspore grains. All of the lenses described above, and a few of the bedding plane replacements, are however of a dark reddish-purple color. This color is due to the large amounts of red diaspore and specularite which are present. A small amount of pyrite in little striated crystals accompanies the diaspore and specularite. The specularite crystals measure up to .25 mm. in size and are easily seen in the hand specimen because of the brilliant reflection from their crystal faces. The specularite is probably due to recrystallization of the red hematite present in the catlinite. Had there been ferrous iron in the catlinite it is possible that magnetite would have formed.

The specific gravity of a specimen of catlinite is 2.746 while that of pyrophyllite is 2.754, as determined by heavy liquids and the Westphal balance. Both the catlinite and the pyrophyllite appear to have little pore space so that the correct densities are probably not far above those given.

The catlinite has a hardness which is somewhat variable but averages about 2.5. The pyrophyllite is approximately 2.0 in hardness. It is commonly believed that catlinite is soft when quarried and hardens upon being dried. A foot or so of water is usually present on the bottom of the Indian quarry so that the lower portion of the catlinite bed is immersed. Visitors to the quarry frequently encounter difficulty in attempting to secure pipestone that lies under the water. The writer was unable to find any difference in hardness between the wet pipestone at the bottom of the quarry and the slabs which had been thrown back on the refuse heap. Samples taken from the bottom of the quarry showed no appreciable difference in hardness six months later. To test the hardness further a piece was sawed in two, one half was saved for comparison and the other half was placed in an oven. After heating 100 hours at 200°C. there was no discernible difference in hardness between the two pieces. The analyzed sample, which showed 0.24 per cent of absorbed water, had been dried three months at room temperature.

Quartzite Beds

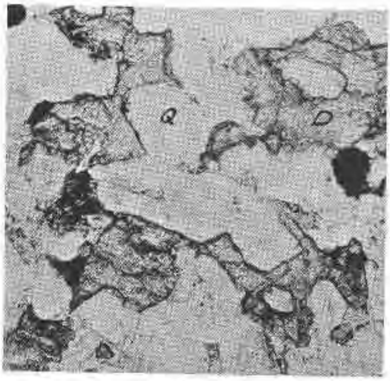
The quartzite beds which overlie the catlinite at Pipestone may be divided into three types on the basis of the cementing material: first, those which are cemented by diaspore and quartz; second, those cemented by diaspore, pyrophyllite and quartz; third, those cemented by pyrophyllite and quartz.

The diaspore quartzites (Figs. 1 and 2) have been described by the writer in a previous paper.[10] They do not extend deeper than 5 or 6 feet from the surface at this locality. At their lower surface they give way to the diaspore-pyrophyllite quartzites in which grains of diaspore appear to be developing in a groundmass of pyrophyllite (Fig. 3). This is the transition zone of figure 1 and is almost 10 feet in thickness. Below this zone there is no diaspore, except that in the catlinite bed. Figures 1, 4, and 5 illustrate the relations of the beds below the diaspore. The quartzite beds immediately below the impervious catlinite layer are pyrophyllitized in the same manner as those immediately above.

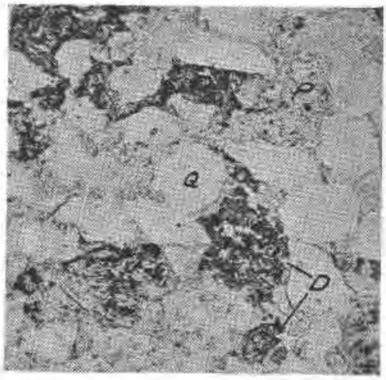
Eighteen thin sections of the various types of quartzite were examined. Two were from the diaspore facies, four from the diaspore-pyrophyllite facies and twelve from the pyrophyllite beds. In addition, several samples from the pyrophyllite zones were crushed and subjected to a bromoform separation. The heavy minerals in each case were iron oxides and zircon. No diaspore was observed. The thin sections showed the presence of quartz, chalcedony, pyrophyllite, diaspore, iron oxides, rutile and zircon in the quartzite beds.

The pyrophyllite in the quartzite beds was identified optically, but as a check several samples of both the red and white varieties of quartzite were crushed, and screened to remove the coarse grains of quartz. The fine grained fraction was *x*-rayed and was found to contain pyrophyllite and quartz.

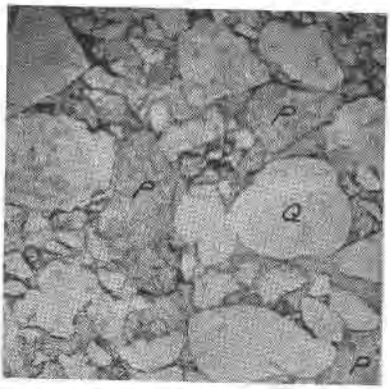
[10] Berg, Ernest L., An occurrence of diaspore in quartzite: *Am. Mineral.*, vol. **22**, pp. 997–999, 1937.



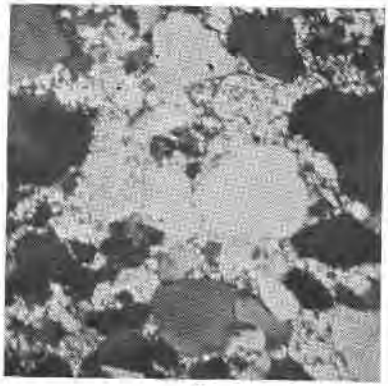
2



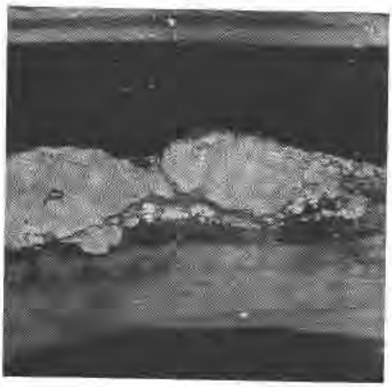
3



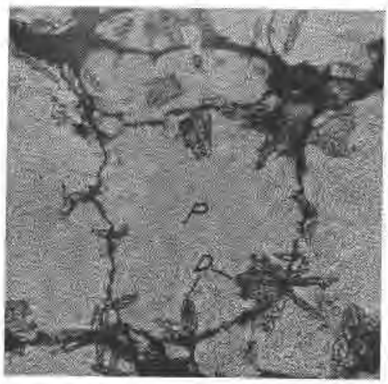
4



5



6



7

PHOTOMICROGRAPHS OF THIN SECTIONS.

FIG. 2. (Upper left) Quartzite cemented by diaspore (D). Plain light (×30)

3. (Upper right) Quartzite cemented by pyrophyllite (P) in which diaspore is beginning to form. Plain light (×30)

4. (Middle left) Quartzite cemented by pyrophyllite. Note the grains of pyrophyllite which are apparently replacements of other minerals. Plain light (×30)

5. (Middle right) Same as figure 4. Crossed Nicols (×30)

6. (Lower left) Pyrophyllite replacement parallel to the bedding of the pipestone. Plain light (×5)

7. (Lower right) Pyrophyllite replacement in pipestone containing minute seams (iron-stained) along which diaspore crystals have formed. Plain light (×60)

In most of the sandy shale horizons the individual quartz grains are completely surrounded by pyrophyllite. Some of the grains are partially or wholly replaced by this mineral. A thin section of the quartzite which immediately overlies the catlinite bed shows that almost all of the quartz grains within half an inch of the catlinite bed have been replaced by pyrophyllite. The identity of the replaced mineral can be determined because a few of the grains have not been entirely replaced. These show a small remnant of quartz. Furthermore, one would not expect to find many grains of a mineral other than quartz in a sandstone. Figures 4 and 5 show several replaced grains in a bed several feet above the catlinite. In this material no remnants of the original material can be observed. It may have been feldspar, quartz or still some other mineral.

All of the thin sections showed that the quartzite formation is well cemented at this locality. Not all of the rocks are quartzites, however, since those cemented by pyrophyllite are too soft to be so classified. Also, some beds are too fine textured to be called quartzite, but the term quartzite may be used to distinguish the rest of the formation from the catlinite bed.

Certainly the most striking feature of the quartzite beds is the relation of the diaspore to the present surface. At the bottom of the section the beds are cemented with pyrophyllite but, as one approaches the surface, small grains of diaspore appear and finally at the surface the pyrophyllite gives way entirely to diaspore.

Probable History of Deposits

Summarizing the foregoing statements it is seen that the Sioux quartzite at this locality is a clastic sedimentary deposit of Algonkian age varying in texture from coarse sand to very fine shale. The formation has been subjected to static metamorphism but not to intense dynamic action since the catlinite bed shows no slaty cleavage and there is no parallelism of grain.

At some time during the consolidation or metamorphism of the formation, the sericite which makes up the bulk of the catlinite, was formed from the minerals of the original shale. Large amounts of sericite are not unusual in metamorphosed shales.[11] Dale[12] has shown that the red slates of Vermont, New York and elsewhere are largely composed of sericite and quartz. He quotes Hutchins[13] as follows:

> . . . the fine mixture of biotite, muscovite, kaolin, the minutest waste of feldspar, and in less degree of quartz . . . under the joint action of pressure, warmth, and mineral solutions, gives rise to various decompositions and recombinations which result, among other things, in the formation of new mica.

However, the absence of quartz in discernible amounts is noteworthy. If the original shale contained only moderate amounts of quartz it might have been consumed in the formation of the sericite, or it might have been removed in solution, or entered into the composition of pyrophyllite when that mineral replaced portions of the sericite. It is possible, of course, that the catlinite was originally a volcanic ash or bentonite bed containing little or no quartz. Twenhofel reports three bentonites which contain only from 3 to 7 per cent of quartz.[14] Wherry[15] reports a deposit which shows no quartz. But analyses[16] of these bentonites show that they are low in alumina and potash, and high in lime and magnesia.

Subsequent to the formation of the sericite, which makes up the catlinite bed, replacement by pyrophyllite began. Very likely the replacement of the quartzite beds took place at the same time. The pyrophyllitization of the quartzite beds implies that they were originally somewhat arkosic and argillaceous. Potash feldspar, kaolin and sericite are commonly present in arkoses and shaly sediments. These minerals are known to yield pyrophyllite under hydrothermal conditions both in the laboratory and in the field.

Buddington[17] suggests the following reaction for the alteration of sericite to pyrophyllite:

$$\underset{\text{(sericite)}}{2KH_2Al_3Si_3O_{12}}+6SiO_2+H_2O \rightleftarrows \underset{\text{(pyrophyllite)}}{6HAlSi_2O_6}+K_2SiO_3$$

It was suggested above that any quartz originally in the catlinite

[11] Van Hise, C. R., A treatise on metamorphism: *U. S. Geol. Survey, Monograph* **47,** 1904.

[12] Dale, T. Nelson, Slate deposits and slate industry of the United States: *U. S. Geol Survey, Bull.* **275,** 1906.

[13] Hutchins, W. M., Clays, shales and slates: *Geol. Mag.*, vol. **7,** p. 317.

[14] Twenhofel, W. H., *Treatise on sedimentation: Second Edition*, p. 270, **1932.**

[15] Wherry, E. T., Clay derived from volcanic dust in the Pierre of S. Dakota: *Jour. Wash. Acad. Sci.*, vol. **7,** pp. 576–583, 1917.

[16] Twenhofel, W. H., *op. cit.*, p. 268.

[17] Buddington, A. F., Pyrophyllitization, pinitization, and silicification of rocks around Conception Bay, Newfoundland: *Jour. Geol.*, vol. **24,** p. 147, 1916.

might possibly have gone into the formation of pyrophyllite according to Buddington's equation. The numerous specks of pyrophyllite found throughout the catlinite could then be interpreted as replacements of quartz. At any rate the equation shows that silica and water must have been added to the sericite, and potassium silicate removed.

Since the formation of pyrophyllite is usually attributed to hydrothermal alteration,[18] and since specularite is commonly thought of as a high temperature mineral,[19] the presence of these minerals implies at least some thermal metamorphism in the rocks of the Pipestone region. There are no known intrusives in the vicinity that are younger than the quartzite. There is, however, some evidence that pyrophyllitization is not limited to the Pipestone area. At New Ulm, Minnesota, 100 miles to the east, pyrophyllite and diaspore are present in the Sioux quartzite. Diaspore, which is associated with the pyrophyllite at Pipestone, is found widely distributed in surface samples of the Sioux quartzite.[20] Pyrophyllitization may, then, be general throughout the formation. Statements as to the temperatures and types of metamorphism should be postponed until more is known of other portions of the formation.

The occurrence of diaspore near the surface strongly *suggests* that pyrophyllite may be unstable under certain environmental conditions, breaking down into diaspore and quartz according to the reaction:

$$\underset{\text{(pyrophyllite)}}{H_2Al_2Si_4O_{12}} \rightarrow \underset{\text{(diaspore)}}{Al_2O_3 \cdot H_2O} + \underset{\text{(quartz)}}{4SiO_2}$$

The silica need not be removed but could be deposited as a secondary growth on the original quartz grains. It must be remembered, however, that diaspore is present in the catlinite bed. Here, too, it is associated chiefly with pyrophyllite and appears to have formed along minute seams (Fig. 7). Nevertheless the catlinite layer is somewhat removed from the surface so that the relation of the diaspore in the catlinite bed to the diaspore in the quartzite is not clear.

Summary and Conclusions

1. The Sioux quartzite at Pipestone, Minnesota, was originally an arkosic sandstone with interbedded argillaceous strata, some of which were very fine grained. The catlinite bed represents the finest of these argillaceous layers.

[18] Buddington, A. F., *op. cit.*
Stuckey, J. L., *Econ. Geol.*, vol. **20**, p. 457, 1925.
Vhay, J. S., (abstract) *Am. Mineral.*, vol. **22**, no. 12, part 2, p. 15, 1937.

[19] Rogers, A. F., Origin of copper ores of the "red bed" type: *Econ. Geol.*, vol. **11**, p. 378, 1916.

[20] Berg, Ernest L., *op. cit.*

2. During consolidation or metamorphism most of the catlinite bed was converted into secondary mica (sericite) and small amounts of free quartz.

3. The catlinite shows neither secondary cleavage nor any evidence of recrystallization under dynamic metamorphism. Metamorphic agencies, probably hydrothermal, produced pyrophyllitization of the quartzite beds and portions of the catlinite bed. Pyrophyllite probably replaced most of the quartz originally present in the catlinite. Specularite was developed locally in the pyrophyllitized pipestone.

4. Near the surface of the outcrop and in the catlinite bed, exposed in the quarry, the pyrophyllite *appears* to have broken down yielding diaspore and quartz.

Acknowledgments

The writer is indebted to Dr. J. W. Gruner for *x*-ray identification of several minerals. Dr. R. B. Ellestad and Mr. Lynn Gardiner gave invaluable assistance in the preparation of this paper.