

ART. XIX.—*Purpurite, a new Mineral*;* by L. C. GRATON
and W. T. SCHALLER.*Introduction.*

IN the central portion of the Carolinas there occurs a belt of metamorphic rocks penetrated by narrow dikes of pegmatite, many of which contain lithium minerals. There can be little question but that the dikes of pegmatite represent the final product of a parent magma which has crystallized as granite and appears almost continuously along the extent of this belt.

Attention was first directed to these pegmatites by the discovery of cassiterite in them. In the autumn of 1904, one of the writers made an examination of these tin deposits for the U. S. Geological Survey. During the course of this study, Mr. J. L. Daniels, superintendent of the Faires tin mine at Kings Mountain, Gaston County, N. C., called attention to a purplish material encountered within a few feet of the surface in the workings of that mine. Thanks are due to Mr. Daniels, who kindly supplied much of the material obtained. Preliminary examination failed to identify the material with any known mineral, although its properties seemed to be those of a definite crystalline compound. Chemical analysis shows that the material is a new mineral, being a hydrous manganic ferric phosphate—the only manganic phosphate known.

The most striking feature of this mineral is its purple or dark reddish color, and for this reason it has been named *purpurite*, from the Latin *purpura*, purple or dark red.

Since the discovery of this mineral in North Carolina, the same mineral has been noticed on some specimens from San Diego County, California. These had been collected by one of the writers, and through the courtesy of Mr. F. M. Sickler, of Pala, several more specimens from this locality have been obtained. They are from one of the lithium-bearing pegmatite dikes on Hiriart Hill, Pala, San Diego County. The mineral occurs with triphylite, and possesses the same purple color as the North Carolina specimens. Under the microscope, the appearance and properties of the mineral from the two localities are identical. There is, however, not enough of the California material for chemical examination.

Occurrence and Physical Properties; by L. C. GRATON.

The mineral purpurite is found in small irregular masses in the tin-bearing pegmatite dikes, and in the near-by schist at the Faires mine. In most cases it occurs in narrow lenses or

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veinlets, and appears to have been deposited from solution in cavities. Occasionally, however, it is found in the midst of the pegmatite as if it were an original mineral.

The question of the origin of purpurite is one of interest. Pegmatite dikes believed to be closely related to the tin-bearing dikes carry the rare-earth phosphate, monazite. Among the primary minerals of the tin-bearing pegmatites are cassiterite, tourmaline, apatite, spodumene, lepidolite, and a yellowish brown, lithia-bearing phosphate which is doubtless lithiophilite. The last two minerals have been found only in small quantities. Partially decomposed specimens of this pegmatite frequently show much manganese dioxide as thin mammillary coating on the other minerals. Ilmenite is often included in crystals of cassiterite. It is evident, therefore, that the elements manganese and iron (as monoxides), lithium, and phosphorus (as phosphate) were primary components of the pegmatite magma.

The mineral presumed to be lithiophilite is always surrounded by a coating of black, secondary material. In one case, a narrow zone of purpurite was found between the lithiophilite and the black mineral. It is believed that this single occurrence furnishes the explanation of the origin of purpurite. A lithia-manganous-ferrous phosphate, probably lithiophilite, was attacked by oxidizing solutions. The lithia was almost wholly carried away, while of the remaining elements, iron and manganese were oxidized to the state of sesquioxides and were recrystallized with the phosphoric acid and water to form purpurite. The trace of lithium which this mineral contains is a remnant of that from the lithiophilite. In some cases the recrystallization took place without transportation of the materials, forming pseudomorphous replacements, but in general the materials were carried in solution to cavities and there deposited.

Purpurite is probably orthorhombic, but no specimens have been found which show crystal outline. A cleavage which is probably pinacoidal is of rather perfect development, but the cleavage surfaces are often curved as if the orientation of adjoining grains were not exactly the same. A second cleavage, presumably at right angles, is considerably less distinct. The mineral has an uneven fracture and is rather brittle. It is scratched without difficulty by the knife, but on the other hand just scratches fluorite, and hence has a hardness of 4-4.5. Mr. Schaller determined the specific gravity as approximately 3.15. In color the mineral is a rich deep red or reddish purple, sometimes with a slight bronzy iridescence, and not uncommonly darker on the cleavage planes. The powder and the streak have a decided purple or deep rose color. The mineral has a peculiar satiny luster or sheen, more noticeable on fracture surfaces than on cleavage planes.

Although transparent in very thin pieces, the ordinary thin section allows the passage of very little light through purpurite. The colors in transmitted light are very beautiful. Pleochroism is noticeable. Parallel to the cleavage the color is a deep scarlet, inclining to rose-red, while across the cleavage the absorption is greater and the color becomes a beautiful purple. This absorption, it will be noticed, is similar to that of tourmaline and a few other minerals, in which the greatest absorption is at right angles to the direction of cleavage or elongation. Extinction is generally parallel; an inclination up to three or four degrees, which has been observed in a few instances, has probably been due to the orientation of the sections examined. It may be, however, that the mineral is monoclinic, with a very small extinction angle. Sections which were transparent were not of sufficient size to give an interference figure. No sections showing the intersecting cleavages were seen, and in all the sections examined the traces of the cleavages are parallel to the direction of greater elasticity of the section; so if the mineral is biaxial, the intersection of the cleavages is parallel to *a*. This is also the direction of least absorption. The refractive index is somewhat greater than that of Canada balsam and probably lies between 1.60 and 1.65. The difference of the indices or the double refraction is high, and although it could not be measured at all accurately, is probably not much below .060. One effect of this high double refraction on the very thin sections examined is that under crossed nicols the mineral appears to transmit as much and as brilliant light as without polarization. The red interference colors are very striking.

The purple mineral is always covered or surrounded by a greater or less thickness of a black or brownish black material of pitchy luster and uneven or sub-conchoidal fracture. This material, which is soluble in hydrochloric acid, has been found by Mr. Schaller to contain iron, manganese, phosphoric acid, and water. Under a lens the black material can be seen to encroach upon the purpurite, eating in along the cleavage planes and gradually replacing the purple mineral. It is undoubtedly a decomposition product of purpurite and is certainly the same as that which surrounds the supposed lithiophilite. Viewed with the aid of the microscope it appears to be a definite mineral, having an imperfect cleavage, and a brownish yellow color in transmitted light. Extinction is nearly or quite parallel to the cleavage, and the trace of the cleavage is the direction of least refractive index of the sections examined. Pleochroism is distinct and, as in the case with purpurite, absorption is greatest across the cleavage. The index of refraction is greater than that of Canada balsam, and the double refraction

tion is probably rather high. It is hoped that sufficient of this material for analysis will soon be obtained.

The occurrence of purpurite in material collected from California by Mr. Schaller throws additional light on the origin and association of this mineral. It occurs with a black material which appears to be identical with that described above, and both are undoubtedly decomposition products of the accompanying triphylite, the iron-rich member of the lithia-manganous-ferrous phosphate series, of which lithiophilite is the manganese-rich end.

The small number and rarity of minerals containing manganic oxide, Mn_2O_3 , may be due to the relative instability of that base in comparison with manganese dioxide.

Chemical Composition ; WALDEMAR T. SCHALLER.

About a gram of pure material was separated by Mr. Graton. This was divided into several portions, using about a fifth of a gram for each determination. The most interesting part of the analysis was to determine the state of oxidation of the manganese. When the mineral is treated with hydrochloric acid, chlorine is readily given off. The manganese present can therefore not be in the manganous state, and the absence of ferrous iron and the presence of ferric iron suggested that the manganese was present as a manganic salt. Such was found to be the case.

A fifth of a gram was dissolved in sulphuric acid with a known amount of ferrous ammonium sulphate. All precautions were observed to avoid the presence of air, the entire operation being conducted in an atmosphere of carbon dioxide. The water used had been boiled and cooled out of contact with air. Just before the iron sulphate was introduced into the flask containing the mineral, an equal quantity was removed from the stock solution and titrated with permanganate. Thus, the amount of ferrous iron introduced into the flask with the mineral was known. After the mineral had been decomposed by the sulphuric acid, the flask was cooled and the solution titrated, the amount of iron sulphate oxidized by the liberation of oxygen from the mineral being determined in this way. From these data the amount of Mn_2O_3 was calculated and found to be 30.47 per cent.

A second sample was decomposed by hydrochloric acid and the chlorine evolved passed into a solution of potassium iodide. The liberated iodine was then titrated with sodium thiosulphate, the latter being standardized with pure copper. Calculating from the results obtained, the amount of Mn_2O_3 was found to be 27.93 per cent. Though these results vary somewhat, yet, considering the small amount of material used

(1/5 gram) and the many operations necessary, the agreement is as close as could be expected. The average of the two results is 29.20 per cent.

A direct determination of the total manganese, weighed as anhydrous sulphate, gave as the amount of Mn_2O_3 in the mineral, 29.35 per cent, which agrees almost exactly with the average of the two indirect determinations.

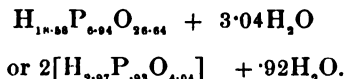
The remaining constituents were determined as follows: A portion of the mineral was dissolved in hydrochloric acid and a known weight of iron added (as ferric chloride). A basic acetate separation was then made, boiling the solution for fifteen minutes, which according to Bunsen will precipitate all the phosphoric acid with the iron and will not precipitate any manganese. The precipitate was dissolved in hydrochloric acid, and reprecipitated by ammonia, after the addition of some ammonium chloride. The two filtrates were united, manganese precipitated by hydrogen sulphide and finally weighed as anhydrous manganese sulphate. Calcium was then thrown out, dissolved and reprecipitated and magnesia found to be absent. The iron-phosphate precipitate was dissolved in hydrochloric acid and divided into two portions. In the one, the iron and phosphoric acid were precipitated by ammonia and weighed. This was then fused up with sodium bisulphate and tested for manganese with silver nitrate and ammonium persulphate. None was present. In the second portion, the iron was reduced by hydrogen sulphide and titrated with permanganate. Phosphoric acid was determined in the usual way and a second value obtained by the difference between the iron and the iron plus phosphoric acid. The alkalis were determined by the Lawrence Smith method. The final solution of chlorides gave a strong spectroscopic test for lithium. The water below 105° was determined directly, using a toluene bath. The total water was determined directly by heating in a glass tube according to Penfield. The water is all given off at a low temperature, that at 105° being given off very readily, and at one time. Further heating at 105° failed to remove any more. The values obtained are as follows:

		Av.	Ratio.	
Fe_2O_3	15.89,	15.89	1.03	} 2.96
Mn_2O_3	29.35, 30.47, 27.93	29.25	1.93	
P_2O_5	47.64, 46.96	47.30	3.47	
H_2O	5.26	5.26	3.04	} .41
CaO	1.48	1.48	.27	
Na ₂ O84	.84	.14	
Li ₂ O	tr.	tr.		
Insol.52	.52		

100.54

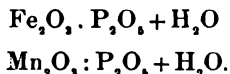
The amount of water given off at 105° is 3.31 per cent. As all of the water is so readily given off, it is most probably present as water of crystallization.

Considering that the calcium and soda require some phosphoric acid, the ratio of $R''',O_3 : P_2O_5 : H_2O$ is approximately 3:3:3. Combining the ratio of the calcium and sodium with that of the iron and manganese, and reducing these to their hydrogen equivalent, the ratio becomes



The acid is therefore H_2PO_4 . The formula for the mineral then becomes $R''',O_3 \cdot P_2O_5 + H_2O$.

It is not known in just what state of combination the calcium and sodium are. They most probably represent some slight impurity. If the manganic and ferric oxides are isomorphous in the sense that manganous and ferrous oxides are, the ratio of Mn_2O_3 to Fe_2O_3 being nearly 2:1 is of no significance and the formula then should not be written $Fe_2O_3 \cdot 2Mn_2O_3 \cdot 3P_2O_5 + 3H_2O$, but $(Mn''', Fe'''),O_3 \cdot P_2O_5 + H_2O$, the mineral purpurite being near the manganic end of an isomorphous series having as its two end members:



There are only a few hydrous phosphates of the normal division in which the base is trivalent, such as scorodite and strengite. All of these, however, contain more water than the mineral here described.

While no manganic phosphates were noted in the literature, there are a number of arsenates containing Mn_2O_3 , with none of which, however, can purpurite be classed. Synadelphite, flinkite, arsenioleite, and perhaps hematolite, contain Mn_2O_3 with Al_2O_3 or Fe_2O_3 , while in durangite and arseniosiderite, Mn_2O_3 is reported in small amounts.

The mineral fuses easily and readily gives off water in a closed tube becoming yellowish brown. It is readily soluble to a clear solution in hydrochloric acid, while in nitric acid a black oxide of manganese separates out. The specific gravity determined on the powdered mineral by the Thoulet solution is approximately 3.15.