

## BRAUNITE FROM MASON COUNTY, TEXAS\*

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The Spiller manganese mine, 15 miles northeast of Mason, Mason County, Texas, was hastily examined by one of the authors (D. F. H.) in May 1934, and subsequent study of the ores has shown that the principal manganese mineral is braunite, which appears to be rare in the United States.

Explorations at the Spiller mine include several open cuts, tunnels, and shafts, which are largely confined to an area about 100 by 600 feet along the crest of a ridge. The deposit was explored in a small way during the war but most of the workings were apparently made prior to 1891.<sup>1</sup> At that time, it was stated "The ore is a hard, steel-gray oxide, blending into a softer, fine-grained crystalline oxide." The presence of garnet (spessartite?) was also noted. This examination confirms the essentials of the description of the local geology as given by Penrose.

The prevailing rock of the explored area is quartzite, which in places contains enough microcline to be regarded as a gneiss. It is a part of the Valley Spring gneiss<sup>2</sup> of the Archean system. This is cut by a few dikes of coarse pegmatite, 5 to 15 inches wide, and by numerous quartz veins as much as 40 inches wide. The laminations of the quartzite trend generally northeast and dip at low angles northwest. They reveal gentle folds but are not plicated. Grains of garnet are distributed in layers in the quartzite but locally also form solid lenses. Tests by Miss J. J. Glass of the United States Geological Survey show that the index of refraction of this garnet is 1.803 and that it is probably a mixture of almandite and spessartite.

The principal manganese mineral is braunite, which is black with sub-metallic luster on polished surfaces. It is the principal constituent of the lenses that have been mined and shipped. One of these attains a maximum width of 3 feet and has been explored horizontally about 75 feet. It lies parallel to the lamination of the quartzite.

The common oxides of manganese, such as pyrolusite, manganite, psilomelane, and wad, seem to be conspicuously absent. As the principal manganese mineral is braunite, with garnet and albite as accessories, the deposit is unique in the United States. It resembles some of the Indian deposits which Fermor has described.<sup>3</sup>

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<sup>1</sup> Penrose, R. A. F., Manganese, its ores, uses, deposits: *Geol. Survey Arkansas*, vol. 1, pp. 442-443, 1891.

<sup>2</sup> Sellards, E. H., Adkins, W. S., and Plummer, F. B., The geology of Texas, vol. 1, Stratigraphy: *Univ. Texas Bull.* 3232, pp. 30-37, 1932.

<sup>3</sup> Fermor, L. L., The manganese-ore deposits of India: *Geol. Survey India, Memoir* 37, Pt. 1, Mineralogy, pp. 52-78, 1909.

In the opinion of the authors, the assemblage of minerals indicates that the deposit has been formed by hydrothermal processes at great depth.

The ore from the Spiller mine varies in texture from a fine-grained compact mass to a coarser aggregate with imperfect crystals up to a centimeter long. Massive cleavable albite (about 95 Ab), garnet, and thin seams of reddish-brown earthy hematite are the only associated minerals noted on the hand specimen.

Three polished surfaces were made and examined by reflected light by Charles F. Park, Jr., of the United States Geological Survey. One was from the same piece from which the material analyzed was obtained, the other two were from different parts of a larger specimen. All three polished surfaces show that neither hematite nor magnetite is present. One surface shows small isolated swarms of an unidentified whitish mineral, probably tetragonal, and strongly anisotropic, which effervesces with  $H_2O_2$  without etching. It was not observed in the material analyzed and in the other specimen was present to the extent of a few per cent only.

The braunite is cut by a network of tiny veinlets of hausmannite showing typical twinning and very strong anisotropism. Hausmannite is estimated to be present to the extent of 5 to 10 per cent of the material, and is, in turn, veined by and appears to be altering to a soft gray undetermined mineral. The braunite also contains remnants of an unknown mineral of about the same hardness as braunite and a little darker gray in color. This unknown mineral is isotropic and reacts negatively to HCl,  $HNO_3$ , KCN, KOH,  $FeCl_3$ ,  $SnCl_2$ ,  $HgCl_2$ , and  $H_2O_2$ .

The chemical analysis and goniometric measurements of the crystals by Schaller identify the black mineral as braunite. Both the color and streak of the Spiller braunite are identical with those of known braunites from other localities.

The crystals are typically octahedral in habit with smaller faces of four other forms, one of which is new for braunite. The usual orientation of braunite (Haidinger, Dana), with  $c=0.9850$ , makes the perfect cleavage form the pyramid of the first order  $\{111\}$ . Goldschmidt turns the crystals  $45^\circ$  and makes the perfect cleavage form the pyramid of the second order  $\{011\}$ , with  $c=1.4032$ . Goldschmidt's orientation yields simpler indices and shows the isozonal relation of the pyramids better than the more generally adopted orientation.

The measured forms and angles are given in the following table, the angles being given in Goldschmidt's orientation.

FORMS AND ANGLES OF BRAUNITE FROM THE SPILLER MINE, MASON COUNTY, TEXAS

| Forms            |                  | Description     | Measured |        | Calculated |        |
|------------------|------------------|-----------------|----------|--------|------------|--------|
| Dana             | Goldschmidt      |                 | $\phi$   | $\rho$ | $\phi$     | $\rho$ |
| <i>c</i> {001}   | <i>c</i> {001}   | Small, square   | .....    | 0 00   | .....      | 0 00   |
| <i>p</i> {111}   | <i>e</i> {011}   | Large, dominant | 0 04     | 54 35  | 0 00       | 54 31  |
| * <i>D</i> {867} | * <i>D</i> {177} | Small, narrow   | 8 03     | 54 49  | 8 08       | 54 47  |
| $\sigma$ {645}   | $\sigma$ {155}   | Medium          | 11 21    | 55 21  | 11 18      | 55 03  |
| $\gamma$ {423}   | $\gamma$ {133}   | Medium          | 18 17    | 55 54  | 18 26      | 55 56  |

The form \**D*{867}, Dana, or \**D*{177}, Goldschmidt, is new for braunite. It is present on a portion of a crystal as two small narrow faces, broader than line faces but narrower than the faces of  $\sigma$  and  $\gamma$ . The average of repeated measurements is given above.

The form lies in the zone

(201).....(111) Dana

or (111).....(011) Goldschmidt

The forms of braunite in the zone segment (011)...(111), Goldschmidt, are:

|                         |          |               |               |               |               |               |          |
|-------------------------|----------|---------------|---------------|---------------|---------------|---------------|----------|
| Forms                   | <i>e</i> | * <i>D</i>    | $\sigma$      | $\gamma$      | $v$           | <i>f</i>      | <i>d</i> |
|                         | 011      | 177           | 155           | 133           | 122           | 344           | 111      |
| <i>p</i> =              | 0        | $\frac{1}{7}$ | $\frac{1}{5}$ | $\frac{1}{3}$ | $\frac{1}{2}$ | $\frac{3}{4}$ | 1        |
| <i>v</i> /1- <i>v</i> = | 0        | $\frac{1}{6}$ | $\frac{1}{4}$ | $\frac{1}{2}$ | 1             | 3             | $\infty$ |
| 2 <i>v</i> =            | 0        | $\frac{1}{3}$ | $\frac{1}{2}$ | 1             | 2             | (6)           | $\infty$ |
| <i>N</i> <sub>3</sub> = | 0        | $\frac{1}{3}$ | $\frac{1}{2}$ | $\frac{2}{3}$ | 1             | 3             | $\infty$ |

The new form *D*{177} fits perfectly in the normal series *N*<sub>3</sub>.

ANALYSIS OF BRAUNITE FROM THE SPILLER MINE, MASON COUNTY, TEXAS

|                                      | Analysis | Analysis*<br>recalculated | Calculated<br>81 per cent 3Mn <sub>2</sub> O <sub>3</sub><br>· MnSiO <sub>3</sub><br>19 per cent 3Fe <sub>2</sub> O <sub>3</sub><br>· MnSiO <sub>3</sub> |
|--------------------------------------|----------|---------------------------|--|
| SiO <sub>2</sub> <sup>b</sup> .....  | 9.90     | 10.01                     | 9.93   |
| MnO.....                             | 66.89    | 68.08                     | 68.72  |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 15.39    | 15.57                     | 14.92  |
| O.....                               | 6.27     | 6.34                      | 6.43   |
| CaO.....                             | 0.06     | —                         | —  |
| MgO.....                             | 0.19     | —                         | —  |
| H <sub>2</sub> O.....                | 0.73     | —                         | —  |
| Insoluble gangue.....                | 0.67     | —                         | —  |
|                                      | 100.10   | 100.00                    | 100.00   |

Sp. gr. = 4.729

\* Recalculated to 100 per cent after changing CaO and MgO to their equivalent of MnO and deducting H<sub>2</sub>O and insoluble gangue.

<sup>b</sup> Soluble silica.

The analysis of the braunite is given above with a comparison of the composition of an isomorphous mixture of the two molecules  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_2$ , and  $3\text{Fe}_2\text{O}_3 \cdot \text{MnSiO}_3$ , in the percentages shown, the analysis showing that a considerable quantity of ferric oxide,  $\text{Fe}_2\text{O}_3$ , is present in the mineral.

The analysis can also be stated in another form by combining the available oxygen (given as 6.34 per cent O in the recalculated analysis) with enough  $\text{MnO}$  to form  $\text{Mn}_2\text{O}_3$ , the remaining  $\text{MnO}$  then being combined with the  $\text{SiO}_2$  to form  $\text{MnSiO}_3$ .

ANALYSIS OF BRAUNITE STATED IN ANOTHER FORM

|                               | Recalculated<br>analysis | Calculated<br>81 per cent $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$<br>19 per cent $3\text{Fe}_2\text{O}_3 \cdot \text{MnSiO}_3$ |
|-------------------------------|--------------------------|--|
| $\text{SiO}_2$ .....          | 10.01                    | 9.93   |
| $\text{MnO}$ .....            | 11.90                    | 11.70  |
| $\text{Mn}_2\text{O}_3$ ..... | 62.52                    | 63.45  |
| $\text{Fe}_2\text{O}_3$ ..... | 15.57                    | 14.92  |
|                               | 100.00                   | 100.00   |

That the  $\text{Fe}_2\text{O}_3$  is an essential part of the braunite and is not due to enclosed hematite, or other iron mineral, is shown by a consideration of the molecular ratios calculated from the above analysis.

The ratios are:

|                               |        |    |      |        |
|-------------------------------|--------|----|------|--------|
| $\text{SiO}_2$ .....          | 0.1666 | or | 1.01 |        |
| $\text{MnO}$ .....            | 0.1678 | or | 1.01 |        |
| $\text{Mn}_2\text{O}_3$ ..... | 0.3959 | or | 2.39 | } 2.98 |
| $\text{Fe}_2\text{O}_3$ ..... | 0.0975 | or | 0.59 |        |

The formula for braunite is  $\text{SiO}_2 \cdot \text{MnO} \cdot 3(\text{Mn}, \text{Fe})_2\text{O}_3$  and all the iron has to be added to the manganic manganese to yield the ratio of 1:1:3, as required by the formula. The absence of hematite, or other iron oxide, was also proven by the examination of three polished surfaces by reflected light.

The presence of hausmannite,  $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ , and the other undetermined, probably manganese, minerals, would tend to raise slightly the ferric oxide content of the braunite itself. The content of  $\text{SiO}_2$  is so close to the calculated value and the ratios of  $\text{SiO}_2 : \text{MnO} : (\text{Mn}, \text{Fe})_2\text{O}_3$  are so close to 1:1:3, as to suggest that the material analyzed contained less than the estimated 5-10 per cent of hausmannite, as indicated by Park's study of the polished surfaces of the ore.

The consideration of the isomorphous replacement of  $\text{Mn}_2\text{O}_3$  by  $\text{Fe}_2\text{O}_3$  in braunite is confirmed by the work of Zachariassen,<sup>4</sup> and Pauling and Shappell<sup>5</sup> on bixbyite, their conclusion being that the formula of bixbyite should be written  $(\text{Mn}, \text{Fe})_2\text{O}_3$ . The formula of the Spiller braunite may then be more accurately written  $3(\text{Mn}, \text{Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$  or, as  $\text{Fe}_2\text{O}_3$  is not an essential constituent of all braunites, and the simpler formula  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$  is usually taken as that of braunite in general, the Spiller braunite may be defined as a ferrian braunite, using the descriptive form suggested by one of us.<sup>6</sup>

The isomorphous relation of  $\text{Mn}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in braunite and bixbyite and in other minerals (the epidote series, purpurite-heterosite, etc.) makes it seem doubtful if their separation in a formula, with definite ratio, is valid, and casts suspicion on such a formula, for example, as is given for sitaparite, namely  $9\text{Mn}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3 \cdot \text{MnO}_2 \cdot 3\text{CaO}$ , and beldongrite, namely  $6\text{Mn}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{MnO}_2 \cdot 8\text{H}_2\text{O}$ . Vredenburgite, with a supposed formula  $3\text{MnO} \cdot 3\text{Mn}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$ , has been shown<sup>7</sup> to be a mixture of jacobsonite,  $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ , and hausmannite,  $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ , and, in the type specimen, with still other manganese minerals.

The Spiller braunite seems to contain the highest reported percentage of  $\text{Fe}_2\text{O}_3$ , namely 15.39, although two other analyses approach this figure closely, namely one of braunite from the Engadine, Switzerland, with 14.55 per cent<sup>8</sup>  $\text{Fe}_2\text{O}_3$ , and another from India with 14.14 per cent<sup>9</sup>  $\text{Fe}_2\text{O}_3$ . Doelter<sup>10</sup> lists six additional analyses of braunite with  $\text{Fe}_2\text{O}_3$  ranging from 11.40 to 12.91 per cent, although there is no assurance for some of the older analyses that the reported  $\text{Fe}_2\text{O}_3$  was not due to impurities.

<sup>4</sup> Zachariassen, William, Über die Kristallstruktur von Bixbyite, sowie vom künstlichen  $\text{Mn}_2\text{O}_3$ : *Zeits. Krist.*, vol. **67**, pp. 455-464, 1928.

<sup>5</sup> Pauling, Linus, and Shappell, M. D., The crystal structure of bixbyite and the C-modification of the sesquioxides: *Zeits. Krist.*, vol. **75**, pp. 128-142, 1930.

<sup>6</sup> Schaller, W. T., Adjectival ending of chemical elements used as modifiers to mineral names: *Am. Mineral.*, vol. **15**, pp. 566-574, 1930.

<sup>7</sup> Dunn, J. A., A study of some microscopical aspects of Indian manganese-ores: *Trans. National Inst. Sciences India*, vol. **1** (no. 7), pp. 103-124, 1936.

<sup>8</sup> Bukeisen, Fried., Mineral-Analysen. z. Braunite: *Sitzungsber. Akad. Wissensch. Wien*, vol. **24**, p. 287, 1857.

<sup>9</sup> Fermor, L. L., The manganese-ore deposits of India: *Geol. Survey India, Mem.* **37**, p. 68, 1909.

<sup>10</sup> Doelter, Cornelius, *Handb. d. Mineralchemie*, vol. **3**, pt. 2, pp. 896-899, 1926.