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A NOTE ON FERROAN GAHNITE FROM MALAYA AND ITS BEARING ON THE PUBLISHED DATA FOR HERCYNITE^{1 2}

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Dark green spinel (gahnite) occurs as fine sub-rounded euhedral crystals, associated with alluvial columbite deposits, at Bakri (Johore) and in the Bedong-Semeling area of Kedah. In the course of detailed examination of the gahnite from Siau Hin Kongsi, Semeling, two samples were obtained by electromagnetic separation. Using a Frantz Isodynamic separator with a side slope of 25° and a forward slope of 15°, a sample x was extracted within the range 0.4 to 0.7 amps and a sample y was extracted within the range 0.7 to 1.0 amps, all the gahnite falling within the range 0.4 to 1.0 amps. These two samples were then cleaned by handpicking and split; one half being used for determining the density (D), refractive index (n) and unit cell dimensions (a), the values for which were as follows:

| Sample - | Density | | | 9 |
|----------|----------------|----------------|---|--|
| | meas.1 | calc. (Dx) | <i>n</i> (Na) | a A |
| x y | 4.507 4.536 | 4.512 4.534 | $\begin{array}{c} 1.782 \pm 0.001 \\ 1.781 \pm 0.001 \end{array}$ | 8.0945 ± 0.0008 8.0923 ± 0.0015 |

¹ By the Berman balance "powder" method using carbon tetrachloride.

Assuming, as for the garnet group, that density, refractive index and unit cell dimension vary linearly with variation in composition (Anderson and Payne 1937, showed a linear variation of refractive index in the Mg-Zn series), the data above indicate that the samples lie between the Zn and Fe end-members, being richer in Zn than Fe, using the published data for the Al_2O_4 series of spinels as tabulated at the top of the next page.

However, the ratio of Zn: Fe varied from 82:18 to 55:45 for x and 87:13 to 64:36 for y, depending on whether refractive index, unit cell or density were considered. In order to obtain the true value, the other half of each sample was chemically analyzed (Table 1).

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| | Dx | n | a Å |
|------------------------------|-------------|-----------------------|--------|
| Mg (spinel) | 3.581 | 1.712 | 8.0800 |
| Zn (gahnite) | 4.608^{1} | 1.778 ± 0.001^{2} | 8.0848 |
| Fe ²⁺ (hercynite) | 4.39 | 1.800 | 8.119 |
| Mn (galaxite) | 4.077 | 1.923 | 8.258 |

Data for Mg and Zn from N.B.S. Circ. 539, Vol. 2, 35-41; for Mn (Dx and a only) from N.B.S. Circ. 539, Vol. 9, 35; for Fe and Mn(n) from Dana's System of Mineralogy, 7th ed., Vol. 1, 689-690.

¹ N.B.S. Circ. quotes 4.607, but the calculation gives 4.608.

² Subsequent adjustment on N.B.S. material (private communication, Dr. H. E. Swanson).

This confirms that samples x and y lie directly on the gahnite-hercynite (Zn-Fe) join; sample x, with a higher proportion of Fe²⁺, being more magnetic than y, as is to be expected. The ratio of Zn:Fe is 66.8:33.2 (*i.e.* 2:1 or a $33.2\%(\frac{1}{3})$ replacement of Zn by Fe) and 74.4:25.6 (*i.e.* 3:1 or a $25.6\%(\frac{1}{4})$ replacement of Zn by Fe) respectively for x and y. Neither of these corresponds to any of the values quoted above. This, together with the variation noted in the latter, indicates that either the assumption of linear variation is not valid or the published data for the end-members are incorrect. The data for Mg, Zn and Mn (except for *n* in the latter)

| | x | У |
|--------------------------------|--------|--------|
| ZnO | 29.26% | 32.60% |
| FeO | 12.80 | 9.95 |
| MgO | 0.40 | 0.20 |
| MnO | 0.02 | 0.01 |
| CaO | trace | trace |
| SiO_2 | 0.50 | 0.52 |
| TiO_2 | 0.04 | 0.11 |
| Al_2O_3 | 56.76 | 56.58 |
| Cr ₂ O ₃ | 0.01 | nil |
| | | |
| Total | 99.79 | 99.97 |

| TABLE | 1. | ANALYSES | \mathbf{OF} | GAHNITE |
|-------|----|----------|---------------|---------|
|-------|----|----------|---------------|---------|

Analyst: G. M. Harral.

The analyses yield the following structural formulae:

 $\begin{array}{l} x\colon (Zn_{5.14}Fe^{2+}_{2.56}Mg_{0.14}Si_{0.11}Ti_{0.01})Al_{15.95}O_{32}\\ y\colon (Zn_{5.76}Fe^{2+}_{1.98}Mg_{0.07}Si_{0.13}Ti_{0.01})Al_{15.94}O_{32} \end{array}$

 SiO_2 and TiO_2 must be considered as replacing the (ZnFe) group in order to obtain a good fit.

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case) is given by the U. S. National Buereau of Standards on synthetic, pure material and may be considered as accurate. The same cannot be said for the data for Fe and it is therefore suggested that linear variation of the three properties considered does in fact occur, and that the published data for hercynite do not refer to the pure end-member.

On this assumption, and taking the data for gahnite and samples x and y, it can be shown that the data for pure hercynite should be

D = 4.32

$$n = 1.790$$

 $a = 8.114$ Å, as follows:

Density. Gahnite=4.608; x=4.512; y=4.534. From x, 33.2% replacement by Fe=4.608-4.512=0.096,

: 100% replacement by Fe = $\frac{0.096 \times 100}{33.2} = 0.289$,

: Dx for hercynite (100% Fe) should be 4.608-0.289=4.319 (*i.e.* 4.32). From y, 25.6% replacement = 4.608-4.534=0.074,

: 100% replacement = $\frac{0.074 \times 100}{25.6} = 0.289$,

: Dx for hercynite should be 4.608 - 0.289 = 4.319 (*i.e.* 4.32).

Refractive Index. Gahnite=1.778; x=1.782; y=1.781. From x, 33.2% replacement = 1.782 - 1.778 = 0.004,

- \therefore 100% replacement = 0.012,
- \therefore *n* for hercynite should be 1.778 + 0.012 = 1.790.

From y, 25.6% replacement = 1.781-1.778=0.003,

 $\therefore 100\%$ replacement = 0.012,

 \therefore *n* for hercynite should be 1.778 + 0.012 = 1.790.

Unit Cell. Gahnite=8.0848 Å; x=8.0945 Å; y=8.0923 Å. From x, 33.2% replacement =8.0945-8.0848=0.0097,

 $\therefore 100\%$ replacement = 0.0292,

 \therefore a for hercynite should be $8.0848 \pm 0.0292 = 8.1140$ (*i.e.* 8.114).

From y, 25.6% replacement = 8.0923 - 8.0848 = 0.0075,

 $\therefore 100\%$ replacement = 0.0293,

: a for hercynite should be 8.0848 + 0.0293 = 8.1141 (*i.e.* 8.114).

Finally, if Dx for hercynite is calculated from the proposed value of a=8.114, a value of 4.321 is obtained which agrees with the proposed value of 4.32 found above.

Using the new values for hercynite, plots of pairs of the three variables are given in Figs. 1a, b and c. The published data for hercynite are indicated as point A. To determine the composition of any point (sample) lying on the Zn-Fe join it is necessary only to measure the distance of the point from one end in relation to the whole.

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FIG. 1. Plots of unit cell, density and refractive index for hercynite and gahnite.





FIG. 2a. Unit cell plotted against density for the Al₂O₄ series of spinels.

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It will be interesting to see how the proposed new values for hercynite compare with data for the synthetic, pure mineral when modern data for it eventually appear. In the meantime, three diagrams (Figs. 2a, b, and c) are appended for determining the composition of the Al₂O₄ series of spinels on the basis of any two of the three properties density, refractive index and unit cell. From these it can be seen that point A in Figure 1 lies



FIG. 2b. Unit cell plotted against refractive index for the Al₂O₄ series of spinels.

towards the Mn end-member, indicating a Mn-enrichment in the sample of hercynite originally examined. Provided accurate data are available it should be possible to extend these diagrams to include the magnetite and chromite series as well.

I should like to express my gratitude to Drs. H. E. Swanson and H. F. McMurdie of the U. S. National Bureau of Standards for providing me with some of their gahnite sample and for checking the refractive index of my samples, and to the Director, Geological Survey, Federation of Malaya for permission to publish this paper.



FIG. 2c. Density plotted against refractive index for the Al₂O₄ series of spinels.

Reference

ANDERSON, B. W. AND C. J. PAYNE (1937) Magnesium-zinc spinels from Ceylon. Mineral. Mag. XXIV, 547-554.

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