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Limonite is goethite.* By W. T. HOLSER, *Department of Geology, Cornell University, Ithaca, N. Y., U. S. A.*

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With reference to the note by Dasgupta & Maitra (1952) the elementary textbooks of Hurlbut, Miers, or Rogers & Kerr cannot be taken as authority that the structure of 'limonite' is amorphous. It is to be regretted that this name continues to be perpetuated as anything other than '... a field or generic term to refer to natural hydrous iron oxides whose real identity is unknown' (Palache, Berman & Frondel, 1944, p. 685). Since the earliest days of X-ray diffraction (Posnjak & Merwin, 1922, p. 1971) it has been known that most mineral specimens labeled

'limonite' are goethite, $\text{HFeO}_2(\alpha\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})$, some are lepidocrocite, $\text{HFeO}_2(\gamma\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})$, and a few are hematite, Fe_2O_3 . Most are only very finely crystalline and hence tend to retain considerable adsorbed water; some are so finely divided that X-ray patterns are diffuse. A brief survey of the A.S.T.M. X-ray diffraction cards indicates that the strong lines of the subject material are within the variations previously reported for goethite (e.g. card 1-0406).

References

* *Editorial note.*—Similar views on the same paper were expressed previous to this note in letters received by the Editor from Prof. Duncan McConnell (Columbus, Ohio, U.S.A., 15 December 1952) and Prof. A. Pabst (Berkeley, Cal., U.S.A., 20 December 1952); these letters contain further references (e.g. Böhme, 1928) in support of the view that limonite is identical with goethite.

- BÖHME, J. (1928). *Z. Kristallogr.* **68**, 567.
 DASGUPTA, D. R. & MAITRA, J. C. (1952). *Acta Cryst.* **5**, 851.
 PALACHE, C., BERMAN, H. & FRONDEL, C. (1944). *Dana's System of Mineralogy*, 7th ed. New York: Wiley.
 POSNJAK, E. & MERWIN, H. E. (1922). *J. Amer. Chem. Soc.* **44**, 1965.

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The low-temperature crystal structure of magnetite.* By H. P. ROOKSBY and B. T. M. WILLIS, *Research Laboratories of The General Electric Company Limited, Wembley, England*

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In a recent communication Abrahams & Calhoun (1953) have presented new evidence concerning the low-temperature structure of magnetite, Fe_3O_4 . They conclude that the structure cell deforms on cooling below 115°K . to give an orthorhombic arrangement rather than the rhombohedral arrangement previously proposed by Tombs & Rooksby (1951).

Since Tombs & Rooksby's paper was written we have obtained additional results that support a rhombohedral deformation. It is the purpose of this note to record these results, and to indicate the difficulties of reconciling them with an orthorhombic low-temperature structure for magnetite.

If Abrahams & Calhoun's evidence for an orthorhombic change is carefully studied, it is found to rely principally on the detection of a splitting of the cubic 800 line into two components at liquid-nitrogen temperature. This line should remain unsplit for a rhombohedral transition. Because the 800 doublet separation, measured by Abrahams & Calhoun with a Norelco spectrometer, was so small, viz. 4 min. of arc ($\text{Fe } K\alpha$ reflection), and the general fit of all our earlier data with the rhombohedral interpretation so close, we undertook further studies by photographic methods. Powder photographs were taken at liquid-air (95°K .) and liquid-nitrogen (80°K .) temperatures using $\text{Co } K$ and $\text{Cr } K$ radiations. In this way we examined the splitting of a wide range of reflexions,

including 440, 444 and 840, in addition to the 533, 731 and 800 lines studied by Abrahams & Calhoun.

Through the courtesy of Dr Abrahams we were able to examine a specimen of his magnetite powder. Results were in every respect similar to results obtained with our own preparations, so that possible ambiguities arising from use of materials of different origins are eliminated.

Planar spacing values for components of split reflexions gave in every instance the separations predicted by a rhombohedral structure cell with dimensions

$$a_R = 5.940 \text{ \AA}, \alpha = 59^\circ 47.5' \text{ at } 80^\circ \text{K}.$$

Making the assumption that the atomic co-ordinates correspond with those in the cubic arrangement, the calculated and observed relative intensities of resolved components agree better with the rhombohedral than with the orthorhombic interpretation. The evidence on lines 440, 533, 444, 800 and 840 is summarized in Table 1.

It may be noted that we have not been able to detect any splitting of 800 photographically, though noticeable broadening might have been expected with a separation of the magnitude indicated by Abrahams & Calhoun. Attention, however, may be drawn particularly to the manner of splitting of 440. The splitting is disclosed clearly in either liquid-air or liquid-nitrogen temperature photographs taken with Cr radiation. Two equally strong components, with a separation of approximately 13 min., occur for the α doublet wave-length, and a corresponding splitting is seen with the β reflexion, in which any intensity ambiguity due to overlaps is naturally absent.

* Communication No. 543 from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.