

## MAGHEMITE IN THE SYDNEY DURICRUSTS

ADETOYE FANIRAN, *Department of Geography,  
University of Ibadan, Ibadan, Nigeria.*

### ABSTRACT

The study of polished sections and powder photographs has confirmed earlier observations on the occurrence of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) in the laterites and ferricretes of the Sydney district, New South Wales. The mineral is confined to the black cores of some pisolites and to similar materials in ferricretes. In profile, the amount of maghemite tends to decrease from top to bottom, being confined mainly to the topmost parts (*i.e.* the upper-indurated zone). The mineral may have been derived from the magnetite in the Hawkesbury Sandstone and or from siderite in the Wianamatta Shales and basic igneous rocks.

### INTRODUCTION

Frankel (1966) reviewed the occurrence of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) in the lateritic rocks of Australia, Northern Ireland, India and various parts of Africa. He also reported the occurrence of the mineral in a laterite from the Sydney district of New South Wales. The mineralogy of the laterites and related rocks of this area is studied here in randomly chosen samples from the northern part of the Sydney district (Fig. 1). In this paper, *laterites* are rocks containing relatively high proportions of the oxides of iron, aluminium, and silicon, particularly those showing concretionary (colloform) textures in hand specimen, and which are found in profiles with mottled—and/or pallid—zone lower layers overlying unweathered or weathering country rock. *Ferricrete* is used for iron-cemented crusts that are underlain by mottled and/or pallid zones. The laterites of this area are associated with shales and sandstones alike, and the ferricretes mostly with coarser-grained (conglomeratic) rocks. It is quite possible that ferricretes belong on the coarsest end of a continuum of laterite types which vary according to the size and content of the constituent quartz; but ferricretes have no colloform textures, and so have been classified separately (Figs. 1 and 2; also Faniran, 1969).

Standard petrographical and X-ray mineralogical methods were used by the author in the Department of Geology and Geophysics, The University of Sydney. Quantitative analyses were undertaken by P. Bayliss, formerly of the University of New South Wales, Kensington (Tables 1 and 2).

### MAGHEMITE IN THE LATERITES

*Identification.* Maghemite was identified in both polished sections and X-ray powder diffraction photographs. Colour, reflectivity, internal reflection, anisotropism or pleochroism, and microhardness were studied. While quantitative measurements were possible in the case of micro-

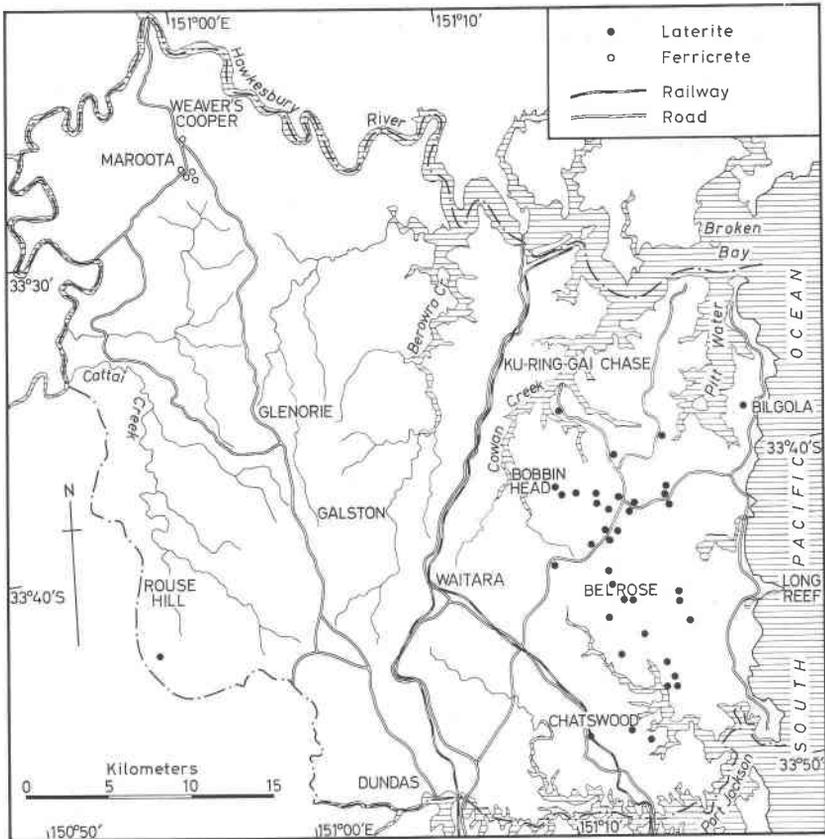
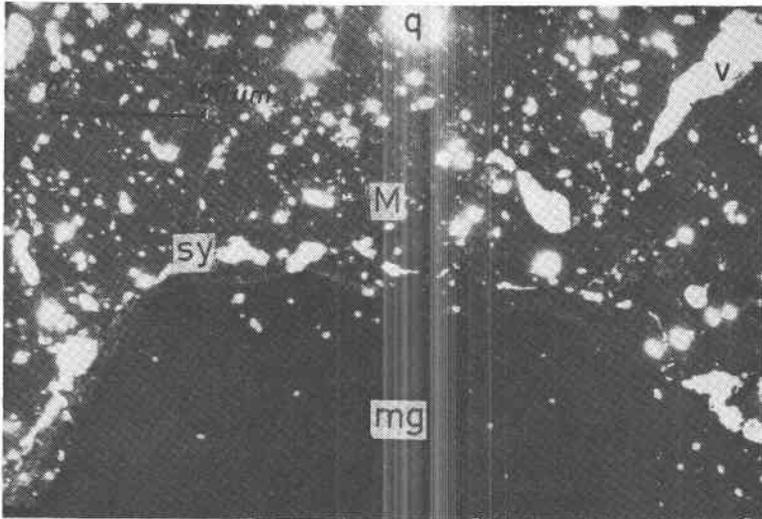
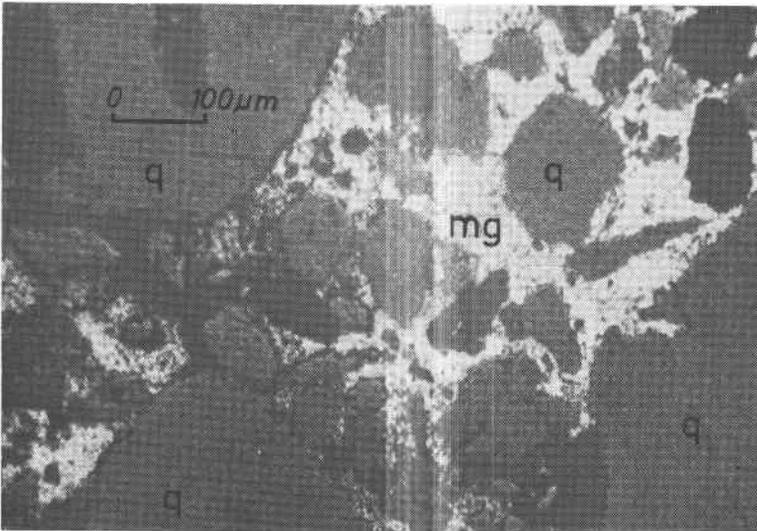


FIG. 1. The distribution of duricrusts in the Northern Sydney district.

hardness using the methods and procedures described by Bowie and Taylor (1958), only semiquantitative measurements were possible for the others. The minerals in the observed samples almost invariably occur as intimate crypto-crystalline aggregates. Maghemite in polished section is generally isotropic, white to bluish white and has high reflectivity, mostly about 25 or more; the same mineral in thin section is completely opaque or black (Figs. 2 and 3; also Bowie and Taylor, 1958, p. 8). These observations agree to a very large extent with Frankel's (1966, p. 115), but the internal reflections which Frankel reported are rarely visible; those observed are mostly green or greenish grey due, perhaps, to the presence of small quantities of titanium in most of the samples (Basta, 1956; Buddington and others, 1963; Glasson, pers. commun.). Moreover, Frankel's conclusion that maghemite is closely associated with goethite



(a)



(b)

FIG. 2. Photomicrographs of the duricrusts of the Sydney district

(a) Laterite in thin section of a fine-grained sandstone sample. Note: (i) The black core of pisolite or birds eye (bottom) (ii) The surrounding voidal space or syneresis (sy) (iii) The goethitic matrix (M, dark grey); and (iv) Few and generally small quartz (q) grains, mostly in the matrix. These are generally whiter (over-exposed) and more rounded than the void spaces, v, which appear, for example, in the top-right corner.

(b) Ferricreted conglomerate in polished section, showing quartz (q) grains of both sand and gravel size, and iron cement, mainly maghemite (mg) and hematite (h).

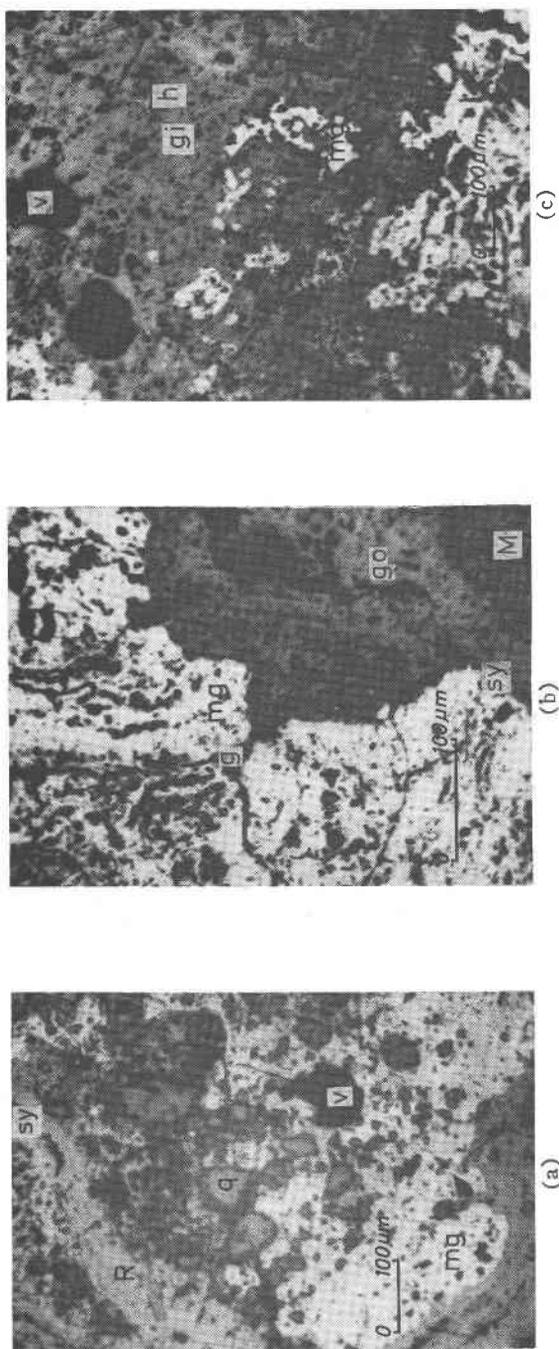


FIG. 3. Progressive replacement of maghemite in the laterites.

a. Sections of three closely-packed maghemite colites, together shrinkage-crack or syneresis (sy) structures. Space between these and the pisolite is filled by goethitic (g) material from the earthy matrix. Gangues (g) are mostly black fine-grained sandstone sample.

b. Section of a pisolite of laterite in coarser grained sandstone than 3(a).

(i) size and number of quartz (q) grains, compared to 2(a) and (ii) peripheral replacement of maghemite. Voids (v) are black.

c. Higher magnification of 3(b) above, showing residual maghemite surrounded by areas of mostly hematite (h) and gibbsite (gi).

TABLE 1. LATERITE (X-RAY-DIFFRACTION) MINERALOGY

Sample <sup>a</sup>	Mineral Content (wt. %) <sup>b</sup>					
	Gibbsite	Goethite	Hematite	Kaolin	Quartz	
Bulk or whole rock	1	30	15	5	25	25
	2	5	30	5	25	35
	3	40	20	5	10	25
	4	35	5	20	30	10
Pisolite texture	5	20	10	25	25	20
	6	20	5	35	30	10
	7	15	10	70	0	5
Matrix	8	50	30	10	5	5
	9	35	15	0	25	25
	10	5	25	5	25	40

<sup>a</sup> All samples belong to the upper-indurated (laterite) zone; samples 2 and 10 are reworked laterites in shale, 1, 3, 5, 7, 8 and 9 are fine-grained sandstones and 4 and 6 coarse-grained sandstone (Table 2).

<sup>b</sup> Estimates of the precision of determination are  $\pm 5\%$  for kaolin,  $\pm 7\%$  for gibbsite and goethite, and  $\pm 10\%$  for hematite and quartz.

was not confirmed in this study. Hematite and maghemite almost invariably occur together here: typically in the pisolites and similar textures. Goethite and gibbsite occur together in the matrix, whereas quartz and kaolin are present in all sections (Table 1).

Although the data on microhardness are certain to be affected by the fineness of the mineral grains, values obtained for hematite and maghemite are generally comparable with those previously reported in the literature. The range of 790–1200 with a mean of 930 for hematite, and of 885–1250 with a mean of 940 for maghemite are close to those reported by Bowie and Taylor (1958, pp. 14 and 19) and by Young and Millman (1964, p. 450).

Maghemite also was identified by X-ray powder diffraction photographs, but not in the quantitative X-ray diffraction analyses of bulk samples shown in Table 1. The latter analysis was designed for the identification of the important minerals in the materials being studied and was not capable of identifying minerals which made up less than 5 percent of the specimens (Bayliss, pers. commun). By contrast, X-ray powder diffraction analysis involved small samples of generally more homogeneous materials taken from thin sections under the microscope. The latter method was designed for the identification of particular minerals observed in thin and polished sections.

TABLE 2. POLISHED SECTION MODAL ANALYSES OF LATERITES IN FINE-GRAINED SANDSTONE,<sup>a</sup> SYDNEY DISTRICT

Sample Reference	Mineral Content (Wt. %)			
	Maghemite	Other Opaques	Rest (mainly quartz)	
Upper—Indurated Zone	1	33.9	53.7	13.0
	2	28.7	62.2	9.1
Middle—Indurated Zone	3	16.2	69.0	14.8
	4	4.6	81.4	14.0
Lower—Indurated Zone	5	3.1	77.8	19.1
	6	1.2	84.4	14.4
	7	0.9	90.0	9.1
	8	0.0	53.7	46.3

<sup>a</sup> Similar trends were observed in respect to laterites formed in shale and in coarse-grained sandstone.

*Distribution.* The relative proportions of the minerals observed in polished sections were estimated by the point counter (Chayes, 1949). However, these minerals mostly occur in intimate mixtures; they were therefore grouped in the broadest forms possible. The sections containing maghemite were measured separately and the other sections were divided into areas containing predominantly other metallic ores, *e.g.* mixtures of hematite, goethite and gibbsite, and those containing mainly nonmetallic substances; the latter section was mainly quartz. These are respectively called maghemite, other opaques, and rest (mostly quartz) in Table 2.

Petrographical modal analyses (Chayes, 1956) showed that maghemite is present in surface and near surface samples and is absent at greater depths (Table 2). This is in agreement with the results of significance tests performed on the data of Table 1, which showed that hematite which in that table also includes maghemite, at least in certain samples occurs mainly in pisolitic textures found mainly in the top (indurated) zones of laterite profiles. On the other hand, goethite and gibbsite typically occur in the matrix. Kaolin and quartz are equally abundant in all sections, presumably on account of the quartzitic parent material.

*Paragenesis.* Various modes of genesis of natural maghemite have been suggested. These include a detrital origin (Baker, 1962), tropical (lateritic) weathering (Schwertmann, 1959; Milner, 1962, p. 334), and low-temperature oxidation of magnetite or dehydration of lepidocrocite (Gruner, 1926; Milner, 1962, p. 447). Lepidocrocite was not identified in the present study but there are at least two possible sources of magne-

tite or other magnetic ores. The Hawkesbury Sandstone, the parent material of much of the laterites of the Sydney laterites, has been reported to contain magnetite (Osborne, 1948, p. xx), and Loughnan and others (1961) have described siderite in the Wianamatta Shales, which overlie the sandstones. Siderite weathers to magnetic ores (Hurlbut, 1949, p. 195; Grebnew, 1957; Yui, 1966) under situations similar to those of tropical (lateritic) weathering. Moreover, magnetite, and possibly also hematite, may have been deposited in the uppermost parts of the laterite profile as gel blebs, and by capillary action during fluctuations of groundwater table. Magnetic ores may also have been leached down into this zone during pedogenic weathering (Mitchell, 1965). In both these cases, the magnetite may have since oxidized to maghemite, and in some cases have been replaced by hematite (Fig. 3).

Bastin (1950, pp. 25–26) has described the development of colloform textures by the deposition of gels of spheroidal form in voids. He stated in effect that substances such as the oxides being deposited at or near the surface by capillary action tend, under the influence of surface tension, to assume spherical shapes. It is therefore possible that the pisolitic (colloform) textures of these laterites have formed by the dehydration of the originally deposited gels or blebs. The development of the concretionary textures of the Sydney laterites is discussed in another paper being prepared.

#### CONCLUSION

The maghemite in the Sydney duricrusts occurs mainly in the black cores of some pisolites or in similar materials in ferricretes mostly in association with hematite but to a lesser extent with gibbsite. These latter minerals appear to be replacing maghemite progressively, especially in the peripheral areas (Fig. 3; also Basta, 1956; Ito, 1959; and Welfers, 1967). These observations are contrary to those by Kulp and Trites (1951, p. 39) that aluminium and ferric iron ions are geochemically separated under normal weathering conditions, Colombo and others (1965) that the presence of hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ) necessarily implies complete oxidation of magnetite to hematite, or Frankel (1966) that maghemite is usually associated with goethite. On the contrary, goethite, and also gibbsite, mostly occur in the matrix, or in weathered pisolites, where they may have been derived from hematite on the introduction of water and air (Threadgold, pers. commun.). Similar reasons may be advanced for the conversion of maghemite to hematite, but other factors, including the influence of  $\text{Al}_2\text{O}_3$ , may be involved.

The association of maghemite and hematite with pisolites suggest that these were originally formed by deposition of magnetite, and probably

also of hematite, by capillary activity, at or near the surface. Some of these materials may, in addition, have been leached out of and carried down from former iron-rich cover rocks. These propositions are further supported by the fact that the concentrations of maghemite and hematite decrease from top to base of the duricrust profile, just as the number and the colloform shapes of pisolites decrease with depth. These minerals and textures are virtually absent from the lower portions of the indurated zone of the duricrust profile. Alternatively, the maghemite and hematite in these lower portions may have all been converted to goethite and possibly also gibbsite, under the influence of ground water. The absence of the undehydrated forms of maghemite (lepidocrocite) from these lower portions, however, seems to rule out this possibility.

#### ACKNOWLEDGEMENT

This paper is slightly modified from a Ph.D thesis supervised by Professor G. H. Dury and financed by the Commonwealth of Australia Government and the Department of Geography, the University of Sydney. Comments by Professor Kevin Burke of the Department of Geology, University of Ibadan, have been found most useful.

#### REFERENCES

- BAKER, G. (1962) Detrital heavy minerals in natural accumulates. *Australas. Inst. Min. Metall. C.S.I.R.O. (Aust.) Monogr.* **1**, 146p.
- BASTA, E. Z. (1956) Some mineralogical relationships in the system  $Fe_2O_3$ - $Fe_3O_4$  and the composition of titanomaghemite. *Econ. Geol.* **54**, 698-719.
- BASTIN, E. S. (1950) Interpretation of ore textures. *Geol. Soc. Amer. Mem.* **45**, 101p.
- BOWIE, S. H. U. AND K. TAYLOR (1958) A system of ore mineral identification. *Mineral Mag.*, **99**, 337-345.
- BUDDINGTON, A. F., FAHEY, J., AND A. VLISIDIS (1963) Degree of oxidation of Adirondack iron oxides and iron-titanium oxide minerals in relation to petrogeny. *J. Petrology*, **4**, 138-169 [*Mineral. Abstr.* **17**, 324].
- CARROLL, D. AND N. K. JONES (1947) Laterite developed on acid rocks in southwestern Australia. *Soil Sci.*, **64**, 1-15.
- CHAYES, F. (1949) A simple point counter for thin section analysis. *Amer. Mineral*, **34**, 1-11.
- (1956) *Petrographical Modal Analysis*. John Wiley, New York, 113p.
- COLOMBO, V., F. GAZZARRINI, G. LANZAVECCHIA, AND G. SIRONI (1965). Magnetic oxidation: a proposed mechanism. *Science*, **147**, 1033 [*Mineral Abstr.* **17**, 667].
- FANIRAN, ADETOYE (1969) Duricrusts, relief, and slope populations in the Sydney district, New South Wales. *Nigerian Geog. J.* **12**, 53-62.
- FRANKEL, J. J. (1966) Some mineralogical observations on Australian lateritic rocks. *Aust. Jour. Sci.*, **29**, 115-117.
- GREBNEV, S. K. (1957) Production of low-arsenic concentrate on calcining magnetic concentrations of Kerch ores. *Sb. T. Nauch. Issled. Gornorud. Inst. Ukr. SSSR*, **1**, 420-427 [*Chem. Abstr.* **55**, 3355h].
- GRUNER, J. W. (1926) Magnetite-martite-hematite. *Econ. Geol.*, **21**, 375-393.
- HURLBUT, C. S. (1949) *Dana's Minerals and How to Study Them*. John Wiley, New York, 323p.

- ITO, KENZU (1959) The maghemite in the effluent fume from the open hearth furnace. *Ganseki Kobutsu Koch Gakkaishi*, 43, 203-207 [*Chem. Abstr.* 53, 187a].
- KULP, J. L. AND A. F. TRITES (1951) Differential thermal analysis of natural ferric oxides. *Amer. Mineral*, 36, 23-44.
- LOUGHMAN, F. C., R. E. GRIM, J. VERNET (1961) Weathering in some Triassic shales in the Sydney area. *J. Geol. Soc. Aust.* 8, 245-258.
- MILNER, H. B. (1962) *Sedimentary Petrography 4th. Ed., Vol. 2*, Allen and Unwin, London, 715p.
- MITCHELL, B. D. (1965) Thermal analysis in the investigation of naturally inorganic materials. *Proc. Soc. Anal. Chem.* 2, 170-172 [*Mineral Abstr.* 17, 454].
- OSBORNE, G. D. (1948) A review of some aspects of the stratigraphy, structure, and physiography of the Sydney basin. *Proc. Linn. Soc. N.S.W.*, 73, iv-xxxvii.
- SCHWERTMANN, U. (1959) Die fraktionierte Extraktion der freien Eisenvoxyde in Boden, ihre mineralogischen Formen und ihre Entstehungsweisen. *Z. Pflanzenernaehr., Dueng., Bodenk.* 84, 194-204 [*Mineral. Abstr.* 14., 246].
- WELFERS, K. (1957) Phasenbeziehungen in System  $Al_2O_3-Fe_2O_3-H_2O$ . *Z. Erzmetall* 20(2), 71-75.
- YOUNG, R. E. AND A. P. MILLMAN (1964) Microhardness and deformation characteristics of ore minerals. *Trans. Inst. Min. Met.* 73, 437-466.
- YUI, SHUNZO (1966) Decomposition of siderite to magnetite at lower oxygen fugacities—a thermochemical interpretation and geological implications. *Econ. Geol.* 61, 768-776 [*Abstr. N. Amer. Geol.* Dec. 1966, p. 1373].

*Manuscript received, April 29, 1969; accepted for publication, September 8, 1969.*