

A Mössbauer study of some Australian iron ore minerals

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ABSTRACT. Six specimens of Australian iron ore, three hematite-rich and three goethite-rich, have been investigated by Mössbauer spectroscopy at both 300 K and 4.2 K. The resulting spectra provide data relevant to crystallite particle size variations in the hematite and goethite, the extent of isomorphous replacement, and the existence within one specimen of a poorly defined goethite-like material.

THE mineralogy of iron ore is of considerable interest, both because of the widespread occurrence of such ores and because of their economic importance. The Australian continent contains very large deposits of high-grade iron ore and Australia is well known as the world's largest iron ore exporter. The ore is essentially hematite derived from the desilicification and iron-enrichment of banded iron formations of Proterozoic age. The major ore bodies are situated in the north west of Western Australia. This area also contains large deposits of pisolitic limonite of Tertiary age which have great potential as future commercial sources of iron ore.

The mineralogy of these ores has been described in a number of papers including Harms and Morgan (1964), Macleod (1966), Trendall and Blockley (1970), Ayres (1971, 1972), and Klein and Gole (1981). Although the techniques used by these investigators include optical microscopy, electron probe microanalysis, and X-ray diffraction, there are indications that not all of the mineralogical features of the ores have been determined (Ostwald, 1981*a*). Precise definition of iron ore mineralogy is not simply academic, as iron ore mineralogy (and microtexture) influences the blast furnace reduction of lump ore and the characteristics of iron ore

sinter (Ostwald, 1981*b*; Burghardt and Grover, 1981).

For this reason we have attempted to obtain additional information on the major minerals comprising Australian iron ores by the use of Mössbauer spectroscopy (e.g. Bancroft, 1973). This technique is particularly suitable for the study of the iron species present in soils and clays, as it is usually able to provide quantitative analyses for finely divided materials which are not amenable to X-ray diffraction investigation. One particularly useful feature of such measurements is the ability to determine the degree of isomorphous lattice replacement of the iron minerals, and Fysh and Clark (1982*a, b*) have recently published the data required in order to make such determinations for aluminous goethites and hematites.

Hematite and goethite are by far the most commonly occurring iron-containing minerals in Australian iron ores, and so we have carried out Mössbauer analysis on a variety of specimens which represent the major microtypes of these minerals as they occur in such ores.

Specimens examined. Six specimens, three composed essentially of hematite and three essentially of goethite were selected for this study. They were chosen from a range of iron ores because they represented differing modes of genesis of the minerals. Brief descriptions of the ores from which the specimens originated, and their locations, are given below.

(1) Marra Mamba ore (23° 30' S., 120° E.), Western Australia. This ore results from the desilicification and iron enrichment of Proterozoic banded iron formations containing abundant diagenetic iron silicates such as stilpnomelane and minnesotaite (Neale, 1975). The resulting iron ore contains abundant micro-fibrous goethite (fig. 1*a*) as well as smaller amounts of other oxides.

(2) Deepdale ore (22° S., 116° E.), Western Australia, was formed by colloidal deposition of iron oxides in the

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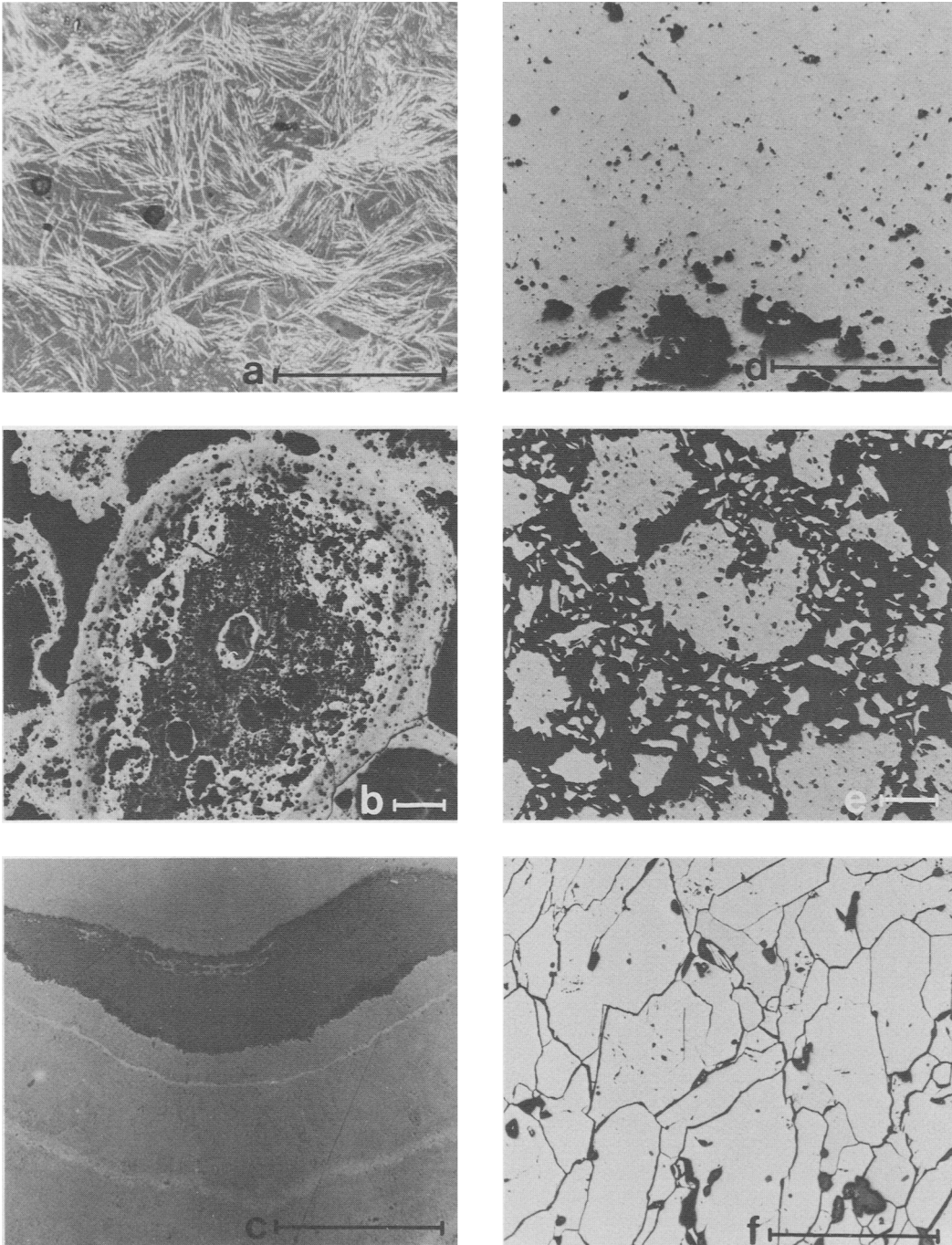


FIG. 1. Photomicrographs of polished sections of the specimens examined. The scale bar represents 20 μm in each case. (a) Marra Mamba. (b) Deepdale. (c) Whyalla. (d) Whaleback. (e) Whaleback scree. (f) Koolan.

form of pisoliths along river valleys during the Mesozoic. Erosion of the strata of essentially goethite pisoliths (fig. 1*b*) during the Tertiary resulted in mesasform deposits. (Harms and Morgan, 1964.)

(3) Metacolloidal goethite from the Middleback Ranges iron ore [Whyalla ore] (33° S., 137° E.), South Australia. A specimen of goethite occurring as a fracture-filling veinlet in the hematite ores of the above area was chosen as a third example of goethite. Microscopy shows the presence of colloform structures (fig. 1*c*) and suggests a metacolloidal origin.

(4) Polycrystalline hematite ore (fig. 1*d*), Mt. Whaleback deposit (23° 30' S., 120° E.), Western Australia. This ore is the result of desilicification and iron enrichment of Proterozoic banded iron formations, accompanied by subsequent recrystallization.

(5) Hematite scree ore, Mt. Whaleback deposit. This ore is comprised essentially of particles of the above polycrystalline hematite cemented by finely porous hematite (fig. 1*e*).

(6) Dense polycrystalline hematite ore, Koolan Island (16° 08' S., 123° 15' E.), Western Australia. This ore consists of mosaics of dense hematite grains (fig. 1*f*) and is apparently the result of iron enrichment of metamorphosed clastic sediments.

Mössbauer analysis. Spectra of the ores have been taken at both 300 K and 4.2 K, using the same methods as have been described previously (Fysh and Clark, 1982*a*). The shape of the Mössbauer spectra observed for Fe in hematite and goethite has been discussed extensively (Fysh and Clark, 1982*a, b*). In these earlier studies the Mössbauer spectra of synthetic hematites and goethites could be fitted by broadened Lorentzian lines, the broadening being the result of the presence of a range of Fe nuclear environments in the Al-substituted structures. In naturally occurring minerals, the range of Fe environments may be so large that the observed line shape is no longer well approximated by a Lorentzian. Fysh (1982) has shown that such spectra may be fitted by the pseudo-Lorentzian line shape

$$(1) \quad y(x) = \frac{1}{1 + \left(\frac{2x}{\Gamma}\right)^{\alpha}} \quad 2 \leq \alpha \leq 3.45$$

which is due to Price (1981). This line shape has been used to fit the spectra taken here.

Results and discussion

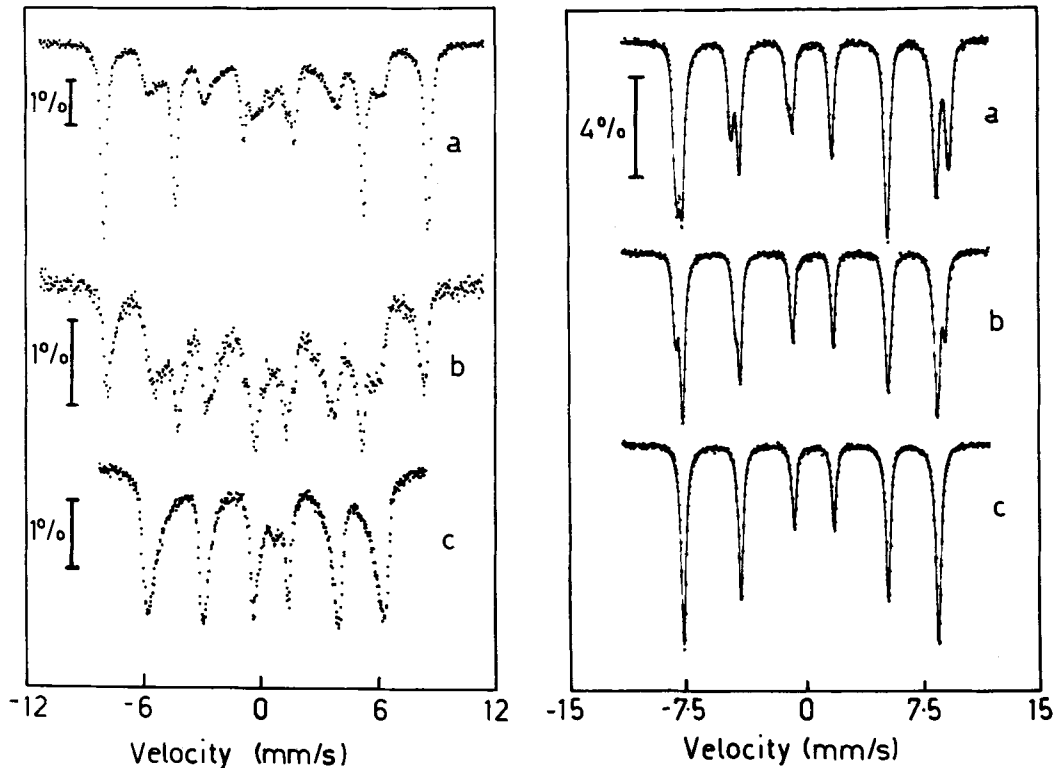
Goethitic ores. The room-temperature spectra of the Marra Mamba, Deepdale, and Whyalla specimens are shown in fig. 2. That of the Marra Mamba ore consists of the superposition of a sharp, well-defined magnetically split spectrum on a relaxed magnetically split subspectrum. The relaxed subspectrum has a much smaller splitting. There is also a doublet between the inner peaks of the relaxed spectrum, and the origin of this will be considered shortly. On the basis of their approximate splittings, the large and small field subspectra

may be identified as being due to hematite and goethite respectively. The spectrum of the Deepdale sample (fig. 2*c*) is qualitatively similar to that of the Marra Mamba ore, but the spectral lines of the outer (hematite) hyperfine split field are asymmetrically broadened. The relative goethite content is apparently greater for the Deepdale ore, and for the Whyalla specimen it appears that only goethite is present.

The asymmetrically broadened (relaxed) appearance of all of the goethite subspectra, as well as that of the Deepdale hematite subspectrum, is due to *superparamagnetic* (SPM) relaxation of the mineral microcrystals (e.g. Bean and Livingston, 1959; Dunlop, 1981; Fysh and Clark, 1982*a*). The magnetic moments of small single domain crystallites fluctuate rapidly, resulting in a reduced (or even zero) time-averaged magnetic field at the Fe nucleus. The asymmetry of the spectral lines is the result of the presence of a range of mineral domain sizes.

Some authors (e.g. Murad, 1979) have interpreted such spectra (obtained for goethites) as being a consequence of the isomorphous replacement of Fe in the crystal structure. However, both decreasing particle size (i.e. SPM) and lattice dilution have been shown (Fysh and Clark, 1982*a, b*) to have the same effect on room-temperature iron oxide spectra, so that the relative contribution of each can only be assessed by taking spectra at low ($\lesssim 77$ K) temperatures. Fluctuations in the magnetization direction of SPM particles are thermally activated, so that at low temperatures any reduction in hyperfine splitting from that of the pure mineral may usually be assumed to be due to isomorphous lattice replacement. In addition, the spectra are considerably easier to fit in the absence of relaxation effects.

Before considering the 4.2 K spectra of the goethitic specimens, however, it is worth noting that some information may be gained from the relaxed 300 K spectra. Thus, for example, the more relaxed shape of the hematite subspectra in the Deepdale ore spectrum cf. that for the Marra Mamba ore is a reasonable indication that the particle size of the hematite in the latter is somewhat greater. The 'particle size' referred to, however, relates to the size of coherent magnetic domains in the hematite. This may not always be coincident with that determined by microscopy and other techniques, due to the possible presence of dislocations, fine cracks, etc. which disrupt the magnetic continuity of 'large' grains. The relationship between true particle size and that determined by Mössbauer and X-ray diffraction methods has been further discussed by Amelse *et al.* (1981).



FIGS. 2 and 3. FIG. 2 (left). Room-temperature Mössbauer spectra of the goethitic specimens. (a) Marra Mamba. (b) Deepdale. (c) Whyalla. FIG. 3 (right). 4.2 K Mössbauer spectra of the same goethitic specimens.

The 4.2 K spectra of each of the samples are shown in fig. 3. Those of the Marra Mamba and Deepdale samples have been fitted with two magnetically split subspectra (representing hematite and goethite) and that of the Whyalla specimen by one. The relative increase in goethite hyperfine splitting between 300 K and 4.2 K is much greater than for hematite, due to the higher Néel temperature of the latter. The relative hematite and goethite contents of each specimen have been calculated using the recoil-free fraction data of Fysh and Clark (1982*a, b*), and are shown in Table I. The hematite in the Marra Mamba and Deepdale ores is, to within experimental uncertainty (± 2 mol %), indi-

TABLE I. Mössbauer data for goethitic samples

Specimen	Relative goethite content (%)	Relative hematite content (%)
Marra Mamba	63 \pm 2	37 \pm 2
Deepdale	76 \pm 2	24 \pm 2
Whyalla	100	0

cated to be pure, as is the goethite in the Deepdale and Whyalla specimens. The Marra Mamba goethite is aluminium substituted by 4 ± 2 mol %. These results are in good agreement with the electron probe microanalyses (EPMA) of these specimens (Table II), in which the Marra Mamba ore Al contents are significantly higher than those for Deepdale or Whyalla.

The relaxation effects seen in the room-temperature spectra of fig. 2 are thus largely due to the small particle size of the goethite in all of these ores, rather than lattice replacement. By comparison with the Mössbauer and X-ray determined particle size data of Fysh and Clark (1982*a*) it would appear that the mean particle size of the goethite present is of the order of 300 Å.

Also shown in Table II are the EPMA values obtained for a mineral phase in Marra Mamba ore which Ostwald (1981*a*) has briefly described as *ferrihydrite*. This material is characterized by low iron oxide totals (high water contents) in EPMA analyses and by a lack of electron diffraction patterns in fibrous crystallites under the electron microscope. The only X-ray diffraction pattern

TABLE II. Electron probe microanalyses of goethitic specimens (wt. %)

Specimen	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Total
Marra Mamba	90.2	2.3	0.7	93.2
Marra Mamba	88.1	1.8	0.4	90.2
Marra Mamba	86.5	3.2	1.1	90.8
Marra Mamba	88.2	2.6	0.8	91.6
Marra Mamba	86.2	3.4	1.6	91.2
Marra Mamba*	61.9	1.2	1.7	64.8
Marra Mamba*	69.2	1.2	0.7	71.1
Marra Mamba*	66.5	0.7	2.1	69.3
Deepdale	89.6	0.1	0.8	90.5
Deepdale	88.4	0.1	0.9	89.4
Deepdale	86.9	0.8	2.4	90.1
Deepdale	87.1	0.9	1.7	89.7
Whyalla	88.7	0.1	0.2	89.0
Whyalla	89.4	0.2	0.4	90.0

* Tentatively identified as ferrihydrite by Ostwald (1981a).

obtained for bulk samples is similar to that of goethite. The possible presence of a ferrihydrite phase in Marra Mamba ore has been further examined here, using Mössbauer techniques.

At 4.2 K the Mössbauer spectrum of ferrihydrite is reported to be a broadened magnetically split sextuplet, with a hyperfine splitting somewhat less than that exhibited by goethite (Murad and Schwertman, 1980). Numerous other reports (see Bowen, 1979) of the Mössbauer spectra of both synthetic and naturally occurring iron oxide gels, many of which are probably either ferrihydrite or of some very similar structure, also note magnetic ordering at low temperatures, with a hyperfine splitting less than that of goethite. As the 4.2 K spectrum of the Marra Mamba ore is well fitted by just two magnetically split subspectra, with the splitting of the smaller being about 5 kOe greater than the maximum value reported for any amorphous iron oxide, it seems fairly clear that there is no ferrihydrite in this sample, despite the low EPMA iron totals. However, the small central doublet appearing in the room-temperature spectrum of this ore does indicate the presence of a small quantity of either very fine SPM goethite or, possibly, ferrihydrite with such a low relative abundance that its magnetically split subspectrum is not resolved from that of goethite at 4.2 K.

In an attempt to further identify the source of the central doublet a second room-temperature spectrum of the Marra Mamba ore was taken over a smaller velocity range, giving a 'close-up' view of the centre of the spectrum (see fig. 4a). This spectrum consists of the central doublet, plus two

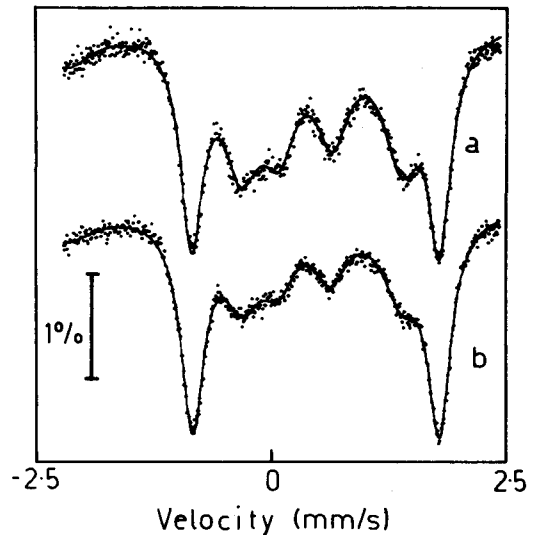


FIG. 4. Low-velocity room-temperature Mössbauer spectra of Marra Mamba ore. The similar decrease in the areas of the two central doublets with respect to the outer (hematite) doublet between the (a) untreated and (b) oxalate extracted ores indicates that they are both due to goethite.

more doublets which are the inner pairs of lines from the hematite and goethite hyperfine split fields. The spectrum has been fitted with three doublets, plus a singlet on the extreme left of the spectrum to account for the next absorption line out. The most interesting parameters of the fit are the quadrupole splitting of the inner doublet, which is 0.56 ± 0.01 mm/s, and its isomer shift, $+0.34 \pm 0.01$ mm/s. These values are very similar to those reported for fully relaxed SPM goethite at 300 K (Fysh and Clark, 1982a). Further, Murad and Schwertman (1980) have reported the quadrupole splitting of the doublet spectrum obtained at room temperature for ferrihydrite to be ~ 0.75 mm/s. Thus it appears that the room-temperature Mössbauer spectrum is also inconsistent with the presence of ferrihydrite in Marra Mamba ore.

Nevertheless, it was decided to examine the effects of a more conventional means of assessing the presence of ferrihydrite on the central doublet present in the 300 K Marra Mamba spectrum. Using the technique of Schwertman (1964), a 500 mg sample of the ore was extracted with one litre of pH = 3.0 acidified ammonium oxalate for 2 hours in a blackened plastic bottle which was constantly shaken. The sample was washed, and dried overnight on a Buchner funnel. A sample of approximately the same mass as the original ore specimen was analysed at the same low velocity as

before (see fig. 4b). The fitting procedure was the same as that employed for the previous run, and reveals a 45% decrease in the ratio

goethite doublet area/hematite doublet area

and a 46% decrease in the ratio

inner doublet area/hematite doublet area.

The other parameters of the fit are unchanged. As the rate of leaching of the inner doublet iron and the goethite are nearly the same, it appears that the previous identification of this phase as finely divided SPM goethite is correct. However, that any goethite is removed at all is hard to explain. Although acidified ammonium oxalate is known to leach goethite in the presence of light, extreme care was taken to exclude all light while the ore was in contact with the solution. Further, the very similar decrease in spectral area for the two different goethite particle sizes seems to indicate that the effect of the oxalate is, at least for the very fine goethite present here, independent of particle size. In order to measure more accurately the decrease in goethite content, the extracted specimen was analysed at 4.2 K (see fig. 5). The

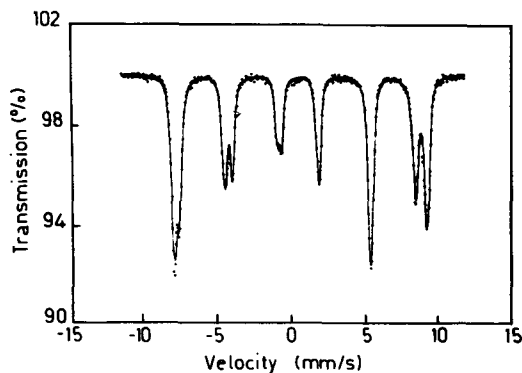


FIG. 5. 4.2 K Mössbauer spectrum of oxalate extracted Marra Mamba ore.

decrease in intensity of the goethite subspectrum relative to that of the hematite can be seen quite clearly by comparing fig. 5 with the 4.2 K spectrum of Marra Mamba ore in fig. 3. Fitting of the spectrum reveals a 43% decrease in goethite content relative to hematite, in excellent agreement with the estimate made on the basis of the room-temperature spectra. It is worth noting that the decrease in goethite content has been calculated relative to the hematite content, which may also have been affected to some extent by the oxalate treatment. This seems unlikely, however, particularly as both the 300 K and 4.2 K spectra indicate

the hematite present to be of a reasonably large particle size (see later section).

One possible explanation for the dissolution of the goethite by the acidified ammonium oxalate treatment is that traces of Fe^{2+} may be present in the ore, catalysing the reaction. A similar effect was observed in goethitic bog iron ores (Schwertman, 1959) where the presence of siderite as a source of Fe^{2+} resulted in complete dissolution of the ore under similar conditions. Numerous other workers (Baril and Bitton, 1969; McKeague *et al.*, 1971; Gamble and Daniels, 1972; Taylor and Schwertman, 1974; Rhoton *et al.*, 1981) have also noted that the presence of Fe^{2+} leads to increased iron oxide solubility in acidified ammonium oxalate. However, no ferrous iron contribution was noted in the well-resolved 4.2 K spectrum of the Marra Mamba ore, either in clay or oxide minerals. Although Mössbauer spectroscopy is not sensitive to very low (≤ 1 wt. % Fe_2O_3) iron concentrations, especially if the resultant spectrum is magnetically split or nearly coincident with a much stronger absorption line, it is very doubtful that a quantity of Fe^{2+} sufficient to catalyse the dissolution of the goethite to the extent observed has remained undetected in the specimen.

Borggard (1976) has pointed out that in numerous earlier papers (referenced therein) the ability of acidified ammonium oxalate to remove 'poorly crystallized' hematite and goethite has been indicated, and goes on to compare the action of this reagent with that of EDTA on a synthetic mixture of amorphous and crystalline iron oxides. He notes the rapid oxalate extraction of the amorphous (as defined by X-ray and EDTA determinations) fraction, and the subsequent removal of the crystalline material also. In the light of this and the earlier studies Borggard cites, it appears that the extraction of the goethite from Marra Mamba ore is largely due to its small particle size. It may well be that the material extracted would appear amorphous to X-ray or electron diffraction, and the results presented indicate the ability of the Mössbauer technique to differentiate between finely divided oxide phases.

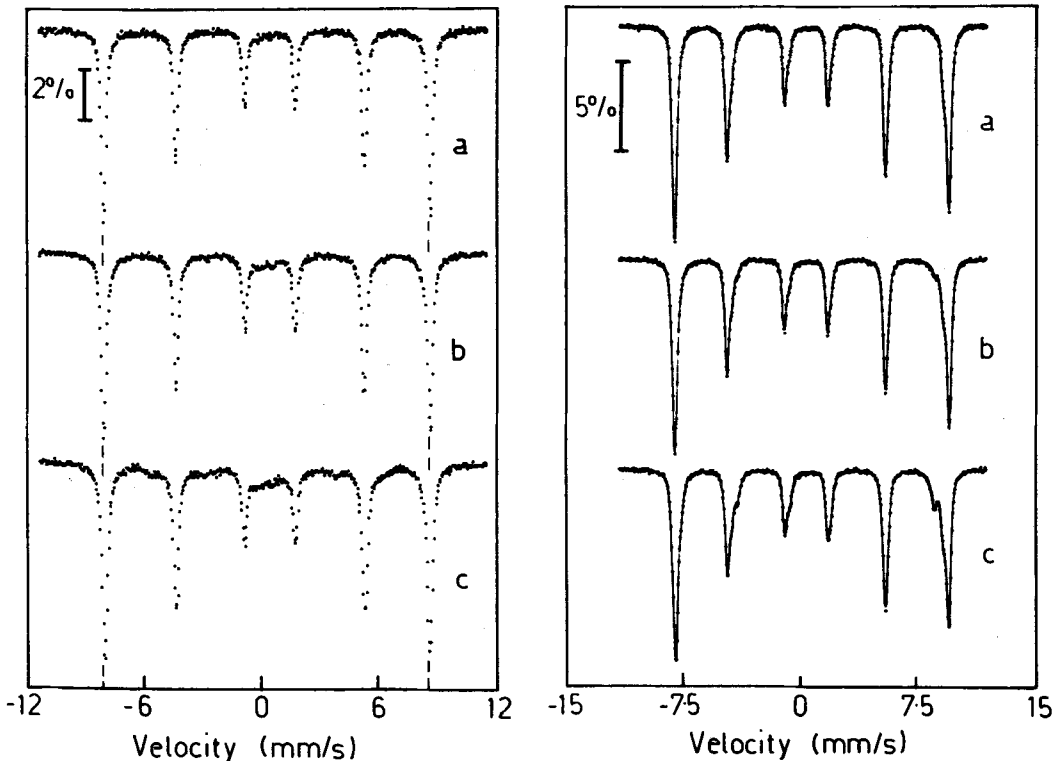
It seems likely that excess water associated with such fine goethite could account for the low EPMA Fe totals observed for the Marra Mamba ore microtypes. Fey and Dixon (1981) have shown that water may actually enter the lattice of poorly crystalline goethite, causing a lattice expansion. Similarly, Wolska (1981) has investigated the presence of bound water in hydrohematite. It has been noted (Fysh and Clark, 1982b) that such bound water probably leads to a reduction in the magnetic splitting of the Mössbauer spectrum of hematite because of the cation vacancy which is necessary

to ensure charge neutrality. A similar reduction would be expected for goethite containing lattice-bound water. Thus it seems likely that at least part of the reduction in 4.2 K goethite hyperfine splitting observed for the Marra Mamba specimen may be associated with the presence of lattice-bound water.

Hematitic ores. The room-temperature spectra of the Koolan, Whaleback, and Whaleback scree ores all indicate that the predominant iron mineral present is hematite (see fig. 6). In each case the hematite spectral lines are similar to those of the Marra Mamba ore, indicating no relaxation due to fine particle size. It has already been pointed out that this is not the case for the Deepdale ore, for which the room-temperature hematite Mössbauer absorption lines are asymmetrically broadened to a considerable extent (see fig. 2). The presence of small quantities of SPM goethite in the Whaleback and Whaleback scree ores makes fitting their room-temperature spectra difficult, and once again quantitative analysis has been performed at 4.2 K. The spectra taken at this temperature (see fig. 7) are somewhat different to those of the Marra

Mamba and Deepdale ores in that there are now three magnetically split subspectra present (most easily seen for the Whaleback scree ore). Examination of the 4.2 K spectra of the Marra Mamba and Deepdale specimens (fig. 3) reveals that the line positions and total splitting of the hematite subspectra in each are quite different. In fact, fitting of the spectra in fig. 7 indicates that the outer two magnetically split subspectra in the hematitic specimens are *both* due to hematite, which is distributed between the two different magnetic states already seen to occur separately in the Marra Mamba and Deepdale ores. The parameters describing the two hematite subspectra are (inner) $\Delta = -0.18 \pm 0.02$ mm/s, $\delta = +0.49 \pm 0.02$ mm/s, $H_{\text{int}} = 536 \pm 1$ kOe and (outer) $\Delta = +0.35 \pm 0.02$ mm/s, $\delta = +0.49 \pm 0.02$ mm/s, $H_{\text{int}} = 543 \pm 1$ kOe, and these indicate that they are due to hematite which is above and below the *Morin* transition respectively (Fysh and Clark, 1982b).

The Morin transition is a magnetic re-ordering which occurs in well-crystallized hematite at about 265 K, and consists of a 90° flip in the orientation of the magnetic moments of individual iron atoms.



FIGS. 6 and 7. FIG. 6 (left). Room-temperature Mössbauer spectra of the hematitic specimens. (a) Koolan. (b) Whaleback. (c) Whaleback scree. FIG. 7 (right). 4.2 K Mössbauer spectra of the same hematitic specimens.

In passing through the transition (from high temperature to low temperature) the hyperfine splitting increases by ~ 7 kOe, and the quadrupole splitting is changed in sign and nearly doubled in magnitude. The effects of particle size and Al substitution on the Morin transition temperature T_M have been discussed elsewhere (Fysh and Clark, 1982b). Both decreasing particle size and increasing Al substitution depress T_M , and Ninninger and Schroerer (1978) have estimated that hematite particles below 200 Å in diameter would not exhibit a Morin transition at all. Thus, it would appear that a variable fraction of the hematite in the iron ores studied is in a very finely divided state. Surprisingly, the only ores containing either *only* 'coarse' or 'fine' (as defined by whether or not $T_M > 4.2$ K) hematite are the two goethitic ores. In all of the hematitic ores there is a range of particle sizes, and the relative goethite and coarse and fine hematite contents of each are given in Table III.

TABLE III. Mössbauer data for hematitic samples

Specimen	Relative goethite content (%)	Relative fine hematite content (%)	Relative coarse hematite content (%)
Koolan	2 ± 2	19 ± 2	79 ± 2
Whaleback	7 ± 2	20 ± 2	73 ± 2
Whaleback scree	21 ± 2	19 ± 2	59 ± 2

Just as for the goethite previously discussed, it is necessary to consider the separate effects of particle size and Al substitution on the spectra. The hematites in all of the iron ores studied have exhibited the full magnetic splitting of pure hematite at 4.2 K, indicating no Al substitution. However, a previous study (Fysh and Clark, 1982b) has shown that the magnetic splitting of 'high-temperature' hematites is not reduced by Al substitution when measured at 4.2 K. This was found to be the case for any hematite subjected to temperatures of about 900 °C, and is thought to be related to a superstructural *c*-axis ordering occurring at these temperatures. The depression of T_M by Al substitution still takes place, with hematites containing greater than about 10 mol % Al exhibiting no Morin transition down to 4.2 K, but exhibiting a magnetic splitting of about the same magnitude as pure hematite at this temperature.

Fortunately, even these high-temperature hematites exhibit a reduction in magnetic splitting with increasing Al content at 300 K, so that if the full hyperfine splitting of 516 kOe is measured at this

temperature then the reduction of T_M observed can be attributed solely to particle size effects. The vertical dashed lines in fig. 6 correspond to the outer lines of the hyperfine split spectrum of pure hematite at 300 K, and indicate clearly that there is no appreciable Al substitution of the hematite in any of these ores. This is confirmed by EPMA. The room-temperature magnetic splitting of the hematite in the Deepdale and Marra Mamba ores is also equal to that of pure hematite. Further, the quadrupole splittings of the spectra in fig. 6 are all in the range -0.19 ± 0.02 mm/s, indicating that the hematite in each is in the *c*-axis disordered state (Fysh and Clark, 1982b). This would be expected, as none of the ores examined are thought to have ever been subjected to extreme (> 900 °C) temperatures during formation.

Thus, because of the varying proportion of hematite above and below the Morin transition it would appear that there is a gradation in hematite particle size within the iron ores studied. The hematite having the greatest average particle size is that in the Marra Mamba ore, with an increasing fraction of very fine (≤ 100 – 200 Å in diameter) hematite in the Koolan, Whaleback, and Whaleback scree ores, and *all* of the hematite in the Deepdale ore being fine. Within the hematitic ores there appears to be a fairly constant proportion of fine hematite, with the main variation between the samples studied being the goethite content.

Conclusions

Mössbauer spectroscopy of the hematite and goethite of Australian iron ores has revealed a number of features of their mineralogy. The goethite of the ores is typically less than ~ 300 Å in particle size, and is in some instances part aluminium substituted. The ability of oxalate to distinguish between very fine particle goethite and ferrihydrite has been examined. Hematite in the ores was found to be non-aluminous; to occur in a range of particle sizes and to not have been subjected to temperatures in excess of ~ 900 °C.

The possible influence of iron mineral lattice-bound aluminium on sintering in the iron-making process has already been considered (Stenlake *et al.*, 1981), and we are currently employing Mössbauer techniques to further investigate both this and the consequences of other aspects (e.g. particle size, hematite/goethite content) of ore mineralogy on ore utilization.

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REFERENCES

- Amelse, J. A., Arciri, K. B., Butt, J. B., Matyl, R. J., Schwartz, L. H., and Shapiro, A. (1981) *J. Phys. Chem.* **85**, 708-11.
- Ayres, D. E. (1971) *Proc. Aus. I.M.M.* **238**, 47-58.
- (1972) *Econ. Geol.* **67**, 1214-33.
- Bancroft, G. M. (1973) *Mössbauer Spectroscopy*, John Wiley and Sons, New York.
- Baril, R., and Bitton, G. (1969) *Can. J. Soil Sci.* **49**, 1-9.
- Bean, C. P., and Livingston, J. D. (1959) *J. App. Phys.* supplement to **30**, 120S-9S.
- Borggard, O. K. (1976) *J. Soil Sci.* **27**, 478-87.
- Bowen, L. H. (1979) *MERDJ*, **2**, 76-94.
- Burghardt, O., and Grover, B. (1981) *Erzmetall*, **34**, 311-16.
- Dunlop, D. J. (1981) *Phys. Earth Planet. Inter.* **26**, 1-26.
- Fey, M. V., and Dixon, J. B. (1981) *Clays Clay Minerals* **29**, 91-100.
- Fysh, S. A. (1982) *Mössbauer Spectroscopy of Bauxite and Synthetic Bauxitic Iron Minerals*. Ph.D. thesis, Monash Univ.
- and Clark, P. E. (1982a) *Phys. Chem. Minerals*, **8**, 180-7.
- (1982b) *Ibid.* (in press).
- Gamble, E. E., and Daniels, R. B. (1972) *Soil Sci. Soc. Am. Proc.* **36**, 939-43.
- Harms, J. E., and Morgan, B. D. (1964) *Proc. Aus. I.M.M.* **212**, 91-124.
- Klein, K., and Gole, M. J. (1981) *Am. Mineral.* **66**, 507-25.
- McKeague, J. A., Brydon, J. E., and Miles, N. M. (1971) *Soil Sci. Soc. Am. Proc.* **35**, 33-8.
- Macleod, W. N. (1966) *Geol. Survey West. Aust. Bull.* **117**.
- Murad, E. (1979) *Mineral. Mag.* **43**, 355-61.
- and Schwertman, U. (1980) *Am. Mineral.* **65**, 1044-9.
- Neale, J. (1975) In *Economic Geology of Australia and Papua-New Guinea*, Vol. 1, Metals. Aust. I.M.M. 1975.
- Ninninger, R. C., and Schroerer, D. (1978) *J. Phys. Chem. Solids*, **39**, 137-44.
- Ostwald, J. (1981a) *BHP Tech. Bull.* **25**(1), 4-12.
- (1981b) *Ibid.* **25**(1), 13-20.
- Price, D. C. (1981) *Austral. J. Phys.* **34**, 51-6.
- Rhoton, F. E., Bigham, J. M., Norton, L. D., and Smeck, N. E. (1981) *Soil Sci. Soc. Am. J.* **45**, 645-9.
- Schwertman, U. (1959) *Z. Pflanzenern. Düng., Bodenkunde*, **84**, 194-204.
- (1964) *Ibid.* **105**, 194-202.
- Stenlake, R. W., Pepper, M. D., and Ostwald, J. (1981) *3rd Int. Symp. on Agglomeration*, Nuremberg.
- Taylor, R. M., and Schwertman, U. (1974) *Clay Minerals*, **10**, 289-98.
- Trendall, A. F., and Blockley, J. G. (1970) *Geol. Survey West. Aust. Bull.* **119**.
- Wolska, E. (1981) *Z. Kristallogr.* **154**, 69-75.

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