

# Characterisation of Australian Iron Ores Using $^{57}\text{Fe}$ NMR

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The  $^{57}\text{Fe}$  nuclear magnetic resonance in the mineral hematite has been measured in Australian iron ore samples categorised according to their petrology. Variable line shift and line broadening occurs for different ore categories, which may be useful for ore characterisation. The variation in response may be qualitatively explained by assuming effects on hyperfine field normally associated with grain size, impurities and crystalline stress.

## 1. Introduction

The petrology of iron ore strongly impacts on bulk handling characteristics, downstream metallurgical performance and ore value. For example, at the mining stage, the ratio of hematite and goethite in primary ore feed is important in determining the ratio of lump and fine product, which in turn affects the ore value. At the iron making stage, the presence of very fine or porous material can impact on blast furnace performance. It would be of significant benefit to the industry if key aspects of the ore petrology could be assessed in real time to control processing. On line analysis would allow for optimised crushing control, ore blending and stockpiling to mitigate variations in feed petrology. However, there currently exist few methods suitable for on-line characterisation of petrology.

One method possibly suited to on-line bulk iron ore characterisation is nuclear magnetic resonance (NMR). Some economically important iron minerals exhibit separate resonances at room temperature without need for application of an external static magnetic field. These resonances arise because of internal magnetic ordering associated with hyperfine interactions. NMR measurement allows the use of non-contact large volume sensors, without need for sample preparation, to provide a bulk ore measurement. The work described here involves an initial appraisal of the use of NMR for Australian iron ore characterisation, particularly applied to hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), a major iron bearing mineral.

## 2. $^{57}\text{Fe}$ NMR in Hematite

Hematite is an antiferromagnet with Néel temperature 960 K, resulting in a static local field at the iron nucleus of approximately 52 T at room temperature [1].  $^{57}\text{Fe}$  nuclei ( $I = 1/2$ ) in each sublattice give rise to one single NMR transition ( $\sim 71.3$  MHz at 294 K), unaffected by quadrupole effects. At temperatures above  $\sim 260$  K (the Morin transition) the antiferromagnetic sublattices are slightly canted, resulting in an associated weak ferromagnetism. Natural samples may in addition exhibit a defect moment. The weak ferromagnetism in hematite allows the formation of magnetic domains. In turn, the response to applied radiofrequency field at the NMR transition frequency yields a signal typically several orders of magnitude larger than expected for material without domains through an enhancement effect [2,3]. This allows relatively straightforward detection of the NMR response, which would otherwise be effectively unobservable owing to the very low NMR receptivity of the  $^{57}\text{Fe}$  isotope. Similar enhancement is observed in the magnetically ordered iron minerals magnetite and maghemite.

The aim of this initial study is to assess whether NMR response varies for iron ore groupings commonly mined in Australia. These groupings relate to macroscopic parameters such as porosity, hardness, friability, grain size, presence of various hematite pseudomorphs and other minerals. In magnetic materials the domain structure, hyperfine field strength and field distribution is typically dependent on crystalline stress, grain size, and level of defects and impurity [4]. Domains and their walls exhibit different levels of enhancement, respond differently to variation in radiofrequency power and can have slightly different transition frequencies. It may therefore be feasible to link NMR response to macroscopic parameters of interest, which could be exploited for ore characterisation.

### 3. Experiment

Ore samples were sourced from the Hamersley province, Western Australia. The samples were classified into groupings listed in Table 1. Classification was conducted by industry geologists by means of visual inspection. The groupings follow standard classification schemes used in the mining industry based on different petrological features. Martite, referred to in Table 1, is a pseudomorph of hematite (hematite replacement after magnetite). In general, groups A-D are harder, blue grey or steel grey in colour, E-F are of lesser hardness and red brown with minor yellow in colour, while G is soft and yellow. The exact mineralogical mix of each sample is unknown but nominally dominated by hematite, except for group G which has significant goethite. All samples were available in the form of coarse powders less than 1 mm sizing. An additional sample of high purity hematite was sourced from the Middleback Ranges, South Australia for use as a comparison sample. This sample was a 150g polycrystalline fragment, very hard, smooth and dark grey-blue in colour. A subsample of the fragment was micronised for room temperature Mössbauer analysis at the University of NSW at ADFA. The Mössbauer spectrum was well fitted with just a single sharp sextet, yielding a local field of 52.04 T. This is in line with the previously measured local field for hematite.

Table 1. Ore groupings represented by samples.

Grouping	Features
A	Very hard, dense, fine grained hematite, smooth
B	Hard microplaty hematite, thick interlocking plates, coarse grained
C	Hard martite, very dense, fine grained, microscopic pores
D	Hard martite/hematite, dense, fine grained, macroscopic pores
E	Medium hardness, hematite matrix+goethite infill
F	Hard, martite matrix+goethite infill
G	Friable soft, martite grains with goethite infill, very porous

The  $^{57}\text{Fe}$  NMR transition was excited using a CSIRO developed conventional pulsed NMR spectrometer, with applied power up to 1 kW and probe bandwidth of approximately 500 kHz. Spin echoes were excited using the Hahn spin echo sequence and averaged over several minutes, with resulting typical integrated signal to noise ratios of over 50. Sample volumes were 20 cm<sup>3</sup>. Over the entire set of results, sample temperature was 294 K, controlled within a 3 K range.

### 4. Results

NMR signals were identifiable in all samples, using power levels from 1-1000 W and Hahn pulse separations of up to 30 ms. Fig. 1(a) shows the echo magnitude with respect to applied radiofrequency power level at 71.30 MHz for the Middleback Ranges sample. Fig.

1(b) shows the hematite spin echo magnitudes for the cases of 11 W and 91 W power. These results were obtained using pulse widths of 10  $\mu\text{s}$  and 20  $\mu\text{s}$  for the 90 and 180 degree pulses of the Hahn sequence respectively, with a pulse separation of 200  $\mu\text{s}$ . Transverse decay times in samples A-F were measured, indicating the existence of two distinct decay periods; a fast decay of about 1 ms, and a longer lived decay of about 15 ms. The relatively short echo duration in these samples indicates that the linewidth is dominated by inhomogeneous broadening.

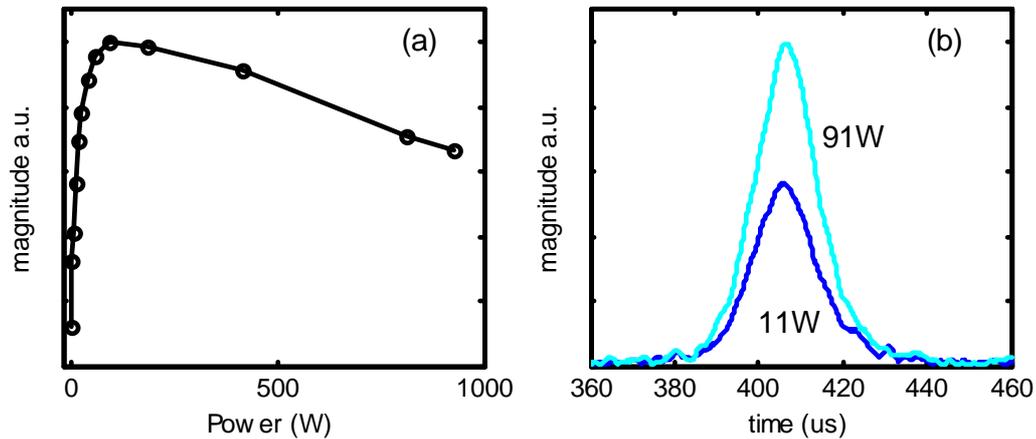


Fig. 1. (a) Hematite response in the Middleback Ranges sample, versus applied radiofrequency power. (b) Examples of Hahn echoes at 11 W and 91 W.

An experiment was performed to measure the spectral distribution of the echo response. Power was fixed at 91 W. The pulse separation of 200  $\mu\text{s}$  was also fixed, therefore encompassing the measurement of spins having short transverse decay time. Echo signals were measured over a range of carrier frequencies, typically stepped at 50 kHz intervals. Fig. 2 illustrates the spectral distribution for the echo response for samples A-G. As the actual relative level of hematite is unknown for each sample, the spectral response has been normalised across all samples.

Several observations can be drawn from Fig. 2. The hardest hematites of Groups A and B exhibit the narrowest spectral distribution and peak response at the highest frequency. The peak response and linewidth in these samples aligns with that of the Middleback Ranges sample. Groups C and D, containing significant martite, have peaks at lower frequency. Groups E and F, containing goethite co-crystallisation, have more complicated multiple peak structure, and stronger broadening. Finally, Group G with higher levels of co-crystallised goethite, exhibit peak response at the lowest frequency.

The frequency shift and broadening observed in the samples could be explained by a number of effects on local field. It is well documented in Mössbauer studies of hematite that both small grain size (through the onset of superparamagnetism) and aluminium substitution tends to reduce the peak local field and broaden the distribution. Further planned assessment of samples by other methods will be required to describe the causes of line variation. However, several comments concerning the samples may be made. Firstly, it is known generally that the mass fraction associated with ultrafine particles ( $< 1\mu\text{m}$ ) is relatively low in the types of ore textures studied, even for friable material like Group G. On the other hand superparamagnetism in hematite usually occurs for grain size well below 100 nm; therefore this effect would presumably be unimportant for the samples studied. Secondly, the known total aluminium contents typical of the ore types studied are not incompatible with the aluminium substitution level required to induce the observed line shifting. For example,

within Group G, an assumed aluminium substitution for iron in hematite of about 1% could explain the observed peak shift [1]. However, in recent measurements of other samples where elemental assays are available (via X-ray fluorescence), strong hematite line variation has emerged despite very low total aluminium content in the samples (< 0.3%). This would suggest that there are additional sources of line variation not directly related to very small grain size or impurity substitution.

The shifting and broadening of  $^{57}\text{Fe}$  NMR signals observed in a number of different samples of natural hematite is encouraging for ore discrimination. Future experiments are planned to elucidate the causes of line variation in natural samples, as well as to extend characterisation to other iron phases using parallel NMR measurements.

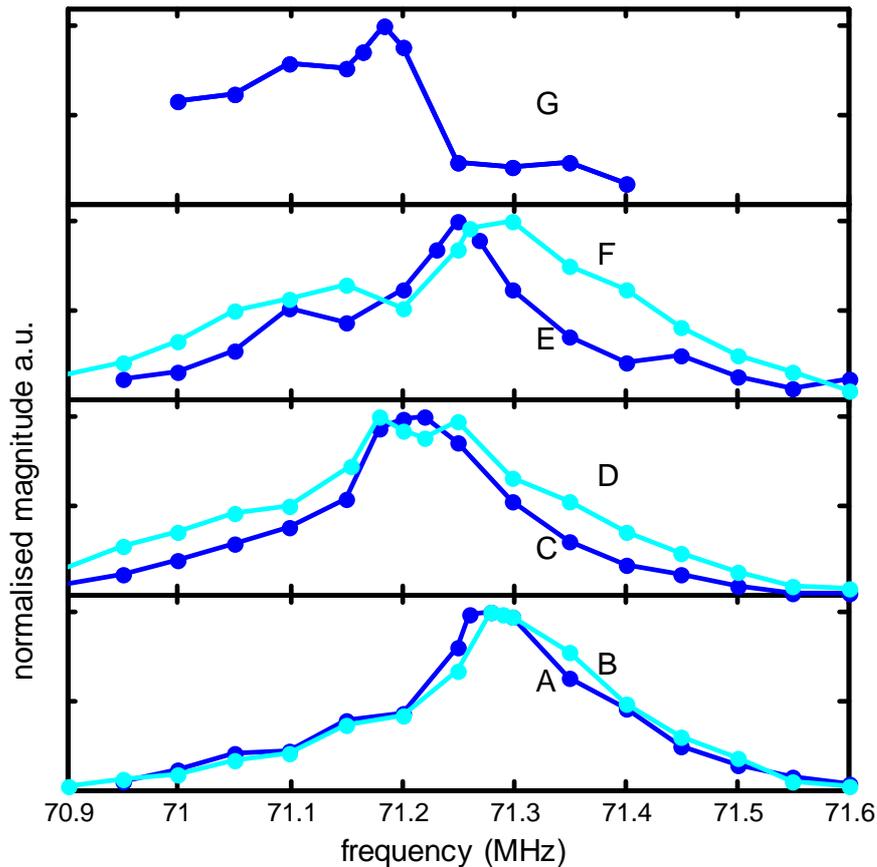


Fig. 2. Spectral distribution of echo response in samples A-G. Each curve is normalised to peak response.

### Acknowledgments

The authors acknowledge useful discussions with Emeritus Prof. Stewart Campbell and Assoc. Prof. Glen Stewart, University of NSW at ADFA. The authors are indebted to Assoc. Prof. Glen Stewart and Mr Banchachit Saensunon for kindly providing Mössbauer analysis on the Middleback Ranges hematite sample.

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