Mössbauer spectroscopy of green shale from banded iron formation

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Abstract. A green shale from the Precambrian banded iron formation of the Bonai Range, Eastern India, is examined by transmission Mössbauer spectroscopy. The constituent phases are identified to be chlorite, siderite and magnetite. The fractional resonance area of each constituent is computed and the ferrous-ferric ratio determined. The variation of this ratio over the sample is examined. Intensity of the magnetite lines reveals that deviation from stoichiometry is negligible. The observations suggest a transition within short range from silicate-rich facies to carbonate-oxide-rich facies in the studied section.

Keywords. Mössbauer spectroscopy; green shale; Precambrian banded iron formation; chlorite, siderite, magnetite; ferrous-ferric ratio; stoichiometry.

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1. Introduction

Information about coexisting iron-bearing phases in a rock can be gathered through Mössbauer spectroscopy (Raclovsky and Egiazorov 1975). Such data may throw light on phase relations, genesis and ultimately on the evolution of iron-bearing formations. The composition of the iron-bearing phases in an iron formation reflects the acid-alkali and oxidation-reduction conditions of the depositional basin. Earlier work has led to the recognition of four distinct chemical facies of iron formation (James 1954), namely, the oxide (almost solely hematite and magnetite), carbonate (dominantly siderite), silicate (chiefly iron phyllosilicate) and sulphide (pyrite) facies. (The term facies in the present case refers to the lithological character of a sedimentary rock unit as expressed by diagnostic mineralogy in relation to depositional environment). The iron formations are metastable chemical systems at the time of their deposition. They may undergo various stages of modifications through recrystallization at relatively low temperature and pressure conditions. They may also be subjected to changes under high pressure and temperature conditions in a metamorphic environment. Thus the processes may produce distinct diagenetic and metamorphic mineral assemblages. A mineral may, however, form and persist over a wide range of physicochemical conditions in the course of transformation of the original sediments into a metamorphic rock. Also superficial alterations may take place in the exposed parts under normal weathering and near-surface conditions.

Mössbauer spectra of the minerals orthopyroxene, calcic clinopyroxene and epidotes from their natural occurrences collected from different parts of India have been studied at Rajasthan University by Tripathi *et al* (1977). They were interested in variations of Mössbauer spectra as related to structure. We shall focus here on different iron-bearing minerals from a typical area of banded iron formations (BIF) (Jones 1934) and try to gather data of geological interest by studying phase assemblages, their spatial variation, the Fe^{2+}/Fe^{3+} ratio and its change. With this in view we report our measurements of Mössbauer spectra of a green shale at room and liquid nitrogen temperature. Subsequent studies will be extended to other distinct facies of BIF.

2. Experimental details

The sample of a green shale, about 20 cm long, was collected from the western edge of the Bonai Range (also known as the Iron Ore range) near Kiriburu (lat. 22°04′N; long. 85°16′E) in Singbhum district, Bihar. The green shale horizon (about 14 m thick) marks a gradual passage from the underlying tuffaceous Lower Shale formation (volcano-genic) to the overlying BIF (oxide facies) and is partly interbedded with the latter. The studied sample represents the base of oxide facies from the BIF typically developed in parts of the Bonai Range.

The lower end of the sample was green in colour and contained mostly chlorite (hydrated magnesium ferrous alumino silicate). The other constituents were carbonate and magnetite. This end was weakly magnetic. The other end of the sample (in the direction of younging) was strongly magnetic and contained relatively more magnetite. Three portions of the rock were examined: the chlorite-rich part, the middle part and the magnetite-rich part to understand the relative variations in coexisting phases. The samples were ground for examination in an ECIL MBS 35 Mössbauer spectrometer coupled to a 2×256 channel recording apparatus constructed by D Das following the design developed at the Tata Institute of Fundamental Research, Bombay. The low temperature data were taken with the samples mounted on a cold finger in contact with liquid nitrogen.

3. Results

Figure 1 shows the Mössbauer spectra at room temperature of the three portions noted above. The spectra are analyzed by LGFIT 2 computer program of von Meerwall (1975). Figure 1a is dominated by the doublet of chlorite; there are weak lines due to small amounts of siderite $FeCO_3$ and magnetite Fe_3O_4. The measured values of the Mössbauer parameters of chlorite are given in table 1, which also gives the values reported by Blaauw *et al* (1980). The values are in agreement confirming our identification. Iron in chlorite is present in the Fe^{2+} state.

Figures 1b and 1c show the spectra of the central and top parts of the sample at room temperature. Besides the chlorite doublet there is a narrower doublet which is identified to be due to siderite by comparing with pure siderite spectrum. The IS (w.r. to α-Fe) and QS values measured are 1.17 ± 0.08 and 1.82 ± 0.08 mm/sec, respectively. The values reported by Ono and Ito (1964) are 1.38 ± 0.02 (w.r. to stainless steel) and 1.87 ± 0.10 mm/sec respectively. At liquid nitrogen temperature (figure 2) the QS is 2.05
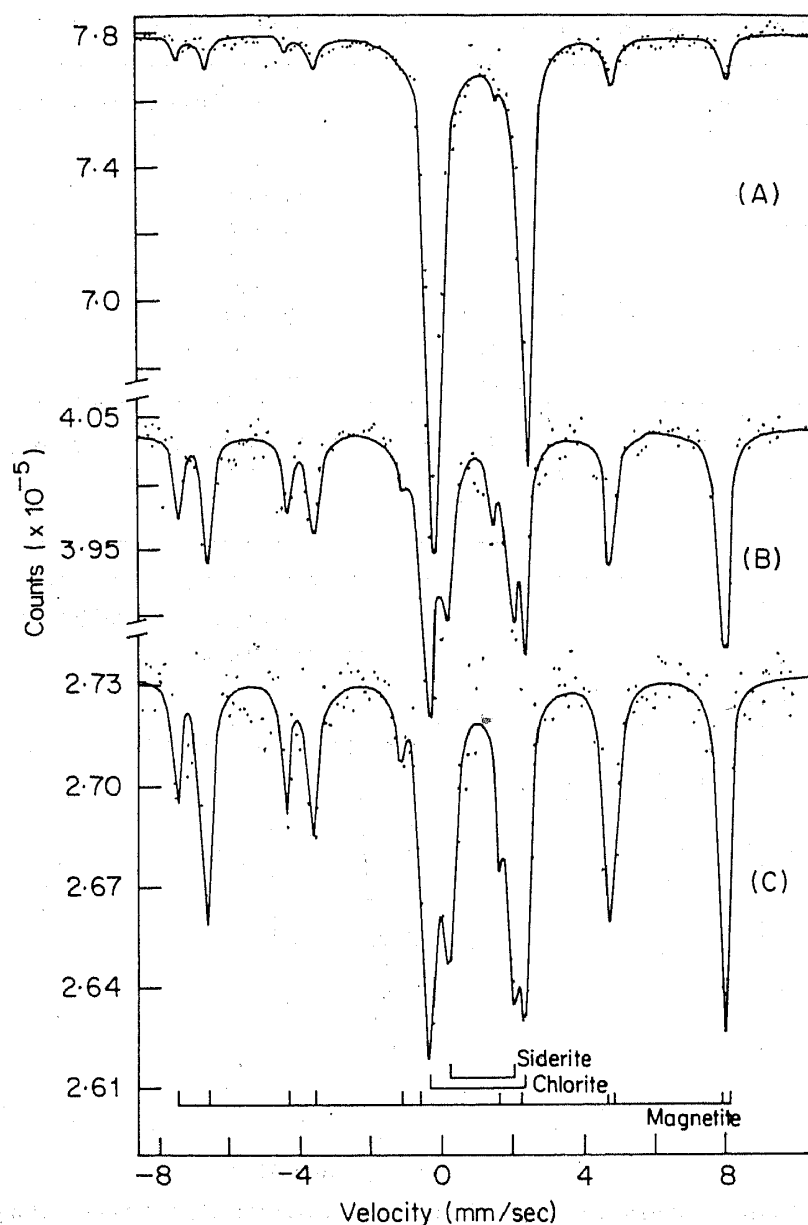
Figure 1. Mössbauer spectra of the green shale: (A) chlorite-rich, (B) middle and (C) magnetite-rich part at room temperature.

± 0.08 mm/sec as compared with their value 2.12 ± 0.10 mm/sec. The agreement is fair. Iron in siderite is, of course, in the Fe^{2+} state.

The remaining peaks in figure 1 are due to magnetite Fe_3O_4, the intensities of the lines increasing with the magnetization of the sample. At room temperature, the IS of the A and B sites are 0.28 ± 0.08 mm/sec and 0.75 ± 0.08 mm/sec, respectively. The magnetic fields at the A and B sites are, respectively, 488 ± 10 kOe and 467 ± 10 kOe. These values are in fair agreement with typical values reported: IS (A) $= 0.25 \pm 0.08$ mm/sec, IS (B) $= 0.65 \pm 0.02$ mm/sec, H (A) $= 493 \pm 3$ kOe, H (B) $= 460 \pm 1$ kOe at 298°K (Evans and Hafner 1969) or IS (A) $= 0.266 \pm 0.010$ mm/sec, IS (B) $= 0.665 \pm 0.010$ mm/sec, H (A) $= 491 \pm 0.5$ kOe, H (B) $= 460.7 \pm 0.5$ kOe (Kündig and Hargrove 1969). At liquid nitrogen temperature (figure 2) we see evidence of the Verwey transition in Fe_3O_4

Table 1. Mössbauer parameters of chlorite (source 5 mCi ^{57}Co in Rh).

	Room temperature		Liquid nitrogen temperature	
	Present measurement mm/sec	Blaauw *et al* (1980) mm/sec	Present measurement mm/sec	Blaauw *et al* (1980) mm/sec
IS	$1\cdot10\pm0\cdot08$	$1\cdot13\pm0\cdot02$	$1\cdot19\pm0\cdot08$	$1\cdot22\pm0\cdot02$
QS	$2\cdot70\pm0\cdot08$	$2\cdot63\pm0\cdot02$	$2\cdot94\pm0\cdot08$	$2\cdot84\pm0\cdot02$
Γ_1	$0\cdot40\pm0\cdot08$	$0\cdot35\pm0\cdot02$	$0\cdot50\pm0\cdot08$	$0\cdot36\pm0\cdot02$
Γ_2	$0\cdot33\pm0\cdot08$	$0\cdot34\pm0\cdot02$	$0\cdot33\pm0\cdot08$	$0\cdot35\pm0\cdot02$

(source 25 mCi ^{57}Co in Rh (Blaauw *et al* 1979)). IS: is isomer shift with respect to α-Fe; QS: quadrupole splitting. Γ_1 and Γ_2: linewidths of the left and right lines, respectively, of the doublet.
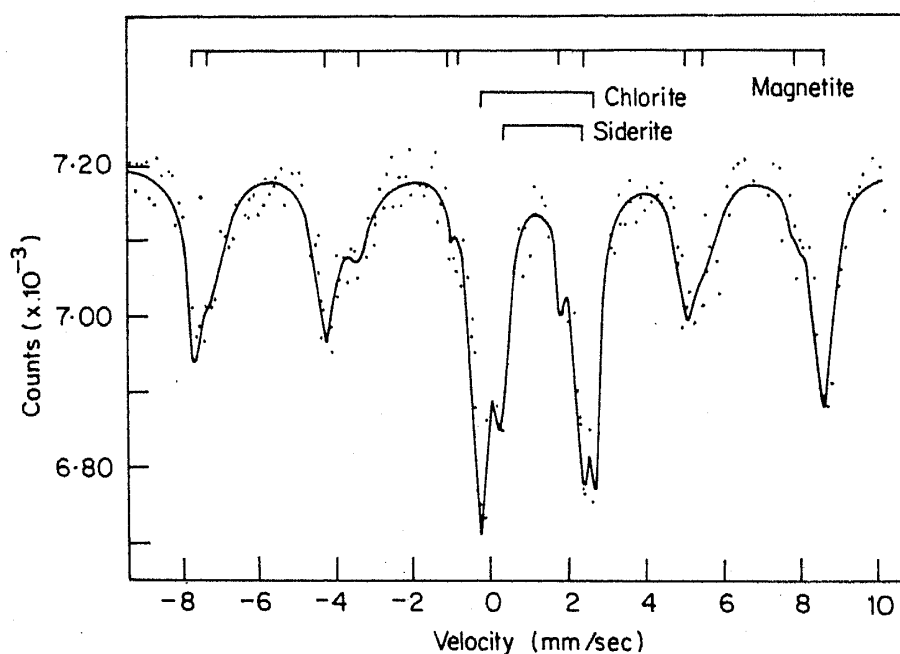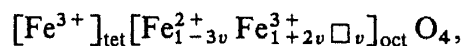

Figure 2. Mössbauer spectra of the magnetite rich part (1(c) of figure 1) at liquid nitrogen temperature. Note the change in the shapes of the magnetite lines.

at 119°K (Bauminger *et al* 1961; Daniels and Rosencwaig 1969). There are still twelve lines, but the intensity pattern has changed. The strong ferric lines correspond to 515 $\pm$ 10 kOe while the weaker ferrous lines correspond to 485 $\pm$ 10 kOe. Typical values reported are 514 $\pm$ 2, 499 $\pm$ 3kOe (Evans and Hafner 1969).

From the intensity of the A and B lines of figure 1 we can conclude that the deviation from stoichiometry in magnetite Fe_3O_4 is negligible. More quantitatively, if the structure of magnetite is represented by

$$[Fe^{3+}]_{tet}[Fe^{2+}_{1-3v}\ Fe^{3+}_{1+2v}\ \square_v]_{oct}\ O_4,$$

v being the concentration of vacancies, the value of $v \simeq 0$ (Coey *et al* 1971; Simmons and Leidheiser 1976).

Table 2. Fractional resonance areas under the three constituents in green shale.

Compound	Fractional resonance area (%)		
	Figure 1a	Figure 1b	Figure 1c
Chlorite	75	27	20
Siderite	10	23	28
Magnetite	15	50	52
Fe^{2+} : Fe^{3+} ratio in bulk sample	90:10	67:33	65:35

The fractional resonance areas under the peaks of the three iron compounds can be calculated from the computer fits in figure 1 and are given in table 2. Because $v \simeq 0$, the ferrous-ferric ratio in magnetite is taken as 1:2 and this ratio in the entire sample is also given. The areas are accurate to about 5%.

4. Discussion

The present sample is located immediately below the oxide facies of BIF and intimately related to volcanogenic sediments developed below it (lower shale). It shows variation in phase assemblage within a short range and contains silicate, carbonate and oxide phases, the latter two particularly dominant towards the upper part. This may be considered to be a short range facies transition from silicate to carbonate-oxide. There may be a genetic relation between the two, but more work will be needed to clarify the exact phase relation between them.

Further work at lower temperature is expected to reveal the known transition of siderite at 38°K and any possible transition of chlorite. To convert the resonance areas of table 2 into ratios of iron atoms in the constituents, one should measure their Lamb-Mössbauer factors (Muir 1971). These are not known. We note, however, that the ratios of figure 1c in table 2 become 20:23:57 at liquid nitrogen temperature (in figure 2). The effect of the Lamb-Mössbauer factors may not be large. This point requires further study by work at several temperatures. We hope to report further analysis of these points and other rocks of the Bonai range shortly.

Acknowledgements

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