

# Characterization of iron bearing minerals from Dagsheri and study of their decomposition behaviour during combustion using $^{57}\text{Fe}$ Mössbauer spectroscopy

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$^{57}\text{Fe}$  Mössbauer spectroscopy has been used to characterize the iron-bearing minerals from Dagsheri (Himachal Pradesh, India). An interesting feature of this sample is, the presence of large amount of haematite and small amount of Jarosite, which decompose into oxide phase, i.e. into haematite, which is likely to have volcanic origin. The decomposition behaviour of these minerals on combustion is studied by Mössbauer technique, after heating the samples at different temperatures. The decomposition route is significantly different from that normally observed in coal samples.

[**Keywords:** Iron bearing minerals, Minerals, Haematite, Jarosith]

## 1 Introduction

For characterizing iron-bearing minerals, various workers have applied Mössbauer technique, as it has certain expedients over other methods. Different environments of iron give rise to different components, in the Mössbauer absorption spectrum. Using computer program, one can separate them. Thus, the chemical state of iron (such as high and low spin  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ) can be easily identified. The Mössbauer spectroscopic procedure enables the analysis to be made in a non-destructive way and in addition, the contribution of iron minerals can be recorded without interference from any other compound present therein. In the present work, characterization as well as the behaviour of decomposition during combustion of one of the samples of sandstone mineral, heated at different temperatures have been studied. The sample was collected from Dagsheri region of Himachal Pradesh, India.

## 2 Experimental Details

The samples collected from Dagsheri region were crushed to obtain fine powders and sieved through a 200  $\mu\text{m}$  gauge. The Mössbauer absorbers were so prepared that a real density was 50  $\text{mg}/\text{cm}^2$  with uniform spread by pressing the powder in the aluminium holder of diameter 10 mm and fixing the open ends with cellophane tapes. The absorption spectra were recorded in transmission geometry at

room temperature. A constant acceleration Mössbauer spectrometer (Austin Science Inc, USA) was used, with a 2 mCi  $^{57}\text{Co}$  single line source in rhodium matrix. In general, several runs were taken to check the reproducibility of the spectra. Total counts collected/channel were close to  $10^6$  or more. The Mössbauer spectrometer was calibrated using a 0.001 in enriched  $\alpha\text{-Fe}$  foil. Calibration spectra with  $\alpha\text{-Fe}$  foil were taken before and after each experiment. The zero velocity channel was determined by locating the point of mirror symmetry (folding point) in each spectrum, using a Fortran program. The experimental data were fitted, using a least squares fitting program assuming Lorentzian lineshape. The solid line through the data points is the result of the computer fit of the data. To study the decomposition behaviour of iron-bearing minerals, samples were heated in atmospheric air for 90 min, in a temperature-controlled furnace. The temperature was maintained within an accuracy of  $\pm 2^\circ\text{C}$ . The Mössbauer absorption spectra of these samples were recorded at room temperature.

## 3 Results and Discussion

The Mössbauer absorption spectra of unheated sample were recorded at room temperature. Then, sample was heat-treated up to different temperatures. However, the Mössbauer spectra of the heat-treated samples were recorded, at room temperature, in transmission geometry. The spectra

Table 1 — Hyperfine interaction parameters computed from Mössbauer absorption spectra recorded at room temperature, isomer shift  $\delta$  is given relative to  $\alpha$ -Fe

Temp* (°C)	Site	Isomer shift ( $\delta \pm 0.01$ ) mm/s	Quadrupole splitting ( $\Delta \pm 0.01$ ) mm/s	Line width ( $\Gamma \pm 0.01$ ) mm/s	$\chi^2$ / degree of freedom	Assignment	$H_{\text{int}}$ ( $\pm 1$ )kOe
RT	M	0.30	-0.12	0.30	1.28	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	511
	D <sub>1</sub>	0.33	0.73	0.36		Fe <sup>3+</sup> high spin state	--
	D <sub>2</sub>	0.36	1.12	0.38		Jarosite	-
525	M	0.36	-0.10	0.32	1.31	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	514
	D	0.35	0.68	0.34		Fe <sup>3+</sup> high spin state	--
825	M	0.34	-0.12	0.32	0.85	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	512
	D	0.38	0.55	0.40		Fe <sup>3+</sup> high spin state	--
1025	M	0.32	-0.11	0.36	0.92	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	516

\*Temperature to which samples were heat-treated

were computer-fitted and the hyperfine parameters i.e. Isomer shift  $\delta$  mm/s, quadrupole splitting  $\Delta$  mm/s, line width  $\Gamma$  mm/s and hyperfine field  $H_{\text{int}}$  kOe were computed using normal procedure<sup>1</sup> and listed in Table 1.

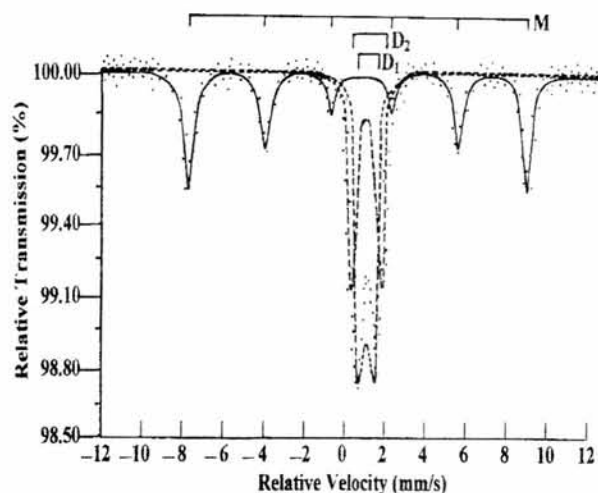


Fig. 1 — Mössbauer absorption spectra of unheated sample recorded at room temperature. (data points represent experimental observation [The solid line & dashed line give the curve obtained by fitting the experimental points])

The Mössbauer absorption spectra were analyzed for one Zeeman sextant and two quadrupole doublets, one zeeman sextant and one quadrupole doublet and one zeeman sextant having Lorentzian line shape using least square fitting computer program with  $\chi^2$  minimization technique.

To study the decomposition behaviour of the iron-bearing minerals, the samples were heated at different temperatures in the range (525-1025 °C).

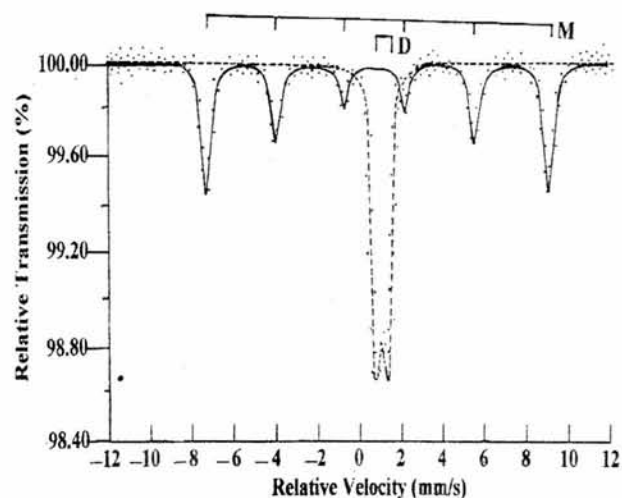


Fig. 2 — Mössbauer absorption spectra of the sample heated at 525 °C and recorded at room temperature [data points represent experimental observation; the solid line and dashed line give the curve obtained by fitting the experimental points]

The Mössbauer absorption spectra of the unheated sample, shown in Fig. 1 exhibits one Zeeman split sextant and two quadrupole doublets. On the basis of observed values of hyperfine parameters, one Zeeman split sextant was assigned to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and one quadrupole doublet corresponds to Jarosite, while the other quadrupole doublet corresponds to Fe<sup>3+</sup> high spin state. On the basis of hyperfine parameters, the presence of Fe<sup>3+</sup> phase

indicate that,  $\text{Fe}^{2+}$  phase (ferrous compounds) which were formed at lower temperature are converted to  $\text{Fe}^{3+}$  phase (ferric compounds) at high temperature as explained by the authors<sup>2-6</sup>. The presence of  $\text{Fe}^{3+}$  phase suggests that, the decomposition of minerals takes place at higher temperatures<sup>6</sup>. There is no change in the hyperfine parameters up to 425 °C.

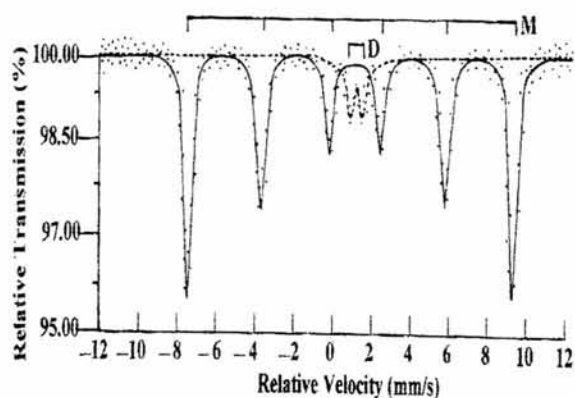


Fig. 3 — Mössbauer absorption spectra of the sample heated at 825 °C and recorded at room temperature [data points represent experimental observation; the solid line and dashed line give the curve obtained by fitting the experimental points]

However, on heating the sample above 425 °C, the parameters do change. The Mössbauer absorption spectrum of the sample, heated at 525 °C is shown in Fig. 2. This was fitted for one normal Zeeman split sextant assigned to  $\alpha\text{-Fe}_2\text{O}_3$  and the single quadrupole doublet assigned to  $\text{Fe}^{3+}$  high spin state. At 525 °C, most of the components corresponding to Jarosite and  $\text{Fe}^{3+}$  phase have decomposed in oxide phase, due to which, the intensity and hyperfine field of oxide phase, i.e.  $\alpha\text{-Fe}_2\text{O}_3$  increases. The Mössbauer absorption spectrum of the heat-treated sample at 825 °C is shown in Fig. 3. It was fitted for a single sextant and single quadrupole doublet having  $\text{Fe}^{3+}$  high spin state. As the sample is heated further to higher temperatures, the  $\text{Fe}^{3+}$  component gradually decreases and the mean hyperfine field gets closer to that for  $\alpha\text{-Fe}_2\text{O}_3$ . The intensity of oxide phase increases as the heating temperature rises. Finally, at 1025 °C as shown in Fig. 4,  $\text{Fe}^{3+}$  phase completely decomposes into oxide phase, i.e.  $\alpha\text{-Fe}_2\text{O}_3$ . At this stage, the intensity of the peaks as well as mean hyperfine field becomes nearly equal to that of  $\alpha\text{-Fe}_2\text{O}_3$ . The presence of  $\alpha\text{-Fe}_2\text{O}_3$  in the sample when heated to 1025 °C shows that, Jarosite is converted into  $\alpha\text{-Fe}_2\text{O}_3$  between 425 and 1025

°C. This would mean that, the characteristic temperature for complete conversion of Jarosite present in the sample collected from Dagsheri into  $\alpha\text{-Fe}_2\text{O}_3$  is around 1025 °C.

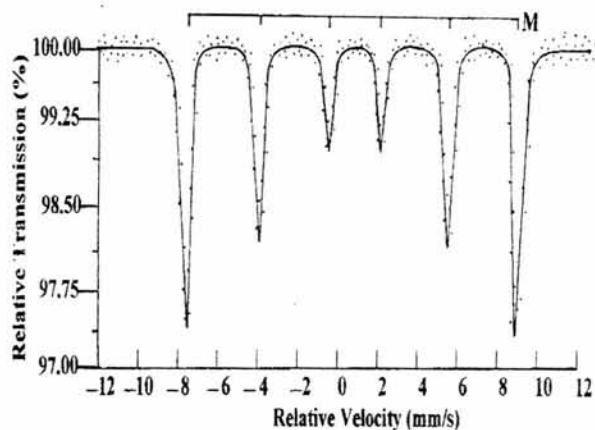


Fig. 4 — Mössbauer absorption spectra of the sample heated at 1025 °C and recorded at room temperature [data points represent experimental observation; the solid line give the curve obtained by fitting the experimental points and gives the total envelope of the fitted curve]

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