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Effect of calcination temperature on Indian Ocean manganese nodules. Mössbauer, XRD, FT-IR and TG-DTA studies

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Abstract

The effect of calcination temperature on the physico-morphological properties of Indian Ocean manganese nodules has been investigated. Mössbauer, XRD, FT-IR spectroscopic and TG-DTA studies on the manganese nodules gave some idea of the phase transformations in the temperature range 110–1000°C. Mössbauer studies reveal that the iron in the untreated nodule is mainly present as γ-FeOOH along with minor amount of iron phosphate and/or silicate. No phase transformation has been observed in the calcined sample up to 500°C and beyond that γ-FeOOH phase transforms to α-Fe_2O_3 and δ-MnO_2 to Mn_2O_3. A solid solution of Fe_2O_3 and Mn_2O_3 is formed above 700°C and beyond that, some amount of Fe exists in magnesium manganese iron oxide form. Insertion of magnesium into the Mg–Mn ferrite structure becomes greater at $\geq$900°C.

Keywords: Manganese nodules; Mössbauer; γ-iron oxyhydroxide; Solid solution

1. Introduction

Studies on Indian Ocean manganese nodules have been a subject of great interest to mineralogists, sedimentalogists and metallurgists. These deep sea manganese nodules are potentially a promising source of many useful metals such as manganese and iron and specially Ni, Co, Cu, etc. [1–4]. Attention has been focused on this material to find an economically feasible way of utilizing it as a mineral resources, since the high-grade land-based ores of these metal elements are being depleted at an alarming rate. As this naturally occurring material exhibits quite remarkable properties to act as a catalyst, investigations have been carried out by different workers to study its catalytic activity [5–7]. The pyrometallurgical processes for the extraction of metals and also the heterogeneous catalytic reactions generally take place at elevated temperatures. It is essential therefore to know the possible phase transformations and the morphological changes taking place during thermal treatment. This study may help in improving the metal extraction processes and establishing the reaction paths of heterogeneous catalytic reactions. There has been limited number of investigations to find the effect of calcination temperature on morphological properties of manganese nodules [8,9]. It was reported that XRD, FT-IR and TG-DTA techniques are not sufficient to characterise the complex material formed during the calcination process of the nodules. The present work reports on the Mössbauer study of Indian

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Ocean manganese nodules.The calcination products at various temperatures are also characterised by Mössbauer spectroscopy in combination with XRD, FT-IR and TG-DTA. To get unambiguous conclusion about the products formed after calcination, synthetic mixtures of δ-MnO_2 and γ-FeOOH has also been studied by Mössbauer spectroscopy.

2. Material and methods

2.1. Sample preparation

Manganese nodules of the Central Indian Ocean Basin were obtained from the National Institute of Oceanography, Goa, India. They were collected during cruises of the Fernela F7. The samples were air dried, powdered, and sieved. The sieved fractions (−75+45 μm) were collected for further studies. About 10 g samples were heated in each batch at a particular temperature (110–1000°C) in a muffle furnace with a suitable controller to maintain offset temperatures to ±5°C. The samples were kept at the desired temperature for 6 h, cooled to ca. 50°C, and then stored in a desiccator over fused $CaCl_2$. For Mössbauer study, synthetic δ-MnO_2 [10] and γ-FeOOH [11] was prepared and mixed keeping the ratio of Mn : Fe exactly same as in the nodules under study.

2.2. Characterization

TG-DTA of the samples (ca. 15 g) was carried out using a Shimadzu DT-40 automatic thermal analyser in the temperature range 30–1000°C at a heating rate of 10°C min^{-1}.

X-ray diffraction patterns of heat-treated samples were recorded on a Philips semiautomatic X-ray diffractometer with auto divergent slits and graphite monochromator using CuK_α radiation operated at 40 kV and 20 mA.

The FT-IR spectra (4000–400 cm^{-1}) of the samples were recorded in KBr using a JASCO Model 5300 spectrometer.

Mössbauer spectra of the samples were measured in a PC-based conventional set up coupled to a 1024 channel multichannel analyzer. Mössbauer spectra of the nodules and synthetic samples calcined at different temperatures were recorded at room temperature in transmission geometry. A Mössbauer spectrum of the air-dried nodules was also recorded at 77 K. A 7 mCi ^{57}Co in Rh matrix was used as the radioactive source and the spectrometer was calibrated with a high purity natural iron foil of 25 μm thickness. Experimental data were analysed with a least-squares fitting programme assuming Lorentzian lineshape.

3. Results and discussion

The analyses of the major and trace elements of the eight different grades of manganese nodules from the Central Indian Ocean Basin are presented in Table 1. It shows that Mn, Fe, Mg and silica are the major components while the trace elements are Cu, Co, Ni etc. are in good agreement with the reported values [12,13].

The TG curve (Fig. 1) of the samples indicate continuous weight loss on increasing the temperature up to 1000°C. A considerable weight loss (14.5%) occurred in the temperature range 30–135°C accom-

Table 1
Chemical analysis (in parts) of Indian Ocean manganese nodules

Sample code	Wt. percent of element/oxides								
	Mn	Fe	Cu	Ni	Co	Mg	Ca	SiO_2	Al_2O_3
Mn-1	24.91	8.23	1.15	0.98	0.126	10.19	1.27	19.9	4.52
Mn-2	22.72	10.02	0.87	0.84	0.149	–	–	25.0	2.56
Mn-3	25.10	9.27	1.13	1.01	0.137	9.67	1.28	21.0	2.67
Mn-4	22.73	12.04	0.92	0.86	0.134	8.42	0.72	22.1	4.40
Mn-5	23.71	9.18	1.21	1.10	0.091	9.39	1.07	22.8	4.17
Mn-6	22.76	9.18	1.43	1.17	0.111	9.92	1.18	24.1	4.66
Mn-7	10.90	12.29	0.26	0.27	0.101	5.96	–	33.3	3.64
Mn-8	18.50	11.90	0.82	0.71	0.090	–	–	27.5	3.81

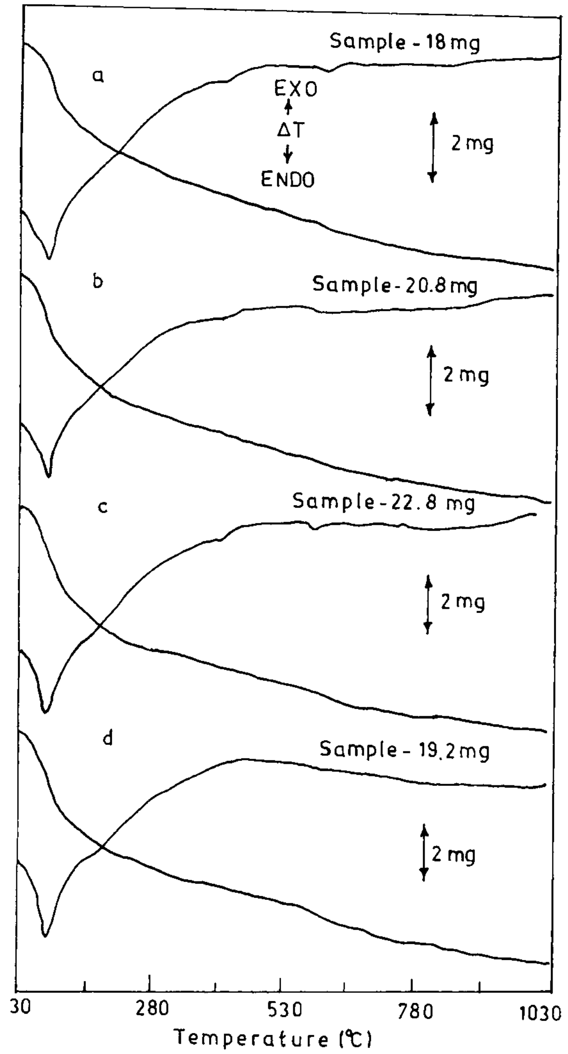

Fig. 1. TG-DTA of air-dried manganese nodules: (a) Mn-1; (b) Mn-2; (C) Mn-3; (d) Mn-5.

panied by a prominent endothermic peak at 82°C corresponds to loss of physisorbed water. The second weight loss (~8%) in the range 135–425°C may be due to decomposition of structural water from hydrous iron oxide and hydrous aluminosilicate phases. Above 450°C, the dehydrated sample further undergoes weight loss (~8%), presumably due to decomposition of oxide phases. The total weight loss at 900°C recorded from the TG (ca. 30%) curve agreed well with that obtained from the mass balance of calcined product at 900°C (isothermal calcination in the furnace).

The XRD patterns of the air-dried manganese nodules and calcined products are illustrated in Fig. 2. It can be seen that the sample dried at room temperature possesses a few diffused and broad peaks which are characteristic of todorokite (9.8 Å) and δ-MnO_2 (2.41 and 1.41 Å). The todorokite phase however, disappeared at 110°C without the development of any new materials. It is interesting to note that the position, as well as the broadness and the intensity of XRD peaks of calcined samples (110–500°C) remains practically unchanged, indicating no change in the structure of the material. The peaks at 3.32 and 3.18 Å indicate the presence of quartz (α-SiO_2) and zeolite minerals, respectively. Calcination at >500°C resulted in the appearance of a strong peak at 2.69 Å due to the formation of α-Fe_2O_3 from iron oxyhydroxides. Around this temperature, δ-MnO_2 also decomposes to γ-Mn_2O_3, as indicated by the appearance of a distinct line at 2.49 Å. This also corroborates to the TG-DTA observation. The sharpness and intensity of the characteristic peaks of α-Fe_2O_3 and γ-Mn_2O_3 increase with increase in calcination temperature beyond 600°C due to improved crystallinity and size of the particles. The XRD patterns of the 700 and 900°C heated samples show some sharp and diffused peaks which may be due to phase transformations/new material formation. The appearance of peaks at 1.42 and 1.66 Å can be attributed to the iron–manganese oxide solid solution $(Fe, Mn)_2O_3$ and the peaks at 1.45 and 2.06 Å may be due to the formation of iron silicate. The phase transition in the manganese magnesium iron oxide is identified from the peaks at 2.93 and 4.91 Å. The XRD patterns and peak positions of the preheated nodules are in good agreements with those reported earlier [8,9].

Fig. 3 displays the FT-IR spectra (4600–400 cm^{-1}) of the heat-treated nodules. The infrared spectra of the nodules are complicated due to their complex matrix. The various absorption peaks are interpreted with special reference to iron, silicon, and manganese oxides/oxyhydroxides and also to water molecules. The presence of OH group as well as H_2O (both adsorbed molecular water within the crystal structures) at lower calcination temperature (<600°C) is revealed by the characteristic absorption peaks at ca. 3400 and 1640 cm^{-1}, respectively, as OH stretching

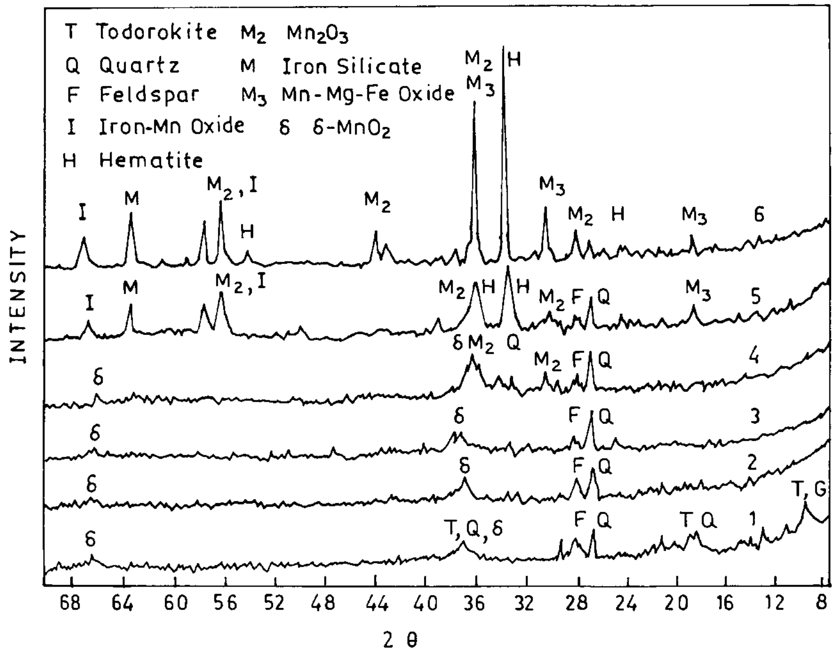

Fig. 2. Powder XRD patterns of heat treated manganese nodules: (1) air-dired; (2) 200°C; (3) 300°C; (4) 500°C; (5) 700°C; (6) 900°C.

and bending modes of vibrations [14]. These peaks either diminished or disappeared with progressive increase in calcination temperature. Surprisingly there is no peak at 3400 cm^{-1} for the sample heated at 110°C. Nodules, generally, exhibit a very strong absorption band at ca. 1020–1040 cm^{-1}, presumably due to Si–O or Si–O–Al vibrations. This band broadens by 50 cm^{-1} with a rise in calcination temperature, indicating that the silicates become more crystalline as reported earlier [9]. Further broadening at >600°C indicates lattice disorder. Appearance of a peak at ca. 570 cm^{-1} with the sample heated above 500°C indicates the formation of α-Fe_2O_3 [9]. A strong peak invariably present at ca. 460–470 cm^{-1} may be assigned to smectite-type clay minerals or Mn–O vibrations [9].

Mössbauer parameters obtained after fitting are tabulated in Tables 2 and 3. Mössbauer spectrum of the air-dried Mn-nodule is shown in Fig. 4(a). A clear doublet with isomer shift (IS) 0.38 mm/s, and quadrupole splitting (QS) 0.66 mm/s indicates that iron in the nodule is in Fe^{3+} valence state. The width of the doublet was found to be 0.49 mm/s, higher than that generally obtained for iron-based minerals [15]. This indicates that more than one iron bearing phase is present in the sample. The doublet could be due to single or mixed oxyhydroxides (α-, β- or γ-FeOOH) and some amount of phosphate and/or silicate present in the nodule as reported earlier [16,17]. The oxyhydroxides are expected to give their characteristic sextet Mössbauer pattern below their Neel temperature (T_N). But presence of very fine particles in the nodule may give rise to superparamagnetic relaxation that causes collapse of the sextet pattern and one gets a doublet even below the Neel temperature of the corresponding oxyhydroxide. As one goes to low temperature the sextet pattern again grows at the cost of the doublet. To check the presence of superparamagnetic particles in the present nodule sample, Mössbauer spectrum of the air-dried sample was taken at 77 K. As can be seen from Fig. 4(b) the doublet observed at room temperature persists even at 77 K without trace of any sextet. This rules out existence of any bulk or superparamagnetic particles of α-FeOOH and β-FeOOH in the sample as their Neel temperatures are well above the liquid nitrogen temperature [18]. It appears that the doublet observed at room temperature and 77 K is due to γ-FeOOH present in the sample. Some amount of ferric phosphate and/or silicate might also be present.

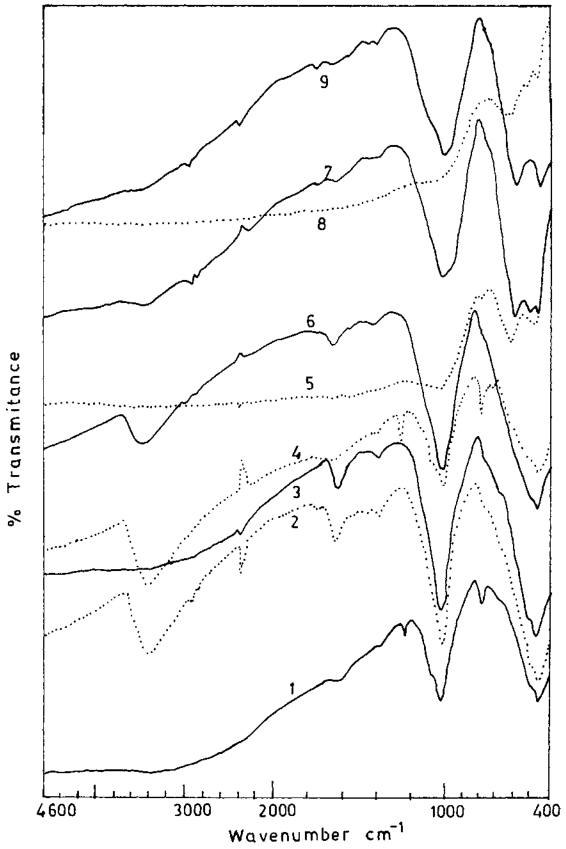

Fig. 3. FT-IR spectra of heat-treated manganese nodules: (1) 110°C; (2) 200°C; (3) 300°C; (4) 400°C; (5) 500°C; (6) 600°C; (7) 700°C; (8) 800°C; (9) 900°C.

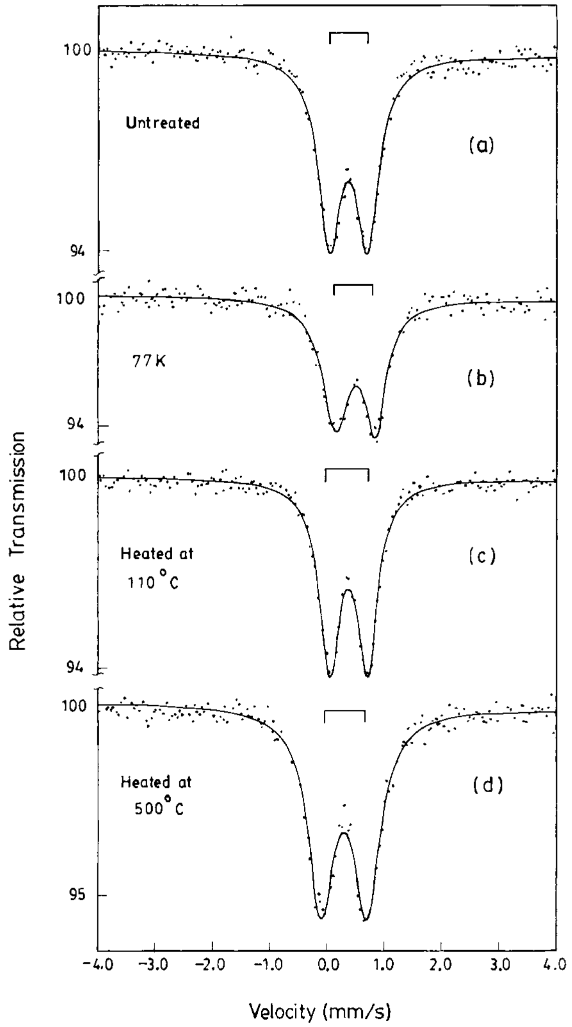

Fig. 4. Mössbauer spectra of manganese nodules: (a) air-dried; (b) 77 K; (C) 110°C; (d) 500°C.

Mössbauer spectra of the nodules at 110° and 500°C (Fig. 4(c) and (d), respectively) show a quadrupole doublet as observed for the air-dried sample indicating no new phase formation upto 500°C. Nodule heated at 600°C shows a sextet superposed on a doublet (Fig. 5(a)). The sextet with IS 0.43 mm/s, QS 0.33 mm/s and H_{int} 485 kOe has been attributed to α-Fe_2O_3 (hematite) which has resulted from the decomposition of oxyhydroxide (γ-FeOOH). The doublet remaining at this heat-treated sample is attributed to ferric phosphate and/or silicate present in the nodule. The nodule heated at 700°C also shows hematite and a doublet (Fig. 5(b)) due to ferric phosphate/silicate.

Mössbauer spectrum of the nodule heated at 800°C (Fig. 5(c)) shows several lines. Two doublets and two sextets were fitted to get a good fit. The sextet with hyperfine field 496 kOe has been attributed to hematite. The other sextet with hyperfine field 395 kOe and nearly zero QS has been attributed to Mg–Mn ferrite. The doublets with QS 1.05 and 0.53 mm/s are assigned to Fe_2O_3–Mn_2O_3 solid solution [19]. This is fairly possible as the air-dried nodule contains δ-MnO_2 and γ-FeOOH which are likely to be transformed to Mn_2O_3 and α-Fe_2O_3, respectively, at much lower temperature (600°C). As magnesium is present in the nodule samples (Table 1), a part of Mn_2O_3 and Fe_2O_3 have combined with MgO to form the Mg–Mn ferrite whereas the remaining part formed the solid

Table 2
Mossbauer parameters of the heat-treated nodule sample

Calcination temperature of nodules (°C)	Site	Isomer shift ($\delta\pm0.02$) mm/s	Quadrupole splitting ($2\varepsilon+0.02$) mm/s	Line width ($\Gamma\pm0.02$) mm/s	Hyperfine field ($H_{\mathrm{int}}\pm2$) kOe
Air dried (RT)	D	0.38	0.66	0.49	—
77 K	D	0.50	0.69	0.47	—
110	D	0.35	0.68	0.45	—
300	D	0.34	0.76	0.49	—
500	D	0.31	0.80	0.56	—
600	D	0.27	0.39	0.60	—
	S	0.43	0.33	0.46	485
700	D	0.29	0.73	0.55	—
	S	0.43	0.27	0.47	493
800	D	0.31	1.05	0.45	—
	D	0.32	0.53	0.46	—
	S	0.37	0.15	0.36	496
	S	0.45	0.03	0.72	395
900	D	0.35	0.45	0.51	—
	S	0.30	0.04	0.76	339
1000	D	0.35	0.53	0.35	—
	S	0.42	0.03	0.82	317

D – Doublet; S – Sextet.

Table 3
Mossbauer parameters of the synthetic mixture (δ-MnO_2+ γ-FeOOH)

Calcination temp. of the synthetic mixture (°C)	Site	Isomer shift ($\delta\pm0.02$) mm/s	Quadrupole splitting ($2\epsilon\pm0.02$) mm/s	Linewidth ($\Gamma\pm0.02$) mm/s	Hyperfine field ($H_{\mathrm{int}}\pm2$) kOe
Air dried	D	0.40	0.55	0.32	—
600	S	0.50	0.15	0.32	505
700	S	0.48	0.15	0.33	504
800	D	0.38	1.11	0.38	—
	D	0.37	0.59	0.32	—
	S	0.47	0.16	0.35	504
1000	D	0.38	1.15	0.36	—
	D	0.37	0.54	0.30	—

S – Sextet; D – Doublet.

solution. Some Fe_2O_3 is left unreacted. It is to be noted that the doublet due to ferric phosphate/silicate as has been seen in the sample heated at lower temperature is masked by the strong absorption due to the solid solution of Fe_2O_3–Mn_2O_3.

Mössbauer spectrum of the sample heated at 900°C (Fig. 5(d)) shows a broad sextet and a doublet at the central region. The sextet with hyperfine field 339 kOe has been attributed to Mg–Mn ferrite. It is to be noted that this field is much less than the field 395 kOe obtained for the sample heated at 800°C. This indicates that the ferrite formed at this temperature has a different composition and most probably contains more Mg which causes the reduction of the hyperfine field. It is reported that the hyperfine field of Mg–Mn ferrite varies by a large amount as the composition varies [20]. The doublet with IS 0.35 and QS 0.45 mm/s is attributed to ferric phosphate/silicate present in the nodules.

Mössbauer spectrum of nodule heated at 1000°C (Fig. 5(e)) also shows the presence of Mg–Mn ferrite and ferric phosphate/silicate. The ferrite field is further reduced indicating more Mg in the composition.

Mössbauer spectrum of the air-dried γ-FeOOH–δ-MnO_2 synthetic mixture shows a doublet (Fig. 6(a))

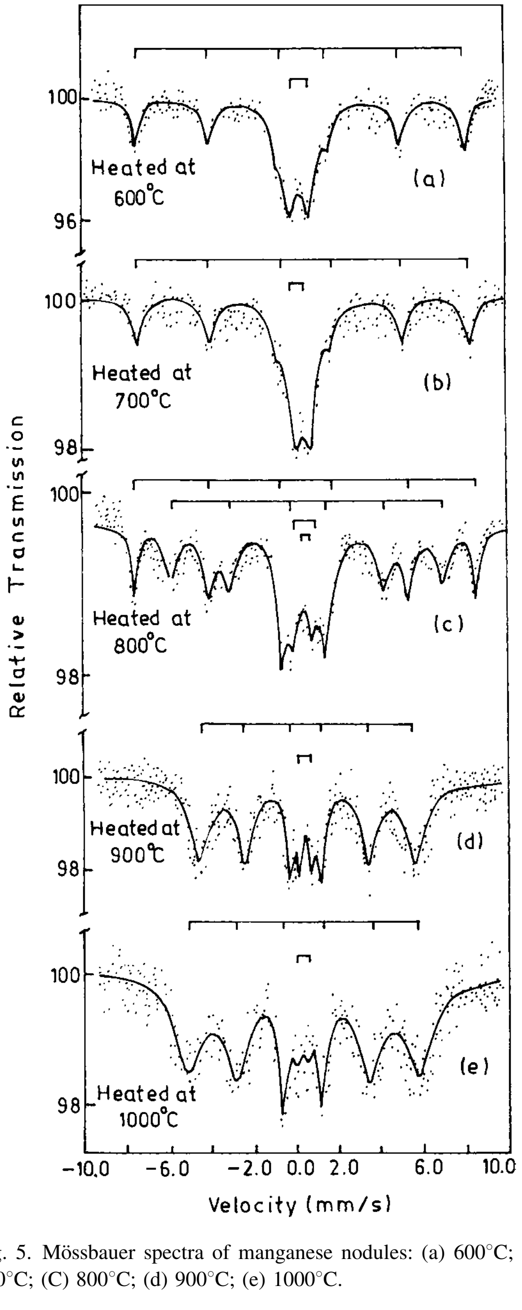

Fig. 5. Mössbauer spectra of manganese nodules: (a) 600°C; (b) 700°C; (C) 800°C; (d) 900°C; (e) 1000°C.

with IS 0.40 and QS 0.55 mm/s. These are close to the parameters obtained for the untreated nodule sample indicating the presence of γ-FeOOH in the nodule. The line width obtained for the synthetic mixture is 0.32 mm/s. This also points that the large line width obtained in the nodules is due to the presence of additional ferric component as discussed earlier.

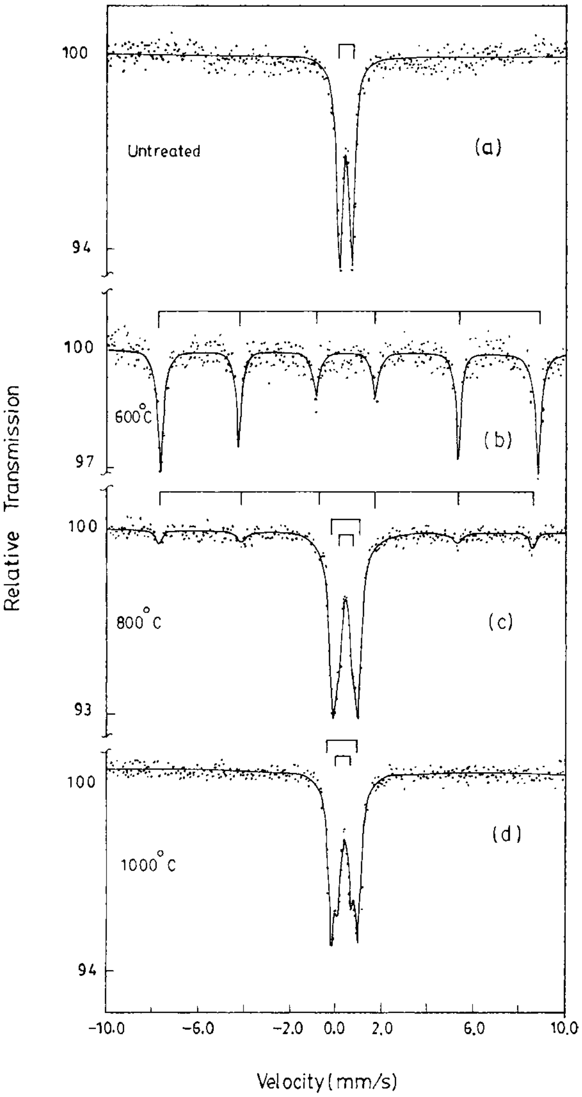

Fig. 6. Mössbauer spectra of synthetic mixture (δ-MnO$_2$ and γ-FeOOH). (a) air-dried; (b) 600°C; (C) 800°C; (d) 1000°C.

On heating the sample at 600°C we obtain a clear sextet (Fig. 6(b)) with IS 0.48 and QS 0.15 mm/s and hyperfine field 504 kOe which has been identified as due to α-Fe$_2$O$_3$. This shows that in the synthetic mixture the γ-FeOOH has completely transformed into α-Fe$_2$O$_3$ when heated at 600°C. Mössbauer spectrum (Fig. 6(c)) of the synthetic mixture heated at 800°C gives a strong absorption at the central region and a weak sextet. The sextet has been identified as due to α-Fe_2O_3. Two doublets have been fitted in the central region and parameters obtained indicate that it is due to the formation of Fe_2O_3–Mn_2O_3 solid solution. Mössbauer spectrum (Fig. 6(d)) of the synthetic mixture heated at 1000°C shows a central absorption where two doublets were fitted. These are identified as due to solid solution of Fe_2O_3–Mn_2O_3. No sextet of hematite could be detected.

4. Conclusions

1. Manganese is present in the form of δ-MnO_2 and iron mainly as γ-FeOOH along with small amount of iron phosphate and/or silicate in manganese nodules of Central Indian Ocean.
2. At 600°C, iron phase is completely transformed into α-Fe_2O_3 and manganese phase into Mn_2O_3.
3. It is evident from Mössbauer studies that at 800°C, formation of magnesium manganese ferrite and solid solution of Fe_2O_3–Mn_2O_3 takes place in case of manganese nodules where as only solid solution of Fe_2O_3–MnO_2 in synthetic mixture of δ-MnO_2 and γ-FeOOH.
4. At 1000°C, magnesium manganese ferrite predominates over the solid solution in manganese nodules but the synthetic mixture still contains mainly the solid solution.

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