2.4 Mossbauer Studies

2.4.1 Mossbauer studies on some ilmenites

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Ilmenite is one of the minerals present in the beach sand deposits of Kerala. While natural ilmenite found in relatively pure underground ore beds is mainly $FeTiO_3$, in the beach sands a significant fraction of the iron atoms exists in the ferric state presumably as a result of weathering effects. The ilmenites from Chavara and Manavalakurichi along the Kerala coast are different in composition - the former containing about two-thirds of all the iron present in the ferric form as against one third in the latter. The nature of the ferric iron in these materials is, however, not clearly understood. Mossbauer studies were carried out on the ilmenite samples from Chavara and Manavalakurichi. Measurements were carried out both at room temperature and at liquid nitrogen temperature to see whether any fresh information can be obtained on the nature of the ferric iron species and also to check the validity of the measurement of ferrous to ferric ratio from Mossbauer data.

The ilmenite samples purified by sieving and magnetic separation were obtained from the Ore Dressing Section of B.A.R.C. Samples containing about 30 mg of the ilmenites were mixed with $LiCO_3$ and pressed into aluminium rings to form absorbers in the Mossbauer studies. Mossbauer measurements were carried out using a constant acceleration spectrometer(1).

The Mossbauer absorption spectra of the ilmenites were measured both at room temperature and at liquid nitrogen temperature. The spectra are shown in Figures 20 and 21. All the spectra are characterised by three absorption maxima and were analysed on a three peak model. A computer programme was used to make a least squares fit of three Lorentzian peaks to the spectra. Efforts to fit four peaks were not successful in any of the cases. In the case of the Manavalakurichi ilmenite, the spectrum taken at liquid nitrogen temperature could not be fitted with even three Lorentzian peaks. Hence in this case only the positions of the peaks are reported. The Mossbauer

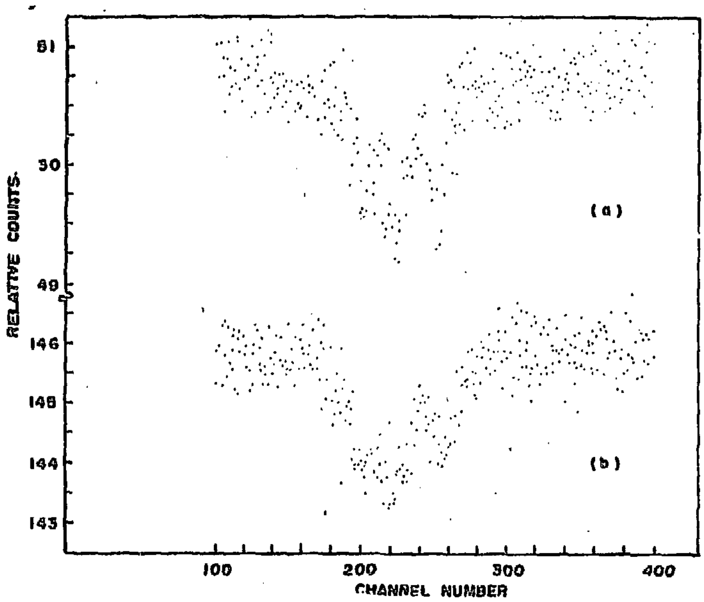

Figure 20 : Mossbauer spectra of Chavara ilmenite at (a) room temperature and (b) liquid nitrogen temperature.

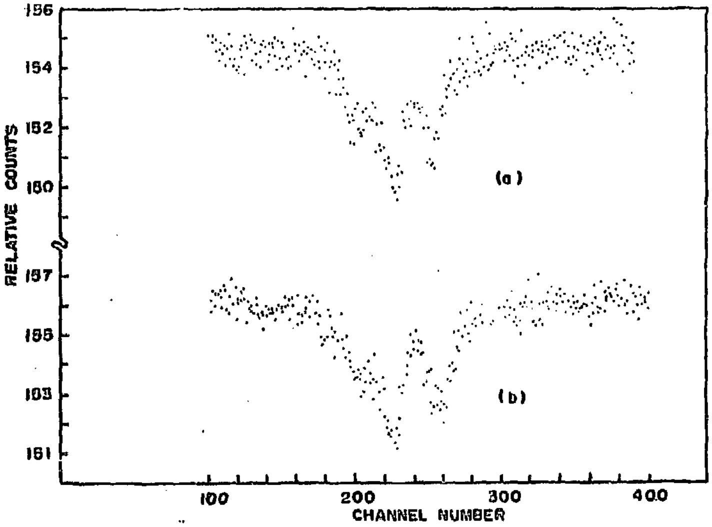

Figure 21 : Mossbauer spectra of Manavalakurichi ilmenite at (a) room temperature and (b) liquid nitrogen temperature.

parameters are given in Table 17. The values are reproducible to within ± 0.025 mm/sec.

TABLE 17

Mössbauer parameters

	Room temperature			Liquid nitrogen temperature		
	Position* mm/sec	Half-width mm/sec	Area (relative)	Position* mm/sec	Half-width mm/sec	Area (relative)
I. Chavara Ilmenite						
Peak 1	0.36	0.50	2.27	0.35	0.60	4.99
Peak 2	0.95	0.46	3.31	0.91	0.68	7.98
Peak 3	1.67	0.21	1.49	1.80	0.74	5.44
II. Manavalakurichi Ilmenite						
Peak 1	0.36	0.48	6.0	0.36		
Peak 2	0.98	0.44	10.9	0.99		
Peak 3	1.71	0.36	7.37	1.82		

* relative to the centroid of the sodium nitroprusside spectrum

In the absence of magnetic hyperfine splitting one would expect these spectra to be composed of the quadrupole-split patterns due to the ferrous and ferric iron. Thus while peaks 1 and 3 would correspond to the outer peaks of the ferrous and ferric doublets respectively, the central peak would be the sum of the other two components of the doublets. The positions of the second and third peaks correspond to natural ilmenite which did not undergo oxidation due to weathering. The isomer shift and quadrupole splitting of the ferrous iron in the ilmenite obtained on the basis of the above interpretation are given in Table 18. Not only the isomer shift but also the temperature dependence of the quadrupole splitting is characteristic of ferrous salts.

TABLE 18

Mossbauer parameters of the ferrous and ferric iron

Sample	Ferrous iron		Ferric iron	
	Isomer shift mm/sec	Quadru-pole mm/sec	Isomer shift mm/sec	Quadru pole mm/sec
I. Chavara				
(a) Room temp.	1.31	0.71	0.66	0.59
(b) Liquid nitrogen temp.	1.36	0.89	0.63	0.56
II. Manavalakurichi				
(a) Room temp.	1.35	0.73	0.67	0.62
(b) Liquid nitrogen temp.	1.41	0.83	0.68	0.63
III. Finish ilmenite(2)				
(a) Room temp.	1.35	0.71		
IV. $FeTiO_3$(3)				
(a) Room temp.	1.35	0.6		
(b) Liquid nitrogen temp.	1.45	1.0		
V. Brazilian ilmenite (from Ref.2)	-	-	0.62	0.67

The parameters agree with those reported for the Finnish ilmenite(2) as well as for $FeTiO_3$(3). The position of the ferric iron peaks is less clear. The fact that only three peaks could be fitted to the observed spectra suggests that if the ferric iron exhibits a simple quadrupole split doublet, the second component of this must coincide with the first component of the ferrous doublet. On the assumption that the positions of peaks 1 and 2 correspond to the positions of the ferric doublet, the Mossbauer parameters of the ferric species were calculated and the results are shown in Table 18. The corresponding data for Brazilian ilmenite, in which the iron is mostly in the ferric state are included for comparison.

Relative amounts of ferric and ferrous iron

Gibb et al(2) obtained the relative amounts of ferric and ferrous iron from Mossbauer spectra by assuming that the areas of peaks 1 and 3 in the ilmenite spectra corresponded to the amounts of ferric and ferrous iron respectively. This assumption is open to question in view of the possible asymmetry of the quadrupole doublets. The results obtained by following the above procedure in the case of the Chavara and Manavalakurichi ilmenites do not agree with the results of chemical analysis as is seen from the data in Table 19.

TABLE 19

Ferric iron content as percentage of total iron :
Comparison of Mossbauer and chemical data

Sample	Percentage of Fe^{3+} in total iron	
	From Mossbauer data	By chemical analysis
Chavara ilmenite		
(a) Room temp.	61%	69%
(b) Liquid N_2 temp.	48%	-
Manavalakurichi ilmenite		
(a) Room temp.	45%	32%
Quilon ilmenite(1)		
(a) Room temp.	71%	68%

The fraction of iron in the ferric state as measured by the above procedure decreases from 61% to 48% on cooling the Chavara ilmenite from room temperature to liquid nitrogen temperature. This can perhaps be understood by considering relaxation effects in interpreting the spectra. When the paramagnetic relaxation time is comparable to the Mossbauer transition period, complex Mossbauer patterns may be expected. A broadened central line with extended wings corresponding to the highly broadened outer lines of the six finger pattern is typical of the spectra to be expected for iron at intermediate relaxation times(4). The presence of quadrupole interaction further complicates the observed spectrum. Fitting one or two Lorentzians to such a pattern is bound to lead to considerable error in the estimates of relative concentrations. This may thus be one of the factors responsible for the lack of reliability in the ferric content estimated from Mossbauer data.

2.4.2 Preparation of ^{145}Pm

With a view to studying Mossbauer effect in ^{145}Nd, the parent nuclide ^{145}Pm is being prepared. ^{145}Pm ($t_{\frac{1}{2}}$ = 18 Y) is formed through the decay of ^{145}Sm ($t_{\frac{1}{2}}$ = 340 d) which is formed by the neutron irradiation on ^{144}Sm. About 100 mg of samarium was irradiated in CIRUS for 10 months and allowed to cool for 3 years. The sample showed very high radioactivity most of which was identified as due to ^{154}Eu. An ion exchange method for separating promethium from other rare earths using α-hydroxy isobutyric acid as the eluting agent was standardized. One cycle of separation was found to be inadequate for decontamination from curie-level ^{154}Eu activity. Further purification of the promethium fraction is in progress.

References

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3. G. Shirane, D.E. Cox, W.J. Takei and S.L. Ruby, J. Phys. Soc., Japan, 17, 1598 (1962).