

⁵⁷Fe Mössbauer studies on natural chromites

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Abstract. Five chromite samples procured from two different belts of India have been studied by ⁵⁷Fe Mössbauer spectroscopy. It is shown that four symmetric doublets are sufficient to fit the chromite spectrum; the Mössbauer parameters and the Fe³⁺/Fe²⁺ ratio are computed. For fully oxidized chromite with only Fe³⁺, two doublets are needed and the parameters are computed.

Keywords. Mössbauer spectroscopy; chromite.

1. Introduction

There has been considerable controversy over the interpretation of the Mössbauer spectra of naturally occurring chromites. They belong to the spinel oxide group with general formula AB₂O₄ where A refers to divalent metal ions (Fe²⁺, Mg²⁺, ...) in tetrahedral coordination and B to trivalent metal ions (Fe³⁺, Al³⁺, Cr³⁺, ...) in octahedral coordination. An ideal chromite FeCr₂O₄ being a direct spinel should have an ordered structure with Fe²⁺ ions in tetrahedral (A) sites and Cr³⁺ ions in octahedral (B) sites. Natural chromites are formed under varied conditions so that ferrous ions could be partially or fully oxidized to ferric ions and the cation distribution be disordered (Da Silva *et al* 1976, 1980). For partial oxidation, Fe²⁺ and Fe³⁺ ions would be found in both A and B sites and four doublets would be expected in the Mössbauer spectrum. If oxidation is complete, Fe³⁺ would be distributed on A and B sites, causing the appearance of two doublets. Actually other types of doublets have also been used in the analysis of chromite spectra, and electron hopping between Fe²⁺ and Fe³⁺ on octahedral sites has been postulated (Fatseas *et al* 1976). It has been argued that next nearest neighbour interactions are responsible for more than one type of A sites in the ordered structure (Osborne *et al* 1981, 1984; Zhe *et al* 1988). So even in an ordered structure and without oxidation, more than one Fe²⁺ site would be present. Any careful fitting of the Mössbauer spectrum must take into account the usual range of isomer shifts (IS), quadrupole splittings (QS) and linewidths as normally observed in minerals (Bancroft 1973; Reiff 1973; Dyar *et al* 1989).

In the first study of natural Indian chromites (Singh *et al* 1978), the interpretation of the Mössbauer spectra was not very satisfactory. Their sample from Sukinda in Orissa contained only Fe³⁺ and they fitted the spectra with Fe³⁺ on A sites and Fe²⁺ on two types of B sites. More recently Mitra *et al* (1991) studied two chromite samples from Sukinda and fitted the Mössbauer spectra of one by three doublets from Fe²⁺ (A), Fe³⁺ (A) and Fe²⁺ (B)

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and of another by three doublets from $\text{Fe}^{3+}(\text{A}_1)$, $\text{Fe}^{3+}(\text{A}_2)$ and $\text{Fe}^{2+}(\text{B})$. They suggested that these chromites had suffered partial inversion during the oxidation process.

In the present Mössbauer study five naturally occurring chromite samples have been examined: three from Sukinda, Orissa, and two from Chimal Pahad, Andhra Pradesh. Two of these samples from Sukinda are fully oxidized, as in the study of Singh *et al* (1978). However, we find two doublets due to $\text{Fe}^{3+}(\text{A})$ and $\text{Fe}^{3+}(\text{B})$ would suffice to fit the spectra. Our other samples can be fitted with doublets due to $\text{Fe}^{2+}(\text{A}_1)$, $\text{Fe}^{2+}(\text{A}_2)$, $\text{Fe}^{2+}(\text{B})$ and $\text{Fe}^{3+}(\text{B})$. Our analysis does not require partial inversion of the spinel structure. But it agrees with that of Dyar *et al* (1989).

2. Experimental

Three chromite samples (C_1 , C_2 and C_3) were collected from the Sukinda valley of Orissa, India. The other two chromite samples (C_4 and C_5) were procured from Chimal Pahad area of Andhra Pradesh, India. In the Sukinda Valley, chromite occurs as persistent layers or as lenses and pockets in the altered dunite–peridotite (Chakravorty and Chakravorty 1984). The chromites of Andhra Pradesh occur as basal member of Chimal Pahad anthrosite complex (Bose 1979). The host rock for chromite pockets are metamorphosed and it is likely that chromite bands have been reconstituted.

The samples were crushed below 200 sieve mesh and boiled in weakly acidic water solution for about half an hour. The powder was then filtered, washed several times in distilled water and dried at room temperature. The dried material was then repeatedly passed through an isodynamic separator to obtain more than 95% pure chromite. For Mössbauer measurements 30 mg of the sample was thoroughly mixed with the required amount of boron nitride powder and in the form of a pellet was spread over an area of 2 cm^2 . The Mössbauer spectra of the samples were taken in a conventional set up consisting of 512 channel multichannel analyzer (Wissel, Germany) coupled to a personal computer. A 6 mCi ^{57}Co radioactive source in Rh matrix was used. The spectrometer was calibrated with a 25 μm thick natural iron foil supplied by Amersham Int plc.. All measurements were taken in transmission geometry. The low temperature measurements were carried out in an indigenously built cryostat where the sample was mounted on a cold finger in contact with boiling liquid nitrogen. A copper-constantan thermocouple and a Philips make micro-voltmeter (PM 2434) were used to record the temperature. The spectra were fitted on a personal computer using a modified version of the least-squares fitting programme of Meerwall (1975). Lorentzian line shapes were assumed for all the peaks. The widths and heights of the component peaks of a doublet are constrained to be equal throughout the analysis. X-ray diffraction studies of the samples were performed in a Philips diffractometer (PW1730) with CuK_α radiation passed through Ni filter. The wet chemical analysis of the major elements present in the samples were performed following the procedure of Dinnin (1959) and the results obtained are presented in table 1.

3. Results

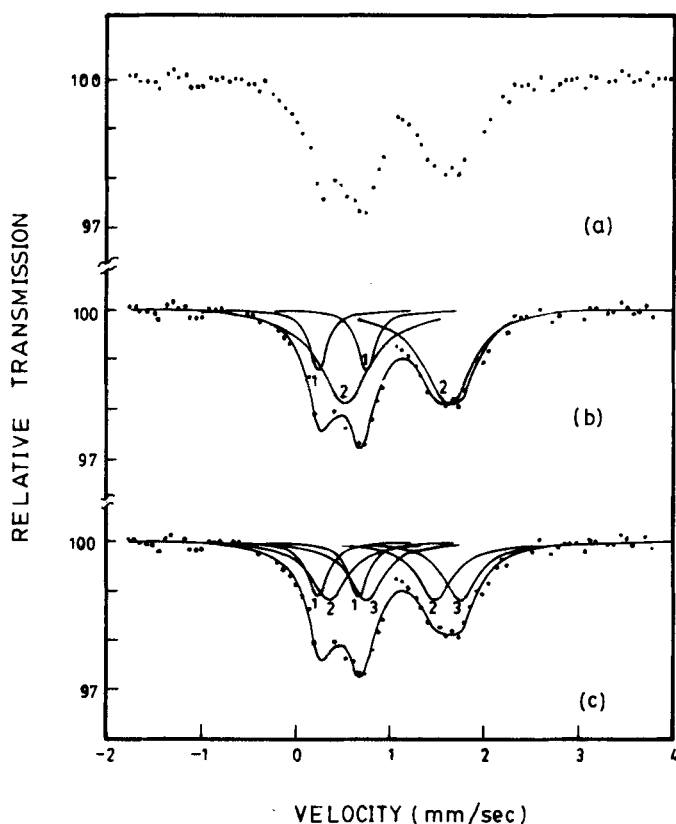
3.1 Mössbauer studies

Figure 1a shows the Mössbauer spectrum of the chromite sample C_1 recorded at room temperature. This and subsequent figures only show the central channels where actual

Table 1. Chemical analysis of the chromite samples.

Oxide (%)	C ₁	C ₂	C ₃	C ₄	C ₅
Cr ₂ O ₃	53.77	59.48	59.06	38.27	37.68
Al ₂ O ₃	10.88	10.95	10.11	12.74	12.82
TiO ₂	0.20	0.22	0.26	0.23	0.24
FeO*	15.25	11.82	13.11	37.50	38.40
MgO	17.23	16.02	14.70	10.6	9.68
NiO	0.82	0.94	0.88	0.18	0.11
MnO	0.11	0.17	0.15	0.13	0.14
SiO ₂	0.94	0.77	0.72	1.06	0.98
Total	99.00	100.37	98.99	100.71	100.05

*All Fe recalculated as FeO

**Figure 1.** Mössbauer spectra of the sample C₁ at room temperature: (a) raw data, (b) 'two doublet' fit and (c) 'three doublet' fit.

absorption took place. Three broad peaks of unequal intensities are observed; they indicate strong overlapping of several doublets. The simplest fit is that of two doublets, as shown in figure 1b. The corresponding hyperfine parameters are shown in table 2. Osborne *et al* (1981) fitted the chromite spectra in a similar way; the doublet with isomer shift (IS) 0.40 mm/s and quadrupole splitting (QS) 0.30 mm/s might be

Table 2. Mössbauer parameters for C_1 at room temperature with different fitting scheme.

Fitting scheme	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Full width at half maximum (mm/s)	Relative intensity (%)	χ^2
'Two doublets'	0.40	0.30	0.23	18	0.99
	1.08	1.09	0.65	82	
'Three doublets'	0.35	0.43	0.26	21	0.88
	0.82	1.12	0.49	41	
	1.15	0.99	0.44	38	
'Four doublets'	0.52	0.44	0.30	23	0.80
	0.88	1.19	0.34	23	
	1.11	1.08	0.36	22	
	1.28	1.06	0.40	32	

attributed to Fe^{3+} in B sites, and the doublet with IS 1.08 mm/s and QS 1.09 mm/s might be attributed to Fe^{2+} in A sites. The difficulty with this kind of fitting is the large linewidths (0.65 mm/s) obtained for the ferrous peak. Generally minerals at room temperature give linewidth in the range of 0.30–0.40 mm/s (Bancroft 1973). The large linewidths obtained in the present case indicate the presence of more than one Fe^{2+} site and a 'two doublet' fit is not satisfactory. A 'three doublet' fit can be done in various ways; each depends on how the component peaks of a doublet are matched up. We have tried many possibilities. A typical 'three doublet' fit is shown in figure 1c, and the corresponding hyperfine parameters are shown in table 2. All 'three doublet' fits give linewidths of the Fe^{2+} peaks in the range 0.44–0.51 mm/s which are larger than what are normally found. Next we have fitted four paramagnetic doublets to the spectrum. Out of the many ways of matching up of the component peaks of the doublets, the one which gives the better χ^2 per degree of freedom and meaningful Mössbauer parameters is shown in figure 2a. The Mössbauer parameters obtained are tabulated in table 2. The linewidths of the ferrous peaks have now fallen in the acceptable range. Fitting of five or more doublets as done by some earlier worker is not needed and has not been tried.

The assignment of different doublets to specific sites in chromite is complicated. To identify the sites we have used the known characteristic temperature variation of the hyperfine parameters. Figure 2b shows the Mössbauer spectrum of the sample C_1 taken at 125 K. Four symmetric doublets are fitted and χ^2 value obtained is reasonable. The computed hyperfine parameters are given in table 3. Comparing them with those at room temperature we note that the isomer shifts of all the sites have increased only slightly, in conformity with the expected increase of the order of 10^{-4} mm/s per K (Schmidbauer 1987). The QS of the Fe^{3+} site has increased by a small amount as expected. The quadrupole splittings of the second and third doublets show large increase (from 1.19 and 1.11 mm/s at room temperature to 2.12 and 2.57 mm/s respectively, at low temperature). We have assigned these doublets to Fe^{2+} at two different tetrahedral sites A_1 and A_2 as the QS of Fe^{2+} in tetrahedral coordination is known to have strong temperature dependence (Greenwood and Gibb 1971). More than one tetrahedral sites can exist in chromite because of next near neighbour interaction as mentioned earlier. The QS of the fourth doublet shows temperature variation of lesser magnitude (from 1.06 at RT to 1.87 mm/s at 125 K). Thus it is more

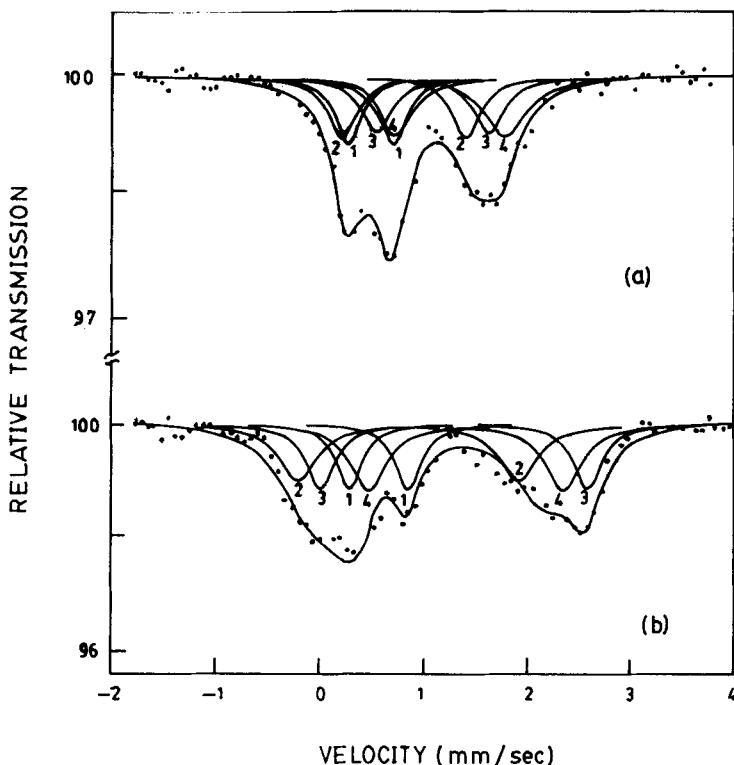


Figure 2. Mössbauer spectra of the sample C_1 with 'four doublet' fit: (a) at room temperature and (b) at 125 K.

logical to assign this doublet to Fe^{2+} at octahedral coordination than to Fe^{2+} at tetrahedral coordination. We have also noted that the area under a particular doublet is found to be temperature independent within the experimental error (table 3). This is to be expected if electron hopping among the sites does not occur in chromite (Osborne *et al* 1984).

Figure 3a shows the Mössbauer spectrum of the sample C_2 recorded at room temperature. A doublet with large linewidth (0.48 mm/s) is seen. Two doublets are fitted as shown in the figure and a good χ^2 and reasonable linewidths (table 3) are obtained. The doublet with IS 0.31 mm/s and QS 0.96 mm/s is assigned to Fe^{3+} in A sites. The other doublet with IS 0.53 mm/s and QS 0.97 mm/s is attributed to Fe^{3+} in B sites. These parameters are well within the range of the hyperfine parameters obtained for iron based compounds with Fe^{3+} ions distributed over tetrahedral and octahedral sites (Reiff 1973). Mössbauer spectrum of the sample C_2 recorded at 125 K (figure 3b) can be fitted with two doublets with acceptable χ^2 and hyperfine parameters (table 3) show the expected temperature dependence.

The sample C_3 gives a Mössbauer spectrum similar to that of C_2 at room as well as at low temperature and a 'two doublet' fit is sufficient (table 3). It must be emphasized that no doublet due to Fe^{2+} has been seen. The spectra of the samples C_4 and C_5 are similar to that of C_1 ; four symmetric doublets are fitted to them (table 3). In these three samples no doublet has been found for Fe^{3+} at A sites.

Table 3. Mössbauer parameters for the chromite samples.

Sample	T (K)	IS (mm/s) (± 0.03)	QS (mm/s) (± 0.03)	RI ($\pm 3\%$)	FWHM (mm/s) (± 0.03)	χ^2	Site assignment
C ₁	300	0.52	0.44	23	0.30	0.80 (300 K)	Fe ³⁺ (B)
	125	0.58	0.56	21	0.30		
	300	0.83	1.19	23	0.34	1.40 (125 K)	Fe ²⁺ (A ₁)
	125	0.37	2.12	26	0.45		
	300	1.11	1.08	22	0.36	1.40 (125 K)	Fe ²⁺ (A ₂)
	125	1.30	2.57	22	0.37		
C ₂	300	1.28	1.06	32	0.40	1.18 (300 K)	Fe ²⁺ (B)
	125	1.42	1.87	31	0.43		
	300	0.32	0.96	35	0.34	0.98 (125 K)	Fe ³⁺ (A)
	125	0.43	0.98	35	0.40		
	300	0.53	0.97	65	0.37	0.98 (125 K)	Fe ³⁺ (B)
	125	0.59	0.98	65	0.44		
C ₃	300	0.34	0.95	54	0.34	0.98 (300 K)	Fe ³⁺ (A)
	125	0.38	0.93	55	0.46		
	300	0.47	0.95	46	0.37	1.33 (125 K)	Fe ³⁺ (B)
	125	0.64	0.94	45	0.49		
	300	0.51	0.63	28	0.30	1.18 (300 K)	Fe ³⁺ (B)
	125	0.56	0.65	30	0.32		
C ₄	300	0.87	1.22	15	0.34	1.39 (125 K)	Fe ²⁺ (A ₁)
	125	0.90	2.53	13	0.35		
	300	1.06	1.33	33	0.40	1.39 (125 K)	Fe ²⁺ (A ₂)
	125	1.27	2.69	35	0.42		
	300	1.36	1.32	24	0.38	1.33 (300 K)	Fe ²⁺ (B)
	125	1.46	1.87	22	0.48		
C ₅	300	0.67	0.50	35	0.30	1.33 (300 K)	Fe ³⁺ (B)
	125	0.68	0.51	35	0.33		
	300	0.89	1.16	13	0.35	2.00 (125 K)	Fe ²⁺ (A ₁)
	125	0.90	1.92	15	0.37		
	300	1.18	0.86	35	0.39	2.00 (125 K)	Fe ²⁺ (A ₂)
	125	1.37	2.27	32	0.48		
300	1.35	1.04	17	0.40	2.00 (125 K)	Fe ²⁺ (B)	
125	1.43	1.52	18	0.41			

IS: Isomer shift, QS: quadrupole splitting, FWHM: full width at half maximum, RI: relative intensity under a doublet

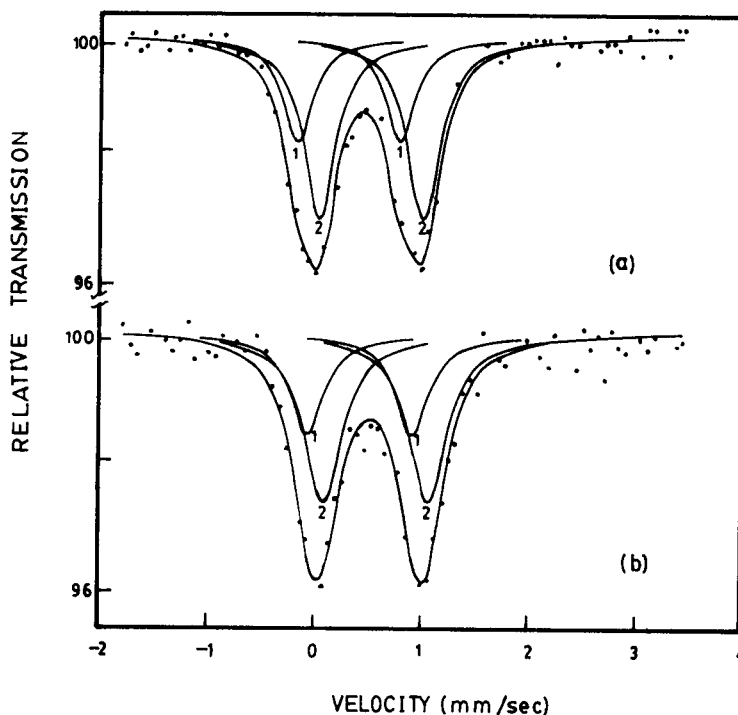


Figure 3. Mössbauer spectra of the sample C_2 : (a) at room temperature and (b) at 125 K.

3.2 X-ray diffraction analysis

X-ray diffraction patterns of the chromite samples have been checked for the spinel structure; a typical diffraction pattern (obtained for the sample C_1) is shown in figure 4. The lattice parameters calculated by taking the average of the several values obtained from each observed peak of known hkl value (taken from ASTM file) are shown in table 4. They compare well with those reported for standard chromite (McGregor and Smith 1963). The spinel structure in the samples is intact. Some weak peaks seen in the diffractogram are due to serpentine which is present in the chromite as gangue material.

3.3 Fe^{3+}/Fe^{2+} ratio, Fe/Cr ratio and chemical formula

As the Mössbauer spectra of the chromite samples at lower temperature are better resolved, the areas under the doublets from the low temperature spectra are utilized to calculate the relative percentage of Fe^{2+} and Fe^{3+} ions in the tetrahedral and octahedral sites and hence the Fe^{3+}/Fe^{2+} ratio. The Lamb-Mössbauer factors are assumed to be the same. The Fe/Cr ratio for all the samples have been calculated from the results of the chemical analysis and are presented in table 4. The known distribution of the Fe ions from Mössbauer analysis is combined with the results of the chemical analysis to construct the chemical formula of all the samples. The approximate

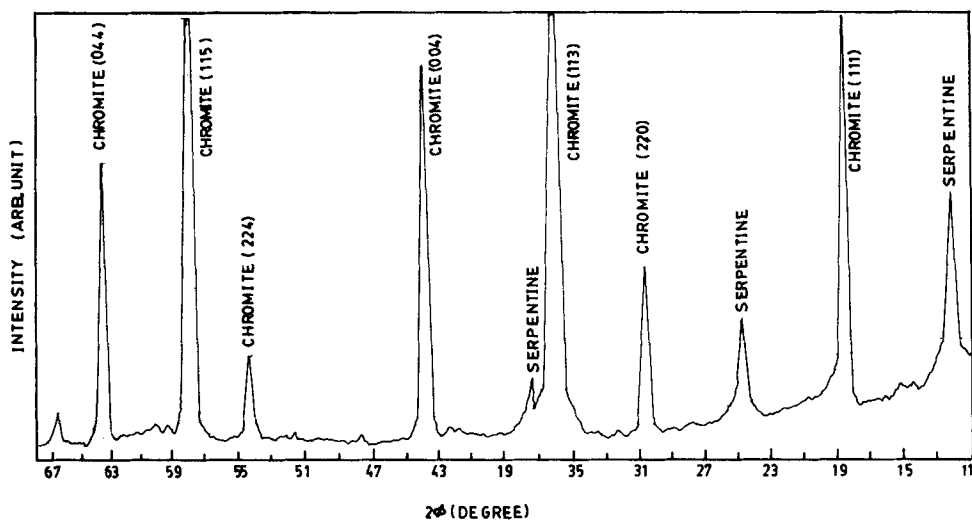
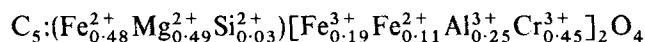
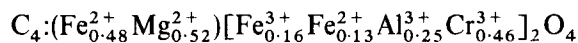
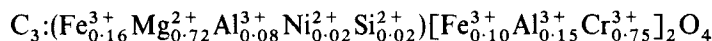
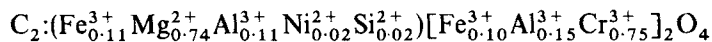
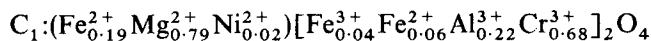


Figure 4. X-ray diffractogram of the sample C_1 .

Table 4. Mössbauer Fe^{2+}/Fe^{3+} ratio, Cr/Fe ratio and lattice parameters.

Sample	Fe^{3+}/Fe^{2+}	Cr/Fe	$a_0(\text{Å})$
C_1	0.26	3.31	8.302
C_2	—	4.74	8.285
C_3	—	4.10	8.310
C_4	0.43	0.88	8.304
C_5	0.54	0.83	8.301

formulas thus obtained are:



where () and [] represent tetrahedral and octahedral sites respectively.

4. Discussion

The samples C_2 and C_3 from Sukinda contain only Fe^{3+} though the sample C_1 from the same place contains both Fe^{2+} and Fe^{3+} . Since the samples were collected from the same ore belt the initial magmatic conditions are likely to be similar. Superficial weathering in the later stage could not be the sole reason for such complete oxidation of

the samples C₂ and C₃. Da Silva *et al* (1976) studied the oxidation process of natural chromites and observed complete oxidation of Fe²⁺ to Fe³⁺ as the samples were heated above 800°C in air, though the spinel structure was retained. We surmise that the samples C₂ and C₃ have been subjected to reheating above 800°C in abundant oxygen. There is some geological evidence that a late intrusive orthopyroxinite in this area caused local heating to 1200°C or so (Chakravorty and Baidya 1978). This, in addition to the normal weathering, is probably the reason for the complete oxidation in C₂ and C₃. The intrusion must have been localized, as C₁ collected from the same chromiferous ultramafic belt about 8 km away has not been fully oxidized.

A comparison of Fe/Cr ratio and the Fe³⁺/Fe²⁺ ratio of the two groups of samples suggest that the major constituents (iron and chromium) were present in different proportions in the chromite forming magmas in these two belts and that the samples C₄ and C₅ were formed under higher oxygen fugacity.

In the ideal chromite we have Fe²⁺ in more than one tetrahedral site. When the chromites are oxidized or subject to thermal effects, the cation distribution is disordered, and Fe²⁺ and Fe³⁺ can occur on both A and B sites. If oxidation is complete only Fe³⁺ is found in both A and B sites. In C₁, C₄ and C₅ we do not see Fe³⁺ on the A site, and we do not have to invoke the inversion of the spinel structure. Our analysis agrees with that of Dyar *et al* (1989) who also fit the spectra by four doublets due to Fe²⁺ (A₁), Fe²⁺ (A₂), Fe²⁺ (B) and Fe³⁺ (B).

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