Petrogenetic implication of the Mössbauer hyperfine parameters of Fe^{3+}-chromites from Sukinda (India) ultramafites

SACHINATH MITRA, TAPAN PAL AND TARAKNATH PAL

Department of Geological Sciences, Jadavpur University, Calcutta 700032, India

Abstract

Chromites from two horizons of the Sukinda area (India) marked as 'grey ore' and 'brown ore' zones have been studied by ^{57}Fe Mössbauer spectroscopy, which revealed that both chromite types are oxidised and have a type of disordered spinel structure in which octahedral sites are occupied by Fe^{2+} ions.

The spectra of the grey ore sample can be fitted to three doublets corresponding to Fe^{2+} (A), Fe^{3+} (A) and Fe^{2+} (B) sites. This sample is less oxidised than the brown ore, in which progressive oxidation in the magmatic (?) stage led to the complete conversion of Fe^{2+} in A sites to Fe^{3+}. The spectra of the brown ore are characterised by two doublets corresponding to two tetrahedral (A) sites of Fe^{3+} with different next-nearest neighbour configurations and a third doublet for Fe^{2+} at the B site. The brown ores have higher chromium and Fe^{3+} content and have lesser amounts of Ni and Al in comparison to the grey ores. Megascopically, the former shows larger crystal sizes. The high Fe^{3+} content in the brown ore suggests that this type of chromite was formed in a region of high f_{O_2} in the magmatic environment. This perhaps occurred at the part of the mantle where the temperature was higher and the rate of cooling was slower than that of the grey ores which crystallised in the magmatic melt.

KEYWORDS: spinel, chromite, electron hopping, electron localisation, Mössbauer spectra, Sukinda, ultramafites, India.

Introduction

CHROMITE is characterised by spinel structure with cubic close packing and space group *Fd*3*m*, Z = 8. In each unit cell, 8 of the 64 tetrahedral and 16 of 32 octahedral sites are occupied by cations. The tetrahedral *A* sites have symmetry T_d and are normally occupied by Fe^{2+} (A) liganded by four oxygens in the first coordination sphere; 12 oxygens and 12 cations in octahedral sites occur in the second coordination sphere.

In recent studies using Mössbauer spectroscopy doubts have been cast on the long-standing view of the assignment of the normal spinel form to chromite (Osborne *et al.*, 1981; Osborne, 1984; Bancroft *et al.*, 1983; Galvao Da Silva *et al.*, 1976, 1980; Fatseas *et al.*, 1976; Robbins *et al.*, 1971; Zhe *et al.*, 1988). These studies indicated that natural chromites have wide range of chemical composition and have both normal and inverse spinel structures. Fatseas *et al.* (1976) have shown that Fe^{3+} may occur in chromite both in the tetrahedral and octahedral sites. Progressive enrichment of Fe^{3+} in the tetrahedral site (commonly occupied by Fe^{2+}), accompanied by concomitant replacement by Fe^{2+} of M^{3+} Fe^{3+}, Cr^{3+}) in the octahedral site, results in a $Fe^{2+} \rightleftharpoons Fe^{3+}$ electron hopping in the octahedral sites.

Galvao Da Silva *et al.* (1980) have studied several natural chromites by Mössbauer spectroscopy and classified them into three groups on the basis of different site occupancies of Fe^{2+} and Fe^{3+} ions. The first group is a normal ordered spinel structure with Fe^{2+} and Fe^{3+} exclusively occupying the tetrahedral and octahedral sites respectively. The second and third group have disordered spinel structures. In the second group the octahedral site is solely occupied by Fe^{3+}, while the tetrahedral site is occupied both by Fe^{2+} and Fe^{3+} ions, with no report of electron hopping at the site. In the third group Fe^{2+} ions are present in both tetrahedral and octahedral sites. These result in an electron hopping of $Fe^{2+} \rightleftharpoons Fe^{3+}$ in the octahedral site which gives characteristic Mössbauer parameters. Osborne *et al.* (1981) questioned the possibility of such disordering in

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chromite, which they maintained to be strictly an ordered normal spinel. Mössbauer spectra of chromite fitted to four doublets, arising out of next-nearest neighbour effect model, have also been reported by Zhe *et al.* (1988). The chromites occurring within the tectonically emplaced Proterozoic (middle) ultramafites (altered) in the Sukinda area (E. India) producing the largest amount of chromite ore in India are investigated by the present authors. The results are discussed in the following sections.

The samples

The chromites of the Sukinda area (Orissa, India) were collected from the chromite bands occurring in association with the ultramafites, composed mainly of dunite, harzburgite, websterite, etc. and their metamorphic (metasomatic) derivatives which occur with intrusive relationship with the host country rocks such as banded hematite ores of the Banded Iron-Formation (*c.* 3 Ga) of E. India (Mitra, 1960). In this area chromite occurs as two distinct varieties which characterise two zones of chromite bodies. These are represented as brown ore and grey ore chromites (Mitra, 1960; 1976*b*).

The brown ore (BCR) and grey ore (GCR) chromites have been investigated using Mössbauer spectroscopy, with evidence from other methods, viz. X-ray powder diffraction, X-ray fluorescence, and susceptibility measurement.

The results are interpreted in terms of plausible distributions of cations in the crystallographic sites and the relevance of this distribution in deciphering the genetic history of these two types of chromites, which are distinctive in their physicochemical properties and petrological association characterising their occurrence in two horizons (Mitra, 1976*b*).

Experimental

As the lower limits of optically measured grain diameters are 0.3 mm and 0.1 mm respectively for the brown and grey ores, the massive ores were crushed and sieved into 0.25–0.42 mm (40–60 mesh) and 0.18–0.25 mm (60–80 mesh) respectively. These were then treated repeatedly with warm dilute HCl and later gravity separated from the lighter silicates using bromoform. These procedures liberated >99% of the chromite from the interstitial silicates; and the separated chromites were used for XRD, XRF, Mössbauer and magnetic studies.

The X-ray powder diffraction (XRD) studies were carried out in a Philips microprocessor controlled PW 1710 diffractometer by using Fe-$K\alpha$ radiation (30 kV, 20 A) and a graphite monochromator.

The XRF study was carried out using a Philips 1212 automatic X-ray Fluorescence Spectrometer; the standard chromite sample from Turkey was analysed by Engin and Hirst (1970). Magnetic susceptibility at 297 K was measured in a Vibrating Sample Magnetometer (Model 155). The Mössbauer spectra for both room temperature (297 K) and low temperature (110 K) were recorded in a spectrometer using a 10 mCi ^{57}Co/Rh source with a constant acceleration drive. The low temperature studies were carried out by mounting the sample in a liquid N_2 cryostat (cold-finger type). The spectra were then fitted to Lorentzian lines with a non-linear least-square fit programme. For each doublet the intensities and line widths of equivalent lines were kept equal and constant. The velocity calibration was performed with respect to a metallic iron (99.991%) standard.

Results and discussion

The brown ores are megascopically coarser in grain size (*c.* 1 cm) than the grey ores ($\leqslant$4 mm). The cell parameters, determined from a number of significant peak positions and corrected using the Nelson-Riley extrapolation, indicate distinct differences in the cell-edges of the two ore types; the brown ores have lower a_0 (8.274 ± 0.06 A°) than those of the grey ores (a_0 = 8.229 ± 0.11 A°).

The room-temperature (297 K) Mössbauer spectra show three sets of doublets corresponding to $Fe^{3+}(A)$, $Fe^{2+}(A)$ and $Fe^{2+}(B)$ for GCR (Fig. 1*a*) and $Fe^{3+}(A_1)$, $Fe^{3+}(A_2)$ and $Fe^{2+}(B)$ for BCR (Fig. 1*b*). For better resolution of the doublets in GCR, low-temperature spectra (110 K) (Fig. 2) were taken. The Mössbauer parameters and the Fe^{3+}/Fe^{2+} ratios in these samples, determined from the fitted spectra, are shown in Table 1. In the fitting procedure the line width and intensities of the peaks in doublets are constrained to be equal. Assuming the recoil free fraction (*f*) at the *A* and *B* sites to be equal, the areas of the doublets would correspond directly to the quantitative occupancies of iron in these sites.

The $Fe^{2+}(A)$ on a regular cubic tetrahedral site in the spinel structure would show a singlet with no quadrupole splitting. The observed quadrupole splitting for $Fe^{2+}(A)$ in our samples may be explained as due to (i) random strain produced by the presence of other ions on the tetrahedral sites, causing the lifting of the degeneracy of the low-lying crystal field states (Leider and Pipkorn,

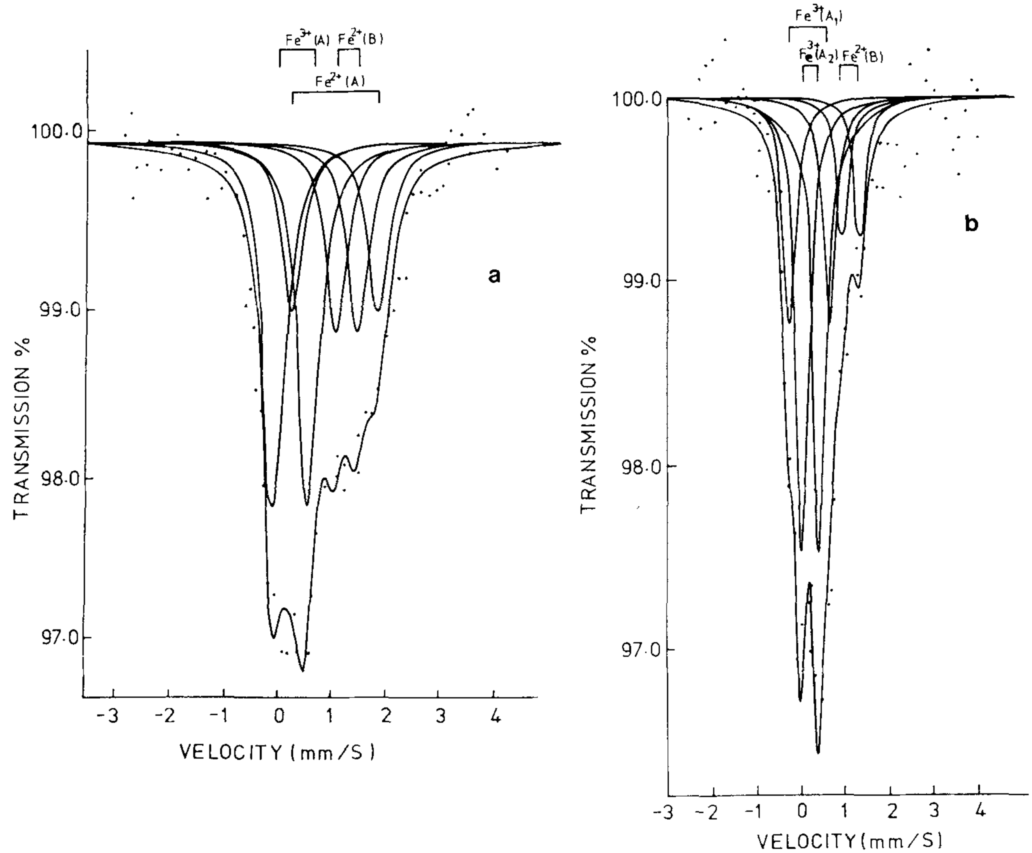

FIG. 1. Room temperature Mössbauer spectra of (*a*) grey ore and (*b*) brown ore chromites.

1968) and/or (ii) by the substitutional distributions of Cr^{3+}, Al^{3+}, Fe^{2+}, etc. of different atomic radii in octahedral sites, causing a comparable strain (Robbins *et al.*, 1971), or distortion of the *A*-site by the next-nearest-neighbour effect. Such an effect can be attributed to an induced anisotropy of the EFG at the Fe^{2+} nucleus by trivalent cation substitution in the next-nearest-neighbour cation sphere. The complex broad spectra of substituted $FeCr_2O_4$ may be explained by partial quadrupole splitting theory (Bancroft *et al.*, 1983), due possibly to the superposition of multiple split doublets assigned to statistically different next-nearest-neighbour (*nnn*) configuration.

The *nnn* effect on QS is more evident for Fe^{2+} (compared to Fe^{3+}) on *A*-sites, because Fe^{3+} is spherically symmetric; and the low lying electron of *e*-orbitals of $Fe^{3+}(A)$ are perhaps less amenable to Jahn–Teller distortion and consequent degeneracy loss than Fe^{2+}. The QS on *A*-sites may also be contributed by the distortion of the site by the presence of vacancies coupled with Fe^{3+}, introduced during oxidation. Quadrupole splitting on octahedral (*B*) sites is generated by trigonal distortion of this site (Mizoguchi and Tanaka, 1963).

Assignment

The room-temperature spectrum for GCR shows three doublets (Fig. 1*a*) with respective isomer shift (IS) 0.19, 0.89, and 1.08 mm/s. The first doublet has been assigned to tetrahedral Fe^{3+}, which is in agreement with previous workers (Galvao Da Silva *et al.*, 1980; Fatseas *et al.*, 1976; Marshall and Dollase, 1984; Dyar *et al.*, 1989). Galvao Da Silva *et al.* (1980) had assigned the doublets with IS (δ) 0.80–1.00 mm/s and QS (Δ) 1.36–1.70 mm/s to $Fe^{2+} \rightleftharpoons Fe^{3+}(B)$ (electron hopping). Similar electron hopping in chromite was also reported by Fatseas *et al.* (1976) but with a lower value of isomer shift. Charge hopping is also present in magnetite. The doublets with $\delta = 0.67$–0.76 mm/s, $\Delta = 1.36$–1.70

mm/s are typical of $Fe^{2.5+}$ (Nolet and Burns, 1979). But some workers do not agree to any possible presence of electron hopping in chrome spinels and have assigned to tetrahedral Fe^{2+} for the doublets with $\delta = 0.85$–0.95 mm/s (Osborne *et al.*, 1981; Marshall and Dollase, 1984; Dyar *et al.*, 1989) and Δ ranges from 0.75 mm/s (Osborne *et al.*, 1981) to 2.09 mm/s (Dyar *et al.*, 1989).

The second doublet of the grey ore shows $\delta = 0.89$ mm/s, $\Delta = 1.37$ mm/s. To reach a better assignment a low-temperature (110 K) spectrum of this sample was taken and the better resolved Mössbauer spectrum showed a doublet of $\delta = 0.96$ mm/s and $\Delta = 2.70$ mm/s. These IS and QS values would rather indicate the presence of Fe^{2+} at tetrahedral (A) sites rather than $Fe^{2+} \rightleftharpoons Fe^{3+}$ at octahedral (B) sites.

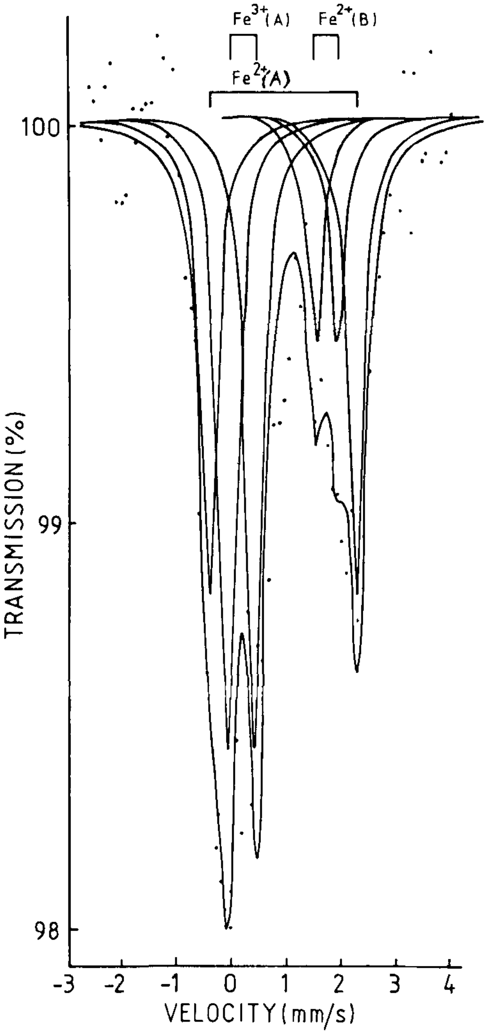

FIG. 2. Mössbauer spectrum of grey ore at low temperature (110 K).

The assignment of a third doublet with $\delta = 1.08$ mm/s may be debatable. The early workers (Galvao Da Silva *et al.*, 1976, 1980; Fatseas *et al.*, 1976; Singh *et al.*, 1978) had assigned this hyperfine parameter to $Fe^{2+}(A)$. Recent work on spinels, however, assign the doublet with $\delta \geqslant 1.02$ mm/s to $Fe^{2+}(B)$ (Marshall and Dollase, 1984; Dyar *et al.*, 1989). The 110 K spectrum showing $\delta = 1.74$ mm/s, $\Delta = 0.39$ mm/s supports the assignment of this doublet as suggested by recent workers. The assignment of the doublets of BCR shows a correspondence with other workers' reported values (Table 1). The presence of two doublets on tetrahedral sites assigned to $Fe^{3+}(A_1)$ and $Fe^{3+}(A_3)$ (Table 1) may be explained by different next-nearest-neighbour configuration effects (Bancroft *et al.*, 1983; Zhe *et al.*, 1989).

Oxidation

Robbins *et al.* (1971), by a study on the $(Fe^{2+}Cr_{2-x}Fe_x^{3+}O_4)$ system, showed that up to $x = 0.68$, Fe^{3+} went into *B* sites and, on further enrichment of Fe^{3+} (in region $0.68 < x < 1.38$), Fe^{3+} then went into *A* sites, displacing corresponding amounts of Fe^{2+} to the *B* site. Schmidbauer (1987) suggested an oxidation mechanism of $FeCr_2O_4$ in which a migration of some Fe^{2+} or Fe^{3+} cations from *A* to *B* sites was assumed. The presence of total iron in the *B* sites as Fe^{2+} has probably not yet been reported. This could be explained by a model as follows. In a spinel lattice electron transfer from one site to another adjacent site is a more probable mechanism than cation migration or diffusion during oxidation, as suggested earlier (Schmidbauer, 1987). In the early crystallising spinels octahedral (*B*) sites were occupied by trivalent cations including Fe^{3+}, while *A* sites were occupied by divalent cations, mainly Fe^{2+}.

During oxidation, Fe^{2+} in *A* sites underwent progressive conversion into Fe^{3+} and the released electron moved from an *A* to *B* site and was localised on $Fe^{3+}(B)$, reducing it to Fe^{2+}. After the full conversion of $Fe^{3+}(B)$ into $Fe^{2+}(B)$, further oxidation transformed the excess Fe^{2+} in the *A* site to $Fe^{3+}(A)$. The area of the doublets indicates a low content of $Fe^{2+}(B)$ in comparison to total iron. This may confirm the view that initially (before oxidation) there was less substitutional Fe^{3+} on *B* sites. A grey ore sample showed both Fe^{2+} and Fe^{3+} on *A* sites, while a brown ore showed Fe^{3+} alone. Therefore,

Table 1 . Mössbauer parameters and distribution of Fe^{2+} & Fe^{3+} at different sites and Fe^{3+}/Fe^{2+} ratio determined from spectra.

	IS (δ) in mm/s	QS (Δ) in mm/s	Distribution	Area of the doublets	Line width in mm/s	λ^2	Fe^{3+}/Fe^{2+}
Grey ore (297K)	0.19	0.54	Fe^{3+}(A)	50.28%	0.38	1.35	1.011
	0.89	1.37	Fe^{2+}(A)	23.37%			
	1.08	0.34	Fe^{2+}(B)	26.35%			
Grey ore (110K)	0.21	0.51	Fe^{3+}(A)	47.22%	0.38	1.73	0.894
	0.96	2.70	Fe^{2+}(A)	35.82%			
	1.74	0.39	Fe^{2+}(B)	16.96%			
Brown ore (297K)	0.16	1.08	$Fe^{3+}(A_1)$	28.00%	0.38	1.52	5.235
	0.23	0.46	$Fe^{3+}(A_2)$	56.09%			
	1.28	0.47	Fe^{2+}(B)	15.91%			

although both the ores are oxidised, GCR is the product of a lower degree of oxidation than BCR. This is also supported by the observed Fe^{3+}/Fe^{2+} ratio, measured by the Mössbauer spectroscopy (Table 1). The process of oxidation is accompanied by cation deficiency on iron sites as $Fe^{2+} + \frac{1}{4}ZO = Z\,Fe^{3+} + (1 - Z)Fe^{2+} + \frac{1}{4}ZO^{2-}$ where Z is the oxidation parameter which determines the proportion of Fe^{2+} ions converted to Fe^{3+} ($0 \leq Z \leq 1$) (Readman and O'Reilly, 1972). For cation-deficient $FeCr_2O_4$, with $Z = 1$ the following cation distribution formulae have been proposed by Gillot *et al.* (1973, 1981).

$$Fe^{3+}_{8/9}\square_{1/9}[Cr^{3+}_{16/9}\square_{2/9}]O_4$$
$$\text{and } Fe^{3+}_{6/9}\square_{3/9}[Cr^{3+}_{16/9}Fe^{3+}_{2/9}]O_4 \qquad (\square = \text{vacancy})$$

The X-ray fluorescence (XRF) data (Table 2), along with Mössbauer analysis, led us to derive the chemical formula of the samples as:

GCR:

$$Mg_{5.762}Fe^{3+}_{1.245}Fe^{2+}_{0.588}Ca_{0.029}Ni_{0.029}Si_{0.059}$$
$$\square_{0.288}(Cr_{10.692}Fe^{2+}_{0.654}Al_{4.324}Ti_{0.236}\square_{0.094})O_{32}$$

BCR:

$$Mg_{4.371}Fe^{3+}_{2.639}Ca_{0.001}Ni_{0.014}Si_{0.295}\square_{0.680}$$
$$(Cr_{11.431}Fe^{2+}_{0.499}Al_{3.514}Ti_{0.029}\square_{0.527})O_{32}.$$

Both the chromite samples show cation deficiency. Distributions of cations other than iron follow the results of other workers (Banerjee *et al.*, 1969; Jensen and Shive, 1973). The greater the conversion of Fe^{3+} from Fe^{2+} and associated vacancy generation, the higher the magnetic susceptibility in chromite is to be expected. The room temperature magnetic susceptibility of brown ore and grey ore were measured as 35.04×10^{-6} and 32.96×10 e.m.u/g respectively. This may be explained by using Schmidbauer's (1987)

Table 2

Chemical composition of brown ore and grey ore chromites [analysed by X-ray fluorescence (XRF)]

Oxide %	Brown ore	Grey ore
SiO_2	1.21	0.25
Cr_2O_3	58.86	54.89
Al_2O_3	12.16	14.95
MgO	11.97	15.47
FeO	15.59	12.20
CaO	0.02	0.12
TiO_2	0.19	1.30
NiO	0.14	0.21
Total	100.14	99.39

* All Fe recalculated as FeO

model where the J_{AB} magnetic coupling of Fe_A^{3+}–O^{2-}–Cr_B^{3+} in BCR is stronger than Fe_A^{2+}–O^{2-}–Cr_B^{3+} in GCR.

The chemical data (Table 2) show that brown ore chromites contain more Cr and less Mg, Al, Ti, Ni and Ca than the grey ore chromites. Since spinels rich in chromium have higher crystallising temperatures than those spinels with higher contents of Al, Ti, Ca etc., the brown ore chromites, with higher Cr-content might have crystallised at an earlier stage and at higher degree of f_{O_2} in the evolution of the Sukinda magma. With progressive crystallisation of Cr-rich chromite and its segregation, the melt became increasingly enriched in Al, and successively crystallising chromite spinels continued to incorporate increasing amounts of Al in the lattice. Thus, when the grey ore chromites crystallised, they became more rich in Al with simultaneous incorporation of other cations, viz. Ni, Ti, Ca. At the initial stage of crystallisation of the mantle, Cr-rich chromites crystallised along with high magnesian olivine (forsterite, Mg_2SiO_4). Nickel, having stronger preference (CFSE) for the smaller and regular octahedron *M*1 in forsterite (Fo), with perfect O_h symmetry site, than the *A* and *B* sites in spinel, entered into olivine structures more readily, while the simultaneously crystallising chromite phases remained depleted in Ni. This process occurred at a condition of high f_{O_2} when the brown ore chromite was simultaneously crystallising with high Fo-olivine to form banded or layered structures in chromite (Mitra, 1960). Crystallisation of olivine at high f_{O_2} condition has been reported earlier by Shinno (1981) using ^{57}Fe Mössbauer spectra of Fe^{3+} in olivines from Japan. Thus the brown ore chromite layers and the host ultramafites (now highly altered) crystallised and settled at high f_{O_2} condition. At a subsequent stage, when the grey ore chromite appeared, the f_{O_2} of the melt decreased and, more significantly, Al^{3+} incorporation in the octahedral (*B*) sites of the crystallising chromites increased. Some workers, however, have distributed Al^{3+} in the tetrahedral (*A*) site (Galvao Da Silva *et al.*, 1980), the basis of which is not clear to the present authors.

Results of chemical analysis of the chromites indicate that both brown ore and grey ore chromites are rich in Mg. The conspicuous unaltered ultramafic rock seen as an elongated body is composed entirely of orthopyroxene. The temperature of crystallisation of the rock on the basis of the $X_{M1}^{Fe} - X_{M2}^{Fe}$ distribution, determined by Mössbauer spectroscopy, was about 800 °C (Mitra, 1976*a*). Thus the high magnesium product (enstatite) at the post-chromite crystallisation stage may also suggest a very high magnesium, high chromium, high f_{O_2}, low Ca and Al ultramafic melt occurring in the mantle in this part of Pangea, dated about 3 Ga. The sequence of chemical changes in the monomineralic rocks (chromitites, enstatites) in Sukinda would therefore depict the crystallising history or mantle sequence underlying this part of India in the Proterozoic period which Mitra (1973) termed the Sukinda magma.

Conclusion

Mössbauer results show that the Sukinda chromites were oxidised to incorporate Fe^{3+} at the magmatic stage, probably in the mantle. At the early stage of magmatic evolution the oxygen fugacity and temperature were high resulting in a total occupation of tetrahedral sites by Fe^{3+}, with simultaneous occurrence of Fe^{2+} in octahedral sites of the crystallised Cr-rich chromites (brown ores). At this stage Ni^{2+} ions entered Mg-rich olivine which crystallised simultaneously with chromite. This was a phase of magmatic crystallisation when f_{O_2} was high and the rate of cooling was probably slow, giving rise to crystalline euhedral octahedrons of chromite up to 1 cm across and having smaller cell edges ($a_o = 8.274 \pm 0.06$ A°) compared to the later evolving chromites of the grey ores ($a_o = 8.299 \pm 0.11$ A°). Al^{3+} and Ni^{2+} did not enter into the chromite lattice at this stage of crystallisation; Ni^{2+} entered the octahedral sites of olivine while Al^{3+} remained mostly in the magmatic liquid. At a later stage of magmatism the rate of cooling increased, f_{O_2} decreased and grey ores appeared with both Fe^{2+} and Fe^{3+} on tetrahedral sites and sole occupancy of Fe^{2+} on octahedral sites, and enrichment of Ni^{2+}, Al^{3+} and Ti^{4+} compared to earlier formed brown ore chromitite layers. Therefore the brown ore and grey ore may be respectively early and late crystallised products of the same ultramafic melt, or alternatively may represent different segments of the heterogeneous mantle under this part of the Proterozoic craton, now manifested by the Sukinda–Naushai ultramafic plutons, with chromite bodies of commercial importance (Mitra, (1976*b*) emplaced in the Banded Iron Formations (*c.* 3 Ga) of eastern India.

Mössbauer studies of different mantle-derived materials provide an insight into the oxidation states of the source regions of those materials. The work of Canil *et al.* (1988) on spinel lherzolite xenoliths from British Columbia and of Dyar *et al.* (1989) on the spinel lherzolites from different localities are very helpful for this purpose. The study on spinel lherzolite by Canil *et al.* (1988)

indicated a depleted oceanic character of that part of upper mantle beneath British Columbia and alkaline lavas in this region were derived from an oxidised source, perhaps at great depth.

The intrinsic oxygen fugacity measurements from the peridotite and megacryst assemblages (Arculus and Delano, 1981; Arculus *et al.*, 1984) and from spinel lherzolites (Canil *et al.*, 1988; Dyar *et al.*, 1989) indicate a lateral as well as vertical heterogeneity in the redox state of the upper mantle.

The composition and stability of solid phases in a given region is related to the composition and redox state of that part of mantle. At present, there is no consensus regarding the oxidation state of the mantle (Virgo *et al.*, 1988). The local heterogeneity in redox state and mantle chemistry as delineated in this area is likely to be a universal phenomenon and we await further supporting evidence from other ultramafic intrusives.

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