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Cation distribution in Cr-spinels from the Sittampundi layered complex and their intracrystalline thermodynamics

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High aluminium chromites occur as bands within anorthosite layered complex of Sittampundi (Tamil Nadu). Cation distribution of two chromite samples is determined by combined electron probe microanalysis and Mössbauer spectroscopy. In the deconvolution of the Mössbauer spectra, the suitability of the best model of spectral fitting has been established with the observation that both Fe^{2+} and Fe^{3+} ions occur at tetrahedral (A) and octahedral (B) sites and $Fe^{3+}/\sum Fe$ found to be ranging between 0.45 and 0.48. Oxygen fugacity (fO_2) has been determined to be about $10^{-7.3}$. Thermodynamic parameters have been determined for the studied chromites using standard models.

Keywords: Cation distribution, chromite, Mössbauer spectroscopy, Sittampundi, thermodynamic parameter.

SPINELS are used as a petrogenetic indicator because their chemical and structural variations are dependent on the

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paragenesis, pressure and temperature of crystallization. The widespread occurrence of spinels is in part a result of the large number of cations that the structure can accommodate. Many crystallographic[1–4] and thermodynamic[4–10] studies have been done on synthetic spinels because of their applications in materials science, metallurgy and earth sciences. However, studies on natural spinel are scarce due to difficulties in assigning major cations present in the tetrahedral (A) and octahedral (B) sites. Among the cations present in spinel, Fe commonly exists in multiple valence states and accurate knowledge of the Fe^{3+}/Fe^{2+} ratio allows us to estimate the oxygen fugacity (fO_2), which controls the magmatic crystallization path and composition of the resulting mineral phases. The aim of the present work is to determine the cation distribution of chromites (Cr-spinel) from the Sittampundi complex, Tamil Nadu, using electron probe microanalysis (EPMA) and room temperature ^{57}Fe Mössbauer spectroscopy (MS) and the intracrystalline thermodynamic parameters of the natural samples.

Sittampundi layered anorthosite complex occurs as a layered igneous body[11]. The study area forms a part of the granulite terrain of South India. Major rock types are chromitite bearing meta-anorthosite, amphibolite, basic granulite, two pyroxene granulite, leptynite, biotite gneiss and pink granite. Chromitite occurs exclusively within the anorthosite as discontinuous bands/lenses. Samples used for crystallo-chemical investigation were culled from chromititites (chromite + rutile + calcic amphibole ± antho-phyllite ± clinochlore). Two samples, #30a and #56 were collected from conformable chromitite lenses on a foot track in the western part of Karungalpatti, Salem district, Tamil Nadu. These two samples are henceforth referred to as Ch_1 and Ch_2.

Chromite samples from the Sittampundi area were studied by the combined EPMA and MS. Samples were analysed by a JEOL-733 superprobe microanalyser with wavelength dispersive method at the Department of Geology, Yonsei University, Seoul. Room temperature (298 K) Mössbauer spectrum was recorded in a Wissel-make conventional constant acceleration spectrometer using a 10 mCi Co/Rh source. The spectrum was fitted to Lorentzian lines with a nonlinear least square fit programme. The velocity calibration was performed with respect to pure metallic iron (99.99%) standard. Detailed processing of the samples and the procedures adopted for data acquisition for the EPMA and MS studies are reported elsewhere[12].

Natural chromite samples having complex compositions or crystallizing in an oxidizing environment, often exhibit disorder of Fe^{2+} and Fe^{3+} distribution between octahedral (B) and tetrahedral (A) sites. We have fitted the spectra considering both the normal and disordered distribution. The spectra fitted in the disordered distribution showed better acceptable χ^2. For natural chromites best-fitting results were obtained using a three-doublet model by Wood and Virgo[13] and a four-doublet model by Dyar *et al.*[14]. Fitting model with four doublets showed better results and

Table 1. Mössbauer parameters and distribution of Fe^{2+} and Fe^{3+} at different sites and $Fe^{3+}/\Sigma Fe$ determined from relative areas

Sample no.	IS (mm/s)	QS (mm/s)	Site	Line width (Γ) (mm/s)	Area (%)	χ^2	$Fe^{3+}/\Sigma Fe$
Ch_1	0.31	0.53	Fe^{3+} (A)	0.46	20.56	1.61	0.48
	0.53	0.43	Fe^{3+} (B)	0.33	27.66		
	0.95	1.62	Fe^{2+} (A)	0.30	20.63		
	1.74	0.58	Fe^{2+} (B)	0.49	31.15		
Ch_2	0.22	0.55	Fe^{3+} (A)	0.40	20.45	2.48	0.45
	0.44	0.52	Fe^{3+} (B)	0.36	24.49		
	0.90	0.52	Fe^{2+} (A)	0.46	21.25		
	1.66	0.56	Fe^{2+} (B)	0.57	33.81		
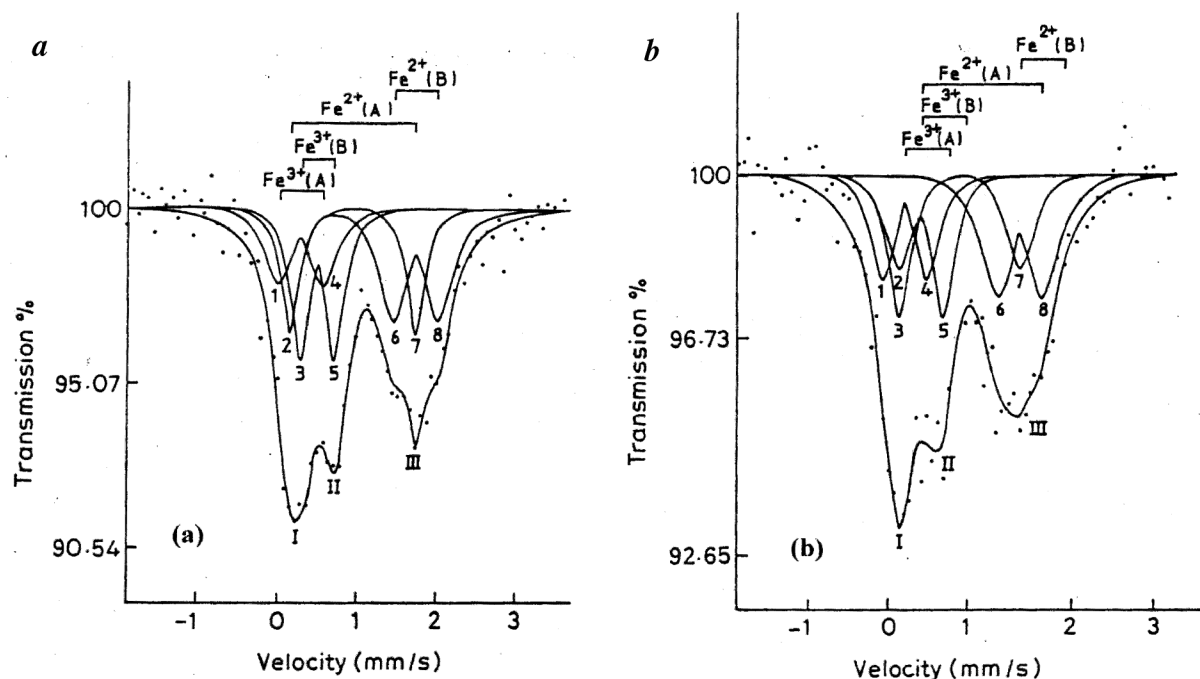
Figure 1. Room temperature ^{57}Fe Mössbauer spectra of chromites: (*a*) sample Ch_1 and (*b*) sample Ch_2.

is considered for the present study. The obtained hyperfine parameters and $Fe^{3+}/\Sigma Fe$ ratios are presented in Table 1 and the spectra are shown in Figure 1.

The first doublet (1–4) with IS 0.31 mm/s (sample Ch_1) and 0.22 mm/s (sample Ch_2) has been assigned to tetrahedral Fe^{3+}. These values correspond to the results reported by earlier workers[14–20]. Doublets (3–5) with IS 0.53 mm/s (sample Ch_1) and 0.44 mm/s (sample Ch_2) are assigned to octahedral Fe^{3+}, which is in accordance with reported by previous workers[16,17,20].

Galvao Da Silva *et al.*[16] have assigned the doublets with IS 0.80–1.00 mm/s and QS 1.36–1.70 mm/s to $Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$ at B site (electron-hopping). Similar electron-hopping in chromite was also reported by Fatseas *et al.*[15], with a lower isomer shift value. However, subsequent workers have discarded the concept of electron-hopping in

spinels[14,17,18,21,22] and assigned the doublets with IS 0.85–0.95 mm/s to tetrahedral[14,17,21] Fe^{2+} and $QS^{14,21}$ ranging from 0.75 mm/s. In the present case the doublets (2–7) with IS 0.95 mm/s (sample Ch_1), 0.90 mm/s (sample Ch_2) and the corresponding QS of 1.62 and 0.52 mm/s respectively, are assigned to Fe^{2+} at A-site rather than $Fe^{2+} \Leftrightarrow Fe^{3+}$ at B-site[14,17–19,21], favouring the view that the present samples showing such hyperfine parameters do not involve $Fe^{2+} \Leftrightarrow Fe^{3+}$ electron hopping.

Assignment of the fourth doublet (6–8) with IS 1.74 mm/s (sample Ch_1) and 1.66 mm/s (sample Ch_2) may be debatable. Early workers[15,16,23,24] had assigned doublet with IS 1.08 mm/s to Fe^{2+} (A). Subsequent studies on spinels, however, assigned the doublet with IS ≥ 1.02 mm/s to Fe^{2+} at B-site[14,17–20]. The presence of four sets of doublets and estimated $Fe^{3+}/\Sigma Fe$ ratios (Table 1), show the oxi-

dized nature of the Sittampundi chromites. Chemical composition of the studied chromites and cation distribution based on combined EPMA and MS studies are presented in Table 2.

Spinel occurs in two types: (i) normal, where divalent cations occupy tetrahedral site and trivalent cations occupy octahedral site and (ii) inverse, where trivalent cations occur in tetrahedral site and octahedral site is occupied by both divalent and trivalent cations. Any partly disordered state may be expressed as a mix of these two end-members, with a general formula $^{[4]}(A_{1-x}B_x)^{[6]}(B_{2-x}A_x)O_4$, where x is the degree of disorder. Characterization of order–disorder phenomenon is central to the understanding of the thermodynamic properties of spinels. So far, application of the postulated thermodynamic models to natural samples is limited. From the combined EPMA and MS data, we have estimated the thermodynamic parameters of the studied samples. Absence of olivine-spinel assemblage does not allow us to determine the equilibrium temperature of the studied chromite samples. We have estimated these equilibrium temperature of an associated basic granulite rock. Using garnet–clinopyroxene geothermometry[25], equilibrium

Table 2. Cation distribution of studied chromites using electron probe microanalysis and Mössbauer spectroscopy (MS)

Oxide	Ch₁*	Ch₂*
SiO_2	0.01	0.15
TiO_2	0.16	0.12
Cr_2O_3	34.68	36.72
Al_2O_3	28.06	25.56
Fe_2O_3	14.26	14.34
FeO	13.77	15.80
MnO	0.23	–
MgO	10.03	7.60
NiO	0.14	0.17
CaO	–	0.17
Na_2O	0.02	0.02
K_2O	0.01	0.01
Total	101.37	100.66

Number of cations on the basis of 32 oxygen

A-site		
Fe^{2+}	1.145	1.307
Fe^{3+}	1.141	1.258
Al	1.901	2.473
Mg	3.726	2.891
Mn	0.045	–
Ni	0.030	0.035
Na	0.010	0.009
K	0.002	0.002
Ca	–	0.025

B-site		
Cr	6.823	7.442
Al	6.329	5.245
Fe^{2+}	1.729	2.079
Fe^{3+}	1.536	1.506
Ti	0.032	0.031
Si	0.003	0.046

Distribution of Fe into FeO and Fe_2O_3 is based on room temperature MS. *Average of seven spots.

temperatures of 950°C (core) and 740°C (rim) are obtained for a heterogenous garnet. We have used the two temperatures for thermodynamic calculations. It can be noted that the calculated intracrystalline thermodynamic parameters of the Sittampundi chromites may not be immediately comparable with the reported synthetic spinel data because of the complex chemistry of the studied samples (Table 2).

In spinel, the degree of exchange between tetrahedral and octahedral sites can be quantified by the degree of disorder, x, giving the fraction of trivalent cations in the tetrahedral site. Complete order has x value of 0 and a value of 1 represents a completely disordered state. For the studied samples, x is found to be 0.38 (Ch₁) and 0.53 (Ch₂), showing their disordered nature. The oxygen positional parameter (u) is sensitive to changes in cation distribution and follows a similar path on heating as the degree of disorder[26]. Oxygen parameter of the studied samples has been estimated using the 3rd polynomial equation, $u = 0.26488 - 0.00118x - 0.0289x^2$. The two determined u values of 0.256137 (Ch₂) and 0.260258 (Ch₁) are close to the reported values of the 2–3 spinels[8,27]; however they are less than that of the measured Nuggihalli chromite $(0.2623)^{[28]}$.

Navrotsky and Kleppa[29] sought a co-relationship between the interchange enthalpy (ΔH_{int}) and the equilibrium cation distribution as a function of temperature. According to them, a knowledge of the equilibrium cation distribution at a temperature is sufficient to estimate interchange enthalpy. For calculation of the parameter, we have used the equation $\Delta H_{int} = -RT\ln[x^2/(1-x)(2-x)]$, where R is the gas constant and the enthalpy of disordering (ΔH_{dis}) is assumed to be the product of degree of disordering and interchange enthalpy. The two enthalpies are calculated for the Sittampundi chromites (Table 3).

The driving force in forming a solid solution is usually configurational entropy of mixing. A solid solution like natural chromite (Cr-spinel) will only be stable if its free energy is less than that of an equivalent mechanical mixture of its components, or of any possible exsolution product. Spinels with a random or highly inverse cation distribution generally have more positive entropy than the largely normal spinels[29]. Calculated configurational entropy due to positional disorder of the cations for the samples using Navrotsky and Kleppa model[29] is presented in Table 3. Positive entropies of the Sittampundi chromites result due to configurational disorder resulting from the mixing of different cations on equivalent structural sites. The values are plotted against the degree of disorder[30] and show their distinct disordered nature (Figure 2).

At equilibrium, interchange enthalpy equals to $\alpha + 2\beta x$, where α and β are the disordering energy and the value of β for 2–3 spinels is taken as -20 kJ/mol[9]. Using the two metamorphic equilibrium temperatures (950 and 740°C), α is calculated for the studied samples. The values of α at the two temperatures for sample Ch₂ are 30.347 and 28.799 kJ/mol, and for sample Ch₁ are 34.981 and 32.565 kJ/ mol, respectively (Table 3).

Table 3. Thermodynamic parameters of Sittampundi chromites

T (K)	ΔH_{int} kJ/mol	ΔH_{dis} kJ/mol	ΔG_{dis} kJ/mol	α_1 kJ/mol	α_2 kJ/mol	α kJ/mol
Sample Ch$_1$: $x = 0.38$; $u = 0.260258$, S$_{conf} = 13.679$ J/mol K						
when $r_1 = [Fe^{3+}]$, $r_2 = [Al]$						
1225	19.741	7.521	24.279	14.044	23.306	34.981
1013	16.325	6.220	20.077	14.251	21.910	31.565
when $r_1 = 1 - ({}^{[4]}X_{Mg} + 2{}^{[4]}X_{Mg})$, $r_2 = 1/2({}^{[4]}X_{Al} + 2{}^{[6]}X_{Al})$						
1225	19.741	7.521	24.279	56.564	65.898	34.981
1013	16.325	6.220	20.077	56.771	64.489	31.565
Sample Ch$_2$: $x = 0.53$; $u = 0.256137$, S$_{conf} = 15.431$ J/mol						
when $r_1 = [Fe^{3+}]$, $r_2 = [Al]$						
1225	9.068	4.824	23.727	16.485	12.552	30.347
1013	7.499	3.989	19.621	16.034	11.992	28.779
when $r_1 = 1 - ({}^{[4]}X_{mg} + 2{}^{[6]}X_{Mg})$, $r_2 = 1/2({}^{[4]}X_{Al} + 2{}^{[6]}X_{Al})$						
1225	9.068	4.824	23.727	55.845	61.232	30.347
1013	7.499	3.989	19.621	55.394	60.671	28.779
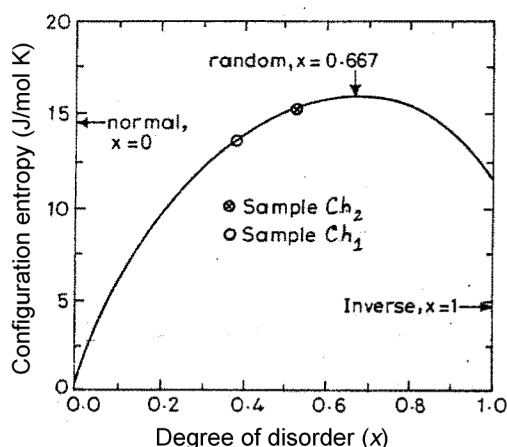
Figure 2. Sittampundi samples plotted in configurational entropy vs degree of disorder curve of Navrotsky and Klappa[29].

The compositional dependence of cation distribution in spinel is due to excess stabilization energy of divalent and trivalent cations in tetrahedral and octahedral sites[31] and is expressed as 'site preference enthalpy'[8,9]. The compositional parameters (r_1 and r_2) of two independent compositional exchange vectors, Fe^{2+} $(Mg^{2+})^{-1}$ and Al^{3+} $(Fe^{3+} + Cr^{3+})^{-1}$ are $r_1 = 1 - ({}^{[4]}X_{Mg} + 2{}^{[6]}X_{Mg})$ and $r_2 = 1/2({}^{[4]}X_{Al} + 2{}^{[6]}X_{Al})$, where ${}^{[4]}X_{Al}$ and ${}^{[6]}X_{Al}$ are the atomic fraction of Al on tetrahedral and octahedral sites respectively. The site preference enthalpies α_1 and α_2 are calculated at the two temperatures from the following equations[13]:

$$-RT \ln \left[\frac{[Fe^{3+}]x(Fe^{2+})}{[Fe^{2+}]x(Fe^{3+})} \right] = \alpha_1 + 2\beta_1[r_1 + r_2],$$

$$-RT \ln \left[\frac{[Al]x(Fe^{2+})}{[Fe^{2+}]x(Al)} \right] = \alpha_2 + 2\beta_2[r_1 + r_2],$$

where $[Fe^{3+}] = Fe^{3+}$ at tetrahedral site and $(Fe^{3+}) = Fe^{3+}$ at octahedral site, and $\beta_1 = \beta_2 = -20$ kJ/mol. The two parameters (α_1 and α_2) are also calculated taking site occupancies (or order parameters r_1 and r_2) for $[Fe^{3+}]$ and $[Al]$ at the two metamorphic temperatures[32]; the values are listed in Table 3.

These data bring out the significant aspect of measuring the relative site preference energy (with respect to Fe^{2+}) of aluminium at both tetrahedral and octahedral sites. Optical spectroscopic techniques widely used for determining the site preference crystal field stabilization energy delimit themselves with transition elements ($3d$ and $4f$) only, not covering amphoteric (non-transition elements like Al). The thermodynamic approach as employed herein may offer a cue for further studies with other amphoteric elements in mixed oxides.

Natural chromites are found to be a reciprocal system and Mg, Fe^{2+}, Al and Fe^{3+} are present in both the tetrahedral and octahedral sites. Cation distributions vary widely in the system. In the thermodynamic model proposed by O'Neill and Navrotsky[8] for a spinel of intermediate cation distribution, the equation for free energy of disordering, $\Delta G_{dis} = x\Delta H_{int} - RT[x \ln x + (1 - x)\ln(1 - x) + x\ln(x/2) + (2 - x)\ln(1 - x/2)]$ has been obtained by combining the interchange enthalpy and configurational entropy. Using this equation, we have calculated the free energy of disordering of the two samples. For sample Ch$_1$, the values are 20.077 and 24.279 kJ/mol and for Ch$_2$, they are 23.727 and 19.621 kJ/mol respectively, at the two equilibrium temperatures.

Change in configurational entropy in disordering (ΔS_{conf}) is also determined at the two temperatures using the equa-

tion: $\Delta G_{dis} = x(\alpha + \beta x) - T(\Delta S_{conf} + \Delta S_{nonconf})$ (see Table 3). The configurational entropy term ($\Delta S_{nonconf}$) is too small and is neglected. In the ordered state, ΔS_{conf} is equal to the configurational entropy (S_{conf}).

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