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Crystal chemical and ^{57}Fe Mössbauer study of chromite from the Nuggihalli schist belt (India)

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Summary

In the Nuggihalli schist belt (India), chromite bodies were affected by intense serpentinization followed by weathering. In spite of the strong oxidation of the chromite grains, some unaltered cores were preserved, and they were characterised using electron probe microanalysis, single-crystal X-ray diffraction and low temperature ^{57}Fe Mössbauer spectroscopy. Results of such investigations revealed that chromite cores from the Nuggihalli schist belt are effectively not oxidised, and their study revealed that chromite was not affected by greenschist-facies metamorphism. The apparently highly ordered cation distribution of the chromites, which would suggest low equilibration temperature, is just caused by the very high Cr contents, which prevent Mg–Al exchange between T and M sites. Using *Fabries* (1979) geothermometer a temperature of about 1180 °C was retrieved (*Mitra* and *Bidyananda*, 2003), which therefore corresponds to the quenched-in igneous equilibrium.

Introduction

Chromite is not only a useful indicator of crystallisation environment, but it also records modifications induced during early hydrous alteration and subsequent prograde metamorphism of host rocks. There are several studies regarding changes in chromite chemistry from ultramafic complexes during metamorphic modification (*Ulmer*, 1974; *Evans* and *Frost*, 1975; *Kimball*, 1990; *Burkhard*, 1993; *Barnes*, 2000). Chromite first becomes rimmed and is progressively replaced by chromian magnetite or ''ferritchromit'', and successively its core composition becomes progressively modified during prograde metamorphism as a result of chemical changes with the surrounding silicates. In general, during metamorphic processes, there is Mg–Fe^{2+} substitution, followed by $Fe^{2+} \rightarrow Fe^{3+}$ transformation. This implies progressive oxidation in chromite.

The oxidation state in spinels has been investigated by means of single crystal X-ray diffraction (*Menegazzo* et al., 1997; *Menegazzo* and *Carbonin*, 1998; *Carbonin* et al., 1999) and Mössbauer spectroscopy (*Mitra* et al., 1991a, b; *Carbonin* et al., 1996). The oxidation state of ferrian spinels may be evaluated by measuring maghemitization and the sometimes observed subsequent martitization of samples. Maghemitization implies transformation of Fe^{2+} to Fe^{3+}, martitization exsolution of α-Fe_2O_3. These two processes cause charge enrichment in higher valent states in the T site, due to trivalent-for-divalent cation substitution and also a decrease in the u oxygen positional parameter. The latter can be easily determined by X-ray diffraction (XRD) in combination with microprobe (EPMA) analyses. Fe^{2+} and Fe^{3+} contents may be indirectly evaluated by stoichiometry via EPMA or directly measured by ^{57}Fe Mössbauer spectroscopy. The latter method discriminates the Fe^{2+}/Fe^{3+} ratio better than EPMA and, in addition, provides their information on Fe^{2+} and Fe^{3+} distribution in T and M sites.

The aim of this work is to verify, by means of single-crystal X-ray diffraction, EPMA and low-temperature ^{57}Fe Mössbauer spectroscopy (MS), the effects of metamorphism on cation distribution and on the oxidation state of some chromite samples from the chromite-bearing Nuggihalli schist belt (India), in order to contribute in reconstructing its thermal history.

Geological setting

The Nuggihalli schist belt occurs as a narrow band of NW–SE trending metamorphosed ultramafic rocks, in the Dharwar craton of South India and is considered to be part of the pristine and primordial crust of Archaean age (>2.5 Ga; *Naqvi* and *Hussain*, 1979). Ultramafic rocks in the study area consist of unaltered dunite, chromite-bearing serpentinite and talc–chlorite–tremolite schist. Other major rock types are amphibolite, metasediments, meta-anorthosite and tonalite tronhdjemite gneisses. The area has been subjected to greenschist to amphibolite facies metamorphism and shows an increase in metamorphic grade from north to south (*Ramakrishnan*, 1981). Chromitite bodies occur as layers, lenses and reefs of varying sizes within serpentinites. The largest chromitite reef at Byrapur (~60 m × 12 m) trends 50° E and dips 50° to 70° S. Thin chromitite layers varying in size from a few centimetres to metres also occur in the schist belt. The variable shapes of the ore bodies appear to be controlled by their structural position in the limbs and hinges of early and later folds and dislocation of the ore bodies by shearing in some areas. In the present study we have selected samples from the large reef (BY) and from a chromite rich layer inside a highly weathered serpentinite (BRG). Spectacular rosy moss-like aggregates of pink Cr-clinochlore occurs as fracture fillings and coatings around grey chromite ore bodies (*Mitra* and *Bidyananda*, 2001).

The chromite–olivine assemblage calibration proposed by *Fabries* (1979) was used to determine the equilibration temperature of chromite ores (*Mitra* and *Bidyananda*, 2003). The following parameters were calculated from coexisting chromite and olivine phases in an unaltered peridotite relict (details to be published elsewhere); $X_{Mg}{}^{Sp} = 0.474$, $X_{Fe}{}^{Sp} = 0.517$, $X_{Mg}{}^{ol} = 0.890$, $X_{Fe}{}^{ol} = 0.109$, $\gamma_{Cr}{}^{sp} = 0.759$, $\gamma_{Fe^{2+}}{}^{Sp} = 0.222$, $K_D = 8.868$, $\ln K_D = 2.18$, $\ln K_D{}^0 = 1.292$. On this basis, the equilibration temperature of Nuggihalli chromite ores was determined at 1178 °C.

Experimental methods

X-ray single crystal diffraction

Several spinel fragments from sample BY were tested, but only a few of them were suitable for single-crystal X-ray diffraction, due to their almost complete alteration. This is probably a consequence of the spinel oxidation accompanying rock serpentinization. Three unaltered fragments were found and selected for X-ray structural study.

Octahedral crystals sizing up to about 7 mm occur in chromite BRG sample. Some of the crystals were crushed, and their outer and inner parts were tested by single-crystal X-ray diffractometer. The fragments containing oxidised outer parts were rejected, and finally just one fragment was selected for X-ray analysis.

X-ray diffraction data were recorded on an automated KUMA-KM4 (K-geometry) diffractometer, using MoKα radiation, monochromatised by a flat graphite crystal, at the University of Trieste (Italy).

Data collection was made, according to *Della Giusta* et al. (1996), up to 55° of 2θ in the ω-2θ scan mode, scan width 1.8 °2θ, counting time 20–50 seconds, depending on intensity standard deviation. Twenty-four equivalent reflections of (12 8 4) peak, at about 90° of 2θ, were accurately centred at both sides of 2θ, and the α_1 peak baricentre was used for cell parameter determination. Corrections for absorption were performed according to *North* et al. (1968).

Structural refinement using the SHELX-93 program (*Sheldrick*, 1993) was carried out against $Fo^2{}_{hkl}$ in the Fd-3 m space group (with origin at $-3\,m$), since no evidence of different symmetry appeared. Refined parameters were scale factor, oxygen positional parameter (u), tetrahedral and octahedral site occupancies, and thermal displacement parameter (U). Scattering factors were taken from the *International Tables for Crystallography* (1974) and *Tokonami* (1965). Two neutral scattering curves, Mg *vs.* Fe in T site and Cr *vs.* Al in M site, were assigned to sites involved in isomorphous replacements, with the constraints of full site occupancy and equal displacement parameters, whereas oxygen was considered to be in a partly ionised state (70%). No constraints were imposed by chemical analyses. Crystallographic data are listed in Table 1.

Chemical microanalyses and cation partitioning

Ten to fifteen spot chemical analyses were performed on the same crystals used for X-ray data collection using a CAMECA-CAMEBAX microprobe operating at 15 kV and 15 nA. A 20-s counting time was used for both peak and total back-

Table 1. *Chemical analyses, cation distribution and structural data of Cr-spinels. Numbers within parentheses are the estimated standard deviations and refer to last digits* m.a.n. *mean atomic number;* U (M), U (T), U (O) *equivalent isotropic temperature factor of octahedral and tetrahedral sites and oxygen atom;* u^* *non-fractional oxygen positional parameter* ($u \times a_0$; Å); chu *charge unbalance* ($q(T)/q(M)$)

	BY-a	BY-b	BY-c	BRG
MgO	8.82 (10)	8.71 (13)	8.58 (10)	8.67 (9)
Al_2O_3	6.52 (7)	6.32 (18)	6.32 (18)	9.56 (1)
SiO_2	0.05 (2)	–	0.05 (2)	0.06 (3)
TiO_2	0.53 (4)	0.53 (3)	0.54 (3)	0.28 (4)
Cr_2O_3	58.03 (78)	57.73 (51)	57.44 (52)	56.57 (33)
MnO	0.41 (7)	0.42 (7)	0.41 (6)	0.44 (4)
FeO	19.64 (36)	19.45 (44)	19.54 (32)	19.85 (33)
Fe_2O_3	5.96	6.06	5.72	3.60
Sum	99.96	99.22	98.60	99.03
T site				
Mg	0.449	0.449	0.439	0.419
Al	0.003	0.003	0.009	0.006
Si	0.002	0.000	0.002	0.002
Mn	0.012	0.012	0.012	0.013
Fe^{2+}	0.499	0.501	0.502	0.530
Fe^{3+}	0.035	0.035	0.036	0.030
Σ	1.000	1.000	1.000	1.000
M site				
Mg	0.000	0.000	0.000	0.017
Al	0.258	0.249	0.250	0.375
Ti	0.014	0.014	0.014	0.007
Cr	1.561	1.570	1.568	1.511
Fe^{2+}	0.053	0.049	0.055	0.028
Fe^{3+}	0.114	0.118	0.113	0.062
Σ	2.000	2.000	2.000	2.000
a_0	8.3370 (3)	8.3374 (1)	8.3316 (6)	8.3198 (3)
u	0.26231 (11)	0.26229 (8)	0.26216 (9)	0.26252 (10)
m.a.n.$_{\text{X-ray}}$	65.15	64.50	64.81	63.76
m.a.n.$_{\text{chem}}$	65.17	65.28	65.28	63.87
N_{refl}	193	193	178	204
U (M)	0.00392 (14)	0.00298 (9)	0.00111 (11)	0.00417 (10)
U (T)	0.00622 (21)	0.00504 (14)	0.00329 (16)	0.00654 (18)
U (O)	0.00566 (26)	0.00471 (18)	0.00286 (22)	0.00610 (24)
R1	3.04	2.40	2.53	2.27
wR2	6.90	4.50	5.44	5.04
GooF	1.330	1.445	1.596	1.347
u^*	2.1868	2.1868	2.1842	2.1842
chu	0.343	0.342	0.344	0.342

ground. Synthetic oxide standards (MgO, FeO, MnO, ZnO, NiO, Al_2O_3, Cr_2O_3, TiO_2, SiO_2) were used. Raw data were reduced by PAP-type correction software provided by CAMECA. Chemical data are listed in Table 1.

Cation partitioning (Table 1) was calculated on the basis of average chemical and crystallographic data, according to the procedure described in *Carbonin* et al. (1996).

Low temperature ^{57}Fe Mössbauer spectra

Mössbauer data on selected chromite cores without evidence of oxidation were recorded in transmission mode at 77 K. Idiomorphic spinel octahedra were crushed under binocular microscope and the altered rims, easily recognisable because of light grey colour, were rejected. Absorbers of chromite samples BY and BRG were prepared by pressing finely ground samples with a powdered acrylic resin (Lucite) to self-supporting discs. Based on EMPA results, 20–25 mg of the two samples were used to prepare the Mössbauer absorbers. This sample amount corresponds to about 2 mg Fe/cm^2 and is well below an absorber density where thickness effects seriously affect Mössbauer results.

Spectra were collected using a conventional spectrometer system operated in constant acceleration mode with a ^{57}Co source of 50 mCi in rhodium matrix. Low temperature measurements were performed using a continuous flow cryostat filled in with liquid nitrogen (LN), with temperature controlled to within ± 0.2 K. Data collection time was about three days, in order to have good statistics (no less than 10000 counts/channel). Spectral data for the velocity range -4 to 4 mm/s were recorded in a multichannel analyser using 512 channels. After velocity calibration against a spectrum of high-purity α-Fe foil (25 µm thick) taken at room temperature (RT), the raw data were folded to 256 channels. The spectra were fitted assuming Lorentzian peak shape and using the commercial fitting program Recoil 1.04. The reduced χ^2 was used to evaluate statistical best fit, and uncertainties were calculated using the covariance matrix. Errors are estimated at about ± 0.02 mm/s for centre shift (CS), quadrupole splitting (QS) and peak width (Γ), and no less then $\pm 3\%$ for doublet areas, due to pronounced overlapping of subspectra especially in the central portion of absorption spectrum.

Low-temperature (LN) Mössbauer spectra of both chromite samples are dominated by a broad asymmetric absorption doublet showing maximum quadrupole splitting up to 3 mm/s, with a complex inner part between zero and 1 mm/s (Fig. 1).

According to the existing literature, the outer part of the absorption envelope may be due to ferrous iron, in tetrahedral and/or octahedral coordination in the spinel structure (*Hålenius* et al., 2002; *Waerenborgh* et al., 1994; *Larsson* et al., 1994). A broad absorption for Fe^{2+} in tetrahedral coordination can be expected due to next-nearest effect (NNN), i.e., the non-spheric cation distribution in the second coordination sphere of this site (*Waerenborgh* et al., 1990). Moreover, inner doublets may be determined by octahedrally coordinated Fe^{2+} (*Larsson* et al., 1994; *Hålenius* et al., 2002). However, these effects may not account for the large asymmetry displayed by the spectra of our chromite samples, hence an absorption band due to ferric iron, which contributes to the area between zero and 1 mm/s, must be considered.

Mössbauer spectra of chromite were interpreted in the literature both considering completely normal cation distribution (*Osborne* et al., 1981, 1984) and intracrystalline cation disorder (*Fatseas* et al., 1976; *Galvao Da Silva* et al., 1980).

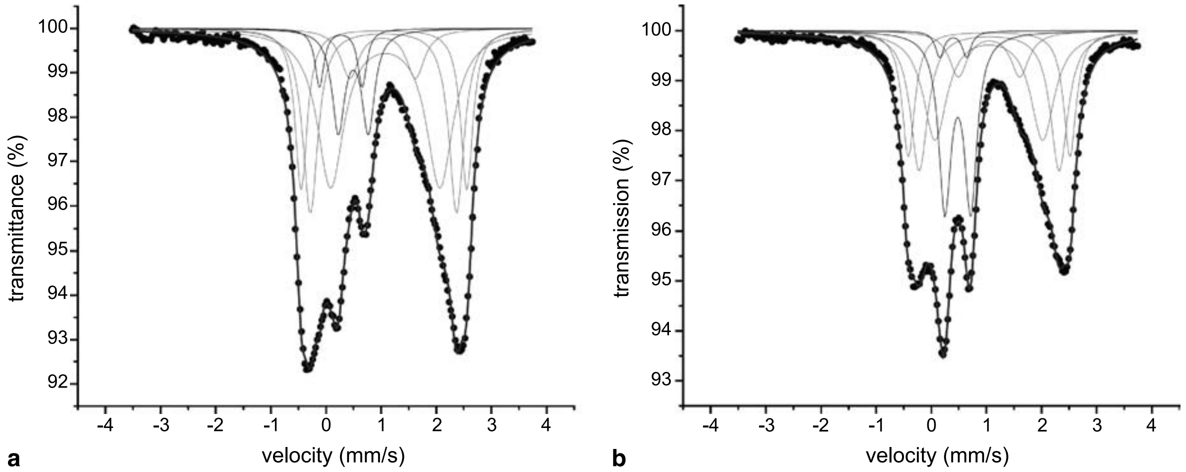

Fig. 1. Liquid Nitrogen ^{57}Fe Mössbauer spectra of chromite BRG (**a**) and BY (**b**). Black dots: experimental data; thick line: calculated fit; thin dark-gray lines: Fe^{3+} doublets; thin light-gray lines: Fe^{2+} doublets

Synthetic $FeCr_2O_4$ is a normal spinel, that is Cr populates octahedral sites and Fe^{2+} the tetrahedral ones, but natural chromite samples rarely have the end member composition and often exhibit disorder of Fe^{2+} and Fe^{3+} between octahedral and tetrahedral sites at high temperature (*O'Neill* and *Navrotsky*, 1983, 1984; *Wood* and *Virgo*, 1989). The studied Indian samples contain appreciable amounts of Mg, Al, and Fe^{3+}, and underwent a complex thermal history, therefore a certain amount of disorder has to be considered possible.

Fitting models adopted in the spinel literature so far were similar but not identical. For natural Cr-bearing spinels, best results were reached by *Wood* and *Virgo* (1989) using a three-doublets model ($2Fe^{2+} + 1Fe^{3+}$), and by *Dyar* et al. (1989) by using a four-doublets model ($3Fe^{2+} + 1Fe^{3+}$). The fitting model is close

Table 2. *Mössbauer parameters for Indian chromite samples* CS *centre shift (with respect to α-iron);* QS *quadrupole splitting;* FWHM *full width at half maximum. Estimated uncertainties are about 0.02 mm/s for CS, QS, FWHM, and no less than 2% for intensity*

Sample	Temperature	CS [mm/s]	QS [mm/s]	FWHM [mm/s]	Intensity [%]	Attribution
BRG	77 K	1.05	3.00	0.26	17	Tetr. Fe^{2+}
		1.04	2.65	0.33	23	Tetr. Fe^{2+}
		1.07	1.98	0.58	36	Tetr. Fe^{2+}
		1.03	1.19	0.40	8	Oct. Fe^{2+}
		0.50	0.54	0.28	11	Oct. Fe^{3+}
		0.27	0.77	0.19	5	Tetr. Fe^{3+}
BY	77 K	1.05	2.93	0.28	16	Tetr. Fe^{2+}
		1.05	2.54	0.28	25	Tetr. Fe^{2+}
		1.04	1.95	0.52	26	Tetr. Fe^{2+}
		1.05	1.12	0.40	8	Oct. Fe^{2+}
		0.48	0.47	0.27	22	Oct. Fe^{3+}
		0.40	0.49	0.19	3	Tetr. Fe^{3+}

to the one used by *Waerenborgh* et al. (1994) for a synthetic spinel solid-solution although they used a quadrupole splitting distribution for modelling the tetrahedral Fe^{2+} absorption. *Li* et al. (2002) used quadrupole splitting distributions to model both tetrahedral Fe^{2+} and octahedral Fe^{3+} of ordered, natural chromites. For a disordered, synthetic spinel solid-solution, *Hålenius* et al. (2002) successfully adopted a five-doublets model, with three tetrahedral Fe^{2+}, one octahedral Fe^{2+} and one octahedral Fe^{3+} contributions.

In this case, the *Hålenius* et al. (2002) model with five doublets was tentatively adopted and a satisfactory fit was obtained. However, comparison with structural analysis suggested to add another component for Fe^{3+}, which was not rejected from calculation routine and led to even better results in terms of hyperfine parameters. Thus a six-doublets model was chosen because it gave the best results. The model used consisted of four doublets representing the broad Fe^{2+} contribution and two doublets due to Fe^{3+} (Fig. 1). The obtained hyperfine parameters are listed in Table 2.

Results and discussion

Crystal chemistry

The three BY spinel fragments show small relative differences in their a_0 and u values, which range between 8.3316 and 8.3374 Å, and 0.2622 and 0.2623, respectively. These values account for good homogeneity of BY sample. The BRG fragment shows a lower a_0 value, 8.3198 Å, and a comparable u value, 0.2625 (Table 1).

Chemical analyses of the three BY fragments (up to 15 measures performed on each crystal from core to rim), confirmed the high homogeneity of this sample, with MgO ranging between 8.58 and 8.82 wt.%, Al_2O_3 between 6.32 and 6.52 wt.%, Cr_2O_3 between 57.44 and 58.03 wt.%, and FeO_{tot} between 24.69 and 25 wt.%. In particular, none of the BY fragments shows chemical inhomogeneities between core and rim (S.D. < 0.78 wt.%, Table 1).

Sample BRG differs from BY in having slightly higher Al_2O_3 and lower FeO_{tot} contents (about 9.56 and 23 wt.%, respectively, Table 1). Inhomogeneities between core and rim of the fragment were not detected (S.D. is even less than 0.33 wt.%, Table 1).

Both in naturally and artificially oxidised spinels, the oxygen positional parameter u decreases as oxidation advances (*Della Giusta* et al., 1996; *Figueiras* and *Waerenborgh*, 1997; *Menegazzo* and *Carbonin*, 1998; *Carbonin* et al., 1999). In different oxidised Cr-spinels, *Carbonin* et al. (1999) showed that the u parameter reaches values down to 0.2616 or 0.2607 when starting from typical values of about 0.2626. Oxidation processes cause charge enrichment in the T site, due to trivalent substitution for divalent cations (i.e., Fe^{3+} replacing Fe^{2+}). A measure of trivalent cations in T site is given by charge unbalance $chu = q(\mathrm{T})/q(\mathrm{M})$, where q(T) and q(M) are the charges in T and M sites, respectively. As evident from Fig. 2, which displays a summary of literature data, normal stoichiometric spinels lie in the region corresponding to $chu < 0.4$ (*Della Giusta* et al., 1996; *Lenaz* and *Princivalle*, 1996; *Lenaz* et al., 2002), whereas Mg–Al rich spinels with vacancies (*Lucchesi* and *Della Giusta*, 1997) and artificially and naturally oxidised samples

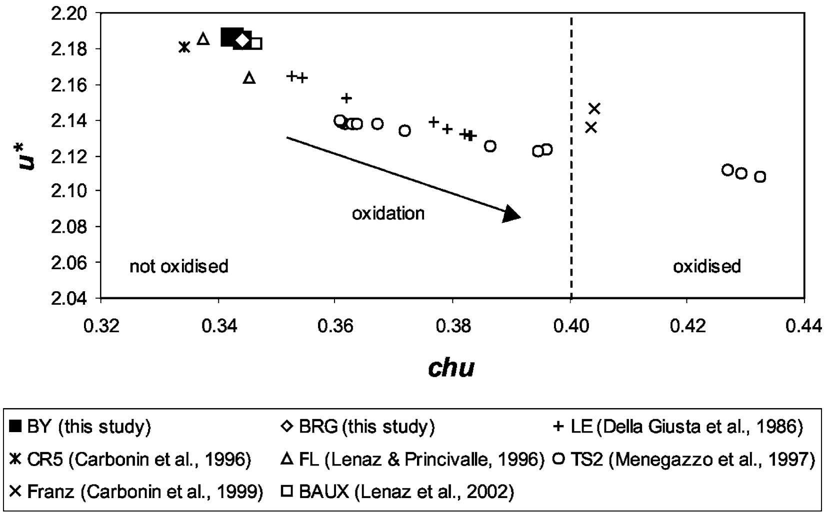

Fig. 2. Plot of u^* against *chu* in samples BY, BRG and in different series and single crystals from the literature. u^* non-fractional oxygen positional parameter ($u \times a_0$; Å); *chu* charge unbalance ($q(T)/q(M)$)

(*Menegazzo* et al., 1997; *Carbonin* et al., 1999) plot in the region with $0.4 < chu < 0.5$. In the same figure, inverse spinels would plot in the region with $chu > 0.5$.

In addition to *chu* values, a comparison between m.a.n.$_{\text{X-ray}}$ and m.a.n.$_{\text{chem}}$, which are the total number of electrons obtained from X-ray diffraction and from microchemical analyses, respectively, may also give the degree of oxidation, because in oxidised spinels m.a.n.$_{\text{chem}}$ is significantly higher than the value obtained from structural refinement.

Results obtained on core fragments of samples BRG and BY show that *u* values are no lower than 0.2622, *chu* values are lower than 0.4 (about 0.34), and differences between m.a.n.$_{\text{chem}}$ and m.a.n.$_{\text{X-ray}}$ are close to 1% relative. These values strongly support the assessment that BY and BRG core fragments are not oxidised. This has been further confirmed by MS results.

^{57}Fe Mössbauer data interpretation

Low-temperature ^{57}Fe Mössbauer data of samples BRG and BY have been analysed following interpretation criteria commonly adopted for spinels (e.g., *Hålenius* et al., 2002; *Waerenborgh* et al., 2002 and references therein). The three doublets with CS 1.04–1.07 mm/s and QS from 3.00 to 1.95 mm/s may be easily attributed to Fe^{2+} in tetrahedral coordination. The observed spread of QS values may be interpreted as the consequence of local disorder around tetrahedral sites (NNN effect). This is a clear indication that the twelve octahedral sites surrounding each tetrahedral site are populated by a large number (three or more) of different cations. The fourth doublet, CS 1.03 and 1.05, QS 1.19 and 1.12 mm/s for BRG and BY samples, respectively, could be interpreted either as tetrahedral Fe^{2+} or as octahedral Fe^{2+}. In the first case it would account for a less disordered cation distribution around T sites, in the second case it could be due to Fe^{2+} inversion due to temperature effect. On the basis of previous work (*Hålenius* et al., 2002), this doublet was assigned to octahedral Fe^{2+}. Moreover, intensity observed for this contribution (8% for both samples), are in close agreement with Fe^{2+} inversion obtained from cation partitioning on the basis of structural data (Table 1).

In Mössbauer spectra collected at room temperature it is common that Fe^{2+}- and Fe^{3+}-doublets are partly or completely overlapped. Moreover, it was pointed out that in spinel the actual content of Fe^{3+} is often overestimated, since the common assumption of equal recoil-free fractions f for Fe^{2+} and Fe^{3+} ions is not true (*De Grave* and *Van Alboom*, 1991). The same authors observed that the assumption of equal f fractions would lead to errors of on the average 15% for the Fe^{2+}/Fe^{3+} ratio evaluated from the relative spectral areas at room temperature. Such an assumption, on the contrary, is definitely more appropriate for spectra collected at liquid nitrogen temperature (LN), because the difference of f fractions for Fe^{2+} and Fe^{3+} becomes very small. As a consequence, a quite good measurement of Fe^{2+}/Fe^{3+} ratio may be obtained simply measuring the spectral areas after a LN experience. In addition, LN spectra have the advantage to be better resolved, as Fe^{2+}-doublets move to high quadrupole splitting values, whereas Fe^{3+}-doublets are less influenced by temperature.

Accordingly, in our case the evaluation of Fe^{3+} content was obtained from the measurement of relative spectral areas at liquid nitrogen. The total Fe^{3+}-contents measured in samples BRG and BY are equal to 17 and 25% with respect to total iron, respectively. The two doublets adopted for Fe^{3+} in both samples show different CS values. On the basis of previous experience on Fe^{3+}-rich spinels (*Andreozzi* et al., 2001), the contribution with higher CS (0.50 and 0.48 mm/s for BRG and BY, respectively) was attributed to octahedrally-coordinated Fe^{3+}, whereas the other one with minor CS (0.27 and 0.40 mm/s for BRG and BY, respectively) to tetrahedrally-coordinated Fe^{3+}. Although the limited amounts observed for tetrahedral Fe^{3+} make its presence almost questionable, at least for sample BY, nonetheless the introduction of this sixth doublet improved the overall quality of fitting, and made final attributions closely matching with cation partitioning on the basis of structural data (Table 1).

Iron quantification and site distribution by crystal chemistry and Mössbauer spectroscopy

The comparison between MS analyses and crystal-chemical data (XRD and EPMA) shows that results of both iron quantification and site distribution from the two approaches are very similar within experimental uncertainties. For BRG sample, in fact, Fe^{2+} measured by MS and crystal chemistry corresponds to 84% and 86% of total Fe, respectively. Fe^{2+} is strongly ordered in tetrahedral site. This was verified both with MS (90% with respect to total Fe^{2+}) and crystal chemistry (95%). Regarding the Fe^{3+} contents (14–16% of total Fe), the agreement observed is even better; both approaches indicate that 31–32% of the total Fe^{3+} is in tetrahedral coordination.

For BY sample, Fe^{2+} measured by MS and crystal chemistry corresponds to 75% and 79% of total Fe, respectively. Similar to the previous sample, 90% of Fe^{2+} is ordered in the tetrahedral site, as deduced from both MS and crystal chemistry data. As regards the Fe^{3+} contents (21–25% of total Fe), its fraction in tetrahedral coordination corresponds to 31% and 24% for MS and crystal chemistry, respectively.

This discrepancy may be due to some inhomogeneities in spinel. Thus, in order to avoid these differences, cation partition obtained from crystal chemistry has been used.

Conclusions

The intra-crystalline Mg–Al distribution between T and M sites of natural spinels mainly depends on the thermal history of the host rocks. The dependence of cation distributions on temperature has been investigated by several authors (*O'Neill* and *Navrotsky*, 1983, 1984; *Della Giusta* and *Ottonello*, 1993; *Nell* and *Wood*, 1991; *Della Giusta* et al., 1996; *Princivalle* et al., 1999). When cooling is very slow, Mg and Al cations strongly order in T and M sites, respectively, whereas fast quenching preserves disordered distribution (*Princivalle* et al., 1989; *Della Giusta* et al., 1996; *Lucchesi* and *Della Giusta*, 1997).

High contents of Cr in the M site do not allow a large-scale Mg–Al cation exchange between T and M sites, and this would simulate an ordered distribution suggesting a low intra-crystalline temperature. This is the case for the spinels examined in this study, since Cr is about 1.5 atoms per formula unit (a.p.f.u.) and Al disordered in tetrahedral site is up to 0.009 a.p.f.u. (Table 1).

Nuggihalli chromite was subjected to greenschist facies metamorphism, therefore a relatively low equilibration temperature (e.g., ca 400–500 °C) for the chromite crystals would be expected. However, studies on chromites in komatiite from the Norseman-Wiluna Greenstone Belt (W. Australia) showed that low-grade metamorphism does not easily affect chromite (*Barnes*, 2000).

The equilibration temperature calculated from co-existing chromite and olivine in the Nuggihalli chromite was determined at 1178 °C (*Mitra* and *Bidyananda*, 2003). This temperature is much higher than greenschist facies conditions. In fact, chromite compositions correspond to equilibration with Mg-rich olivine (Fo_{94-88}) at temperatures in the range 1400 °C to 750 °C. This can only be explained if the chromites are relics of the original igneous stage, and have not been substantially reset during greenschist metamorphism or alteration.

Therefore, the unaltered chromite cores from the Nuggihalli schist belt were not affected by greenschist-facies metamorphism and the temperature of 1178 °C corresponds to the quenched-in igneous equilibrium. Accordingly, the low equilibration temperature indicated by the highly ordered cation distribution has not to be considered as real, but is just caused by the very high Cr contents, which prevent Mg–Al exchange between T and M sites.

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