

## Flux growth of synthetic single crystal spinels in the (Mg, Fe<sup>2+</sup>)(Cr, Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> system

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*Submitted, September 2003 - Accepted, November 2003*

**ABSTRACT.** — Single crystals of spinel with compositions corresponding to (Mg, Fe<sup>2+</sup>)Cr<sub>2</sub>O<sub>4</sub> and Mg(Cr, Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> end members and their solid solutions were synthesised by flux-growth method. Low cooling rates (4°C h<sup>-1</sup>) and linear temperatures profiles were applied in the thermal interval 1200-900°C. Thermal runs were performed in air and in controlled atmosphere. The resulting crystals underwent preliminary structural and spectroscopic characterisation for future thermodynamic and kinetics studies of spinel order-disorder with temperatures.

**RIASSUNTO.** — Cristalli singoli di spinello con composizioni corrispondenti a MgCr<sub>2</sub>O<sub>4</sub>, Fe<sup>2+</sup>Cr<sub>2</sub>O<sub>4</sub> e MgFe<sup>3+</sup><sub>2</sub>O<sub>4</sub> e alle loro soluzioni solide sono stati sintetizzati tramite crescita da flussante. Per la sintesi sono stati utilizzati, nell'intervallo tra 1200 e 900°C, tempi di raffreddamento piuttosto lenti (4°C h<sup>-1</sup>) e profili di temperatura lineari. Tali sintesi sono state effettuate sia in ambiente ossidante che riducente in atmosfera controllata. I cristalli risultanti sono stati caratterizzati in maniera preliminare attraverso uno studio strutturale su cristallo singolo, analisi in microsonda elettronica e una caratterizzazione spettroscopica (assorbimento ottico e Mössbauer) allo scopo di effettuare in futuro studi termodinamici e cinetici di ordine-disordine a diverse temperature.

**KEY WORDS:** *Spinel, flux growth, magnesiochromite, chromite, magnesioferrite*

### INTRODUCTION

Spinel structure is made up by a cubic close-packed array of oxygen atoms with tetrahedral (T) and octahedral (M) sites. One eighth of the T sites and one half of the M sites are filled by heterovalent cations A and B in the ratio AB<sub>2</sub>O<sub>4</sub>, where A = (Mg, Fe<sup>2+</sup>, Zn, Mn) and B = (Al, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ti), in common 2-3 spinels. The crystal-chemistry of spinels is described by the general formula <sup>IV</sup>(A<sub>1-i</sub>B<sub>i</sub>)<sup>VI</sup>(A<sub>i</sub>B<sub>2-i</sub>)O<sub>4</sub>, where *i* refers to the inversion parameter. There are two ordered configuration stable at low temperature, the one with *i* = 0 (normal spinel; e.g., MgAl<sub>2</sub>O<sub>4</sub>, FeAl<sub>2</sub>O<sub>4</sub>, MgCr<sub>2</sub>O<sub>4</sub>, FeCr<sub>2</sub>O<sub>4</sub>) and the other with *i* = 1 (inverse spinel; e.g. MgFe<sub>2</sub>O<sub>4</sub>, FeFe<sub>2</sub>O<sub>4</sub>). When temperature increases, disorder takes place, since A and B cations undergo increasing intersite exchange over the three cations sites per formula unit. The disordering process in spinels is of the non-convergent type, since there is no change of

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the symmetry  $Fd\bar{3}m$ . The completely random distribution of A and B cations over the three cation sites corresponds to  $i = 2/3$ , which is asymptotically approached at very high temperatures (Sack and Ghiorso, 1991a). Modifications of T-O and M-O bond distances to accommodate various chemical compositions and/or cation ordering determine variations in the oxygen positional parameter  $u$  and the cell edge  $a$  (Lavina *et al.*, 2002). Real spinels usually have  $u$  parameters higher than the ideal value 0.25, and this corresponds to larger tetrahedral sites at the expense of decreased octahedral sites, still with fixed coordinates (Hafner, 1960; Hill *et al.*, 1979; O'Neill and Navrotsky, 1983).

Cr is an essential constituent of many spinels in mafic-ultramafic igneous and metamorphic rocks of the crust and the upper mantle. Even if Cr-bearing spinels typically occur as accessory phases they are widely considered as petrogenetic indicators (Irvine, 1965, 1967; Evans and Frost, 1975; Dick and Bullen, 1984; Sack and Ghiorso, 1991b, 1991c). Several petrological studies have shown general relationships between spinel chemistry, rock type and processes but also new knowledge have been achieved on igneous/metamorphic events from analyses of spinel-bearing assemblages (Evans and Frost, 1975; Fujii, 1977; Fabries, 1979; O'Neill, 1981; O'Neill and Wall, 1987; Kamenetsky, 1996; Barnes 2000; Kamenetsky *et al.*, 2001).

Because of the chemical complexity frequently observed in natural spinels and the difficulties in precise site assignment of the major cations synthetic materials of well-defined compositions are crucial to minimise system complexity. Coupled chemical–structural method has already been successfully applied to ordering configurations of both natural and synthetic spinels (O'Neill and Dollase, 1994; Della Giusta *et al.*, 1996; Harrison *et al.*, 1998; Princivalle *et al.*, 1999; Androzzzi *et al.*, 2000; Androzzzi and Lucchesi, 2002; Androzzzi and Princivalle, 2002).

In the present case a flux-growth method was used to obtain high quality spinel crystals with

compositions corresponding to picrochromite  $MgCr_2O_4$ , magnesioferrite  $MgFe^{3+}_2O_4$  end members and their solid solutions, and to picrochromite and chromite  $Fe^{2+}Cr_2O_4$  end members and their solid solutions.

#### CRYSTAL GROWTH

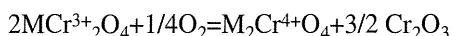
Flux growth is the process of crystal growth from molten salt solvent at high temperatures. To permit growth proceeding at temperatures well below the melting point of the growing phase a high temperature solvent, called flux, is used.

In the present work, single crystals in the  $(Mg, Fe^{2+})(Cr, Fe^{3+})_2O_4$  system were synthesised using a flux-growth method. Analytical grade  $MgO$ ,  $Cr_2O_3$ ,  $Fe_2O_3$  powders were dried at  $900^\circ C$  for 12 h before mixing with  $Na_2B_4O_7$ , used as flux compound. About 5 to 6 g of starting material was ground under acetone in an agate mortar and mixed with flux/nutrient ratio (N) ranging from 2.2 to 3.2 for  $(Mg, Fe^{2+})Cr_2O_4$  spinels and from 2.2 to 0.80 for  $Mg(Cr, Fe^{3+})_2O_4$  spinels depending on nutrient compositions. In fact it was observed that N must be decreased in order to grow spinels with increasing content of  $Fe_2O_3$  and decreasing  $Cr_2O_3$  (which is a refractory oxide) as it was seen also in spinel *s.s.* growth having  $Al_2O_3$  as a refractory oxide (Androzzzi, 1999). The mixtures were loaded in 10cc yttria-stabilised Pt/Au (5%) crucibles and covered with a lid. For thermal runs ENTECH muffle furnace and ENTECH vertical furnace with programmable temperature controllers were used, the former for runs in air and the latter for runs in controlled atmosphere. In order to obtain a homogeneous melt, the load was heated at  $1200^\circ C$  for 24 h. Subsequently the temperature was linearly decreased to  $900^\circ C$  with  $4^\circ C h^{-1}$  cooling rates. The reducing atmosphere was provided by a continuous flow of high-purity  $CO_2$  and  $H_2$  gases into the furnace. The  $CO_2:H_2$  ratio was maintained by TYLAN flow controllers and was kept constant at 1:2. Oxygen fugacity ranged from  $10^{-11}$  to  $10^{-17}$  bars at 1200 and  $900^\circ C$ , respectively, which is

ca. -0.1 log units from the iron-wüstite solid buffer. The thermal runs were ended turning off the furnace and the product was allowed to cool rapidly to room temperature.

Products consisted of spinel crystals, eskolaite, needles of Mg-Cr borate, and a boron-rich glass. By dissolving the glass in warm and dilute HCl (10%) solution, the products were reduced to eskolaite and euhedral and subhedral octahedra of dark spinels, and occasionally borates. It is to notice that, sometimes, small inclusions of eskolaite may be present in our spinels.

When synthesising Mg-chromite spinels in air, O'Neill and Dollase (1994) found a small amount of apparently unreacted Cr<sub>2</sub>O<sub>3</sub>. They believed that the excess Cr<sub>2</sub>O<sub>3</sub> resulted from the presence of Cr<sup>4+</sup> in the chromites at high *f*O<sub>2</sub>, according to the reaction:

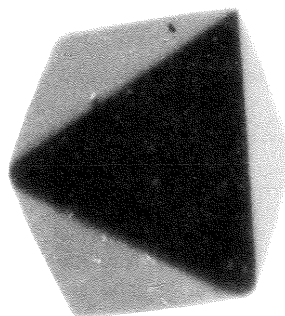


However, optical absorption spectra obtained on our samples, do not show the presence of Cr<sup>4+</sup>. Eskolaite were removed from the samples after repeated cleaning with ultrasonic bath. Unfortunately, the amount of borates is quite large in high-Fe<sup>3+</sup> runs so that it is not possible to remove them completely so that the weight of products for Fe<sup>3+</sup> higher than 30 is considered to be approximately 50 mg.

## RESULTS

### MgCr<sub>2</sub>O<sub>4</sub> end-member

Mg-chromite crystals are dark, translucent crystals sized up to about 300 μm (Fig. 1). Various values for experimental parameters (i.e. oxide proportions, flux/oxide ratio *N*) were tried and the best results are those summarised in Table 1 (MgCr-5). After grinding and polishing the colour of these spinels is dark green. The cell parameter of this end-member was measured by means of a X-ray single-crystal diffractometer KUMA-K4 at the University of Trieste giving a value of *a*<sub>0</sub> equal to 8.3329 (1)



200 micrometers

Fig. 1 – Single-crystal of spinel from MgCr<sub>5</sub> run

Å, *u* (oxygen positional parameter) equal to 0.2612 (1) and T-O and M-O lengths equal to 1.965 and 1.995, respectively, corresponding to the tetrahedral and octahedral bond distances of Mg and Cr calculated by Lavina *et al.* (2002). The chemical composition was measured by electron microprobe giving an average of Mg = 0.991 (9) and Cr = 2.006 (6) atoms per formula unit.

O'Neill and Dollase (1994) studied the crystal structure and cation distribution of MgCr<sub>2</sub>O<sub>4</sub> from powder XRD structural refinements. The lattice parameter was found to be between 8.3339 (1) and 8.3341 (1) for samples annealed at different temperatures. Small differences in the oxygen positional parameter (*u*) were found from the BGI (Bayerische Geoinstitut, Germany) and UCLA (University of California, USA) refinements. In fact the mean *u* values are 0.2612 (2) and 0.2607 (4), respectively. The neutron diffraction study of MgCr<sub>2</sub>O<sub>4</sub> carried out by Infante and Fender (1973), gave *u* equal to 0.2612 (1).

### Mg(Cr, Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> series

During the synthesis of this series, it was noticed that with the increase of the ferrite content there was a decrease of the spinel yield if the same flux ratio (*N*=2.20) was used. This is

TABLE 1

*Flux grown Mg(Cr, Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> spinels. Runs in air: molar proportions of starting oxide mixture, flux/compound ratio (N) and resulting amount of spinel (mg). All runs were performed between 1200 and 900°C, cooling rates 4°C/h.*

Runs	MgCr-5	Fe3-5	Fe3-10	Fe3-20	Fe3-30B	Fe3-40B
MgO	1.00	1.00	1.00	1.00	1.00	1.50
Cr <sub>2</sub> O <sub>3</sub>	1.00	0.95	0.90	0.80	0.70	0.60
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.05	0.10	0.20	0.30	0.40
N	2.20	2.20	2.20	2.20	2.05	1.50
Quantity	980	860	830	250	50	50
Runs	Fe3-50B	Fe3-60B	Fe3-70	Fe3-80	Fe3-90	Fe3-94
MgO	1.50	1.50	2.37	2.37	2.37	2.37
Cr <sub>2</sub> O <sub>3</sub>	0.50	0.40	0.30	0.20	0.10	0.06
Fe <sub>2</sub> O <sub>3</sub>	0.50	0.60	0.70	0.80	0.90	0.94
N	1.30	0.90	0.90	0.80	0.90	0.90
Quantity	50	50	50	50	50	50

clearly seen in Table 1 between the Mg-Cr end-member and 20% of ferrite content (980-250mg) while in the following runs no spinels were present. To obtain spinel crystals with higher MgFe<sup>3+</sup><sub>2</sub>O<sub>4</sub> components the flux/nutrient ratios had to be decreased continuously. It is to be noticed that in some cases, spinels with rounded instead of sharp edges have been found. After polishing and grinding the samples, a change in colour from transparent green to transparent brown was noticed along the series, even with a small amount of Fe<sup>3+</sup> (i.e. from MgCr to Fe<sup>3+</sup> 5%). Moreover, preliminary <sup>57</sup>Fe Mössbauer spectra were measured at room temperature on samples with low Fe-contents using a conventional spectrometer system. The spectra are dominated by a doublet assigned to Fe<sup>3+</sup> in the octahedral position. A weak singlet indicates that some Fe<sup>2+</sup> are also present in the tetrahedral position in these samples. In order to avoid stabilisation of Fe<sup>2+</sup> in the predominantly tetrahedral position an excess of MgO was used in the synthesis runs for compositions with higher

components of MgFe<sup>3+</sup><sub>2</sub>O<sub>4</sub> (cf. Table 1), and Mössbauer spectra of these samples do not indicate any Fe<sup>2+</sup>.

Single crystal X-ray diffraction shows that there is a continuous increase of *a*<sub>0</sub> from 8.3329 (1) Å for Mg-Cr end-member to 8.3734 (4) Å for Mg(Cr<sub>0.2</sub>Fe<sup>3+</sup><sub>1.8</sub>)O<sub>4</sub> spinel (Fig. 2a). The Mg-Fe<sup>3+</sup> end-member was not synthesised, but according to Andreozzi et al. (2001) it is considered to be 8.3841 Å. As concerns the oxygen positional parameter *u* there is a decrease from 0.2612 to 0.2572. T-O and M-O bond distances are inversely related so that with increasing ferrite content M-O distance increases while T-O decreases (Fig. 2b). It is to notice that in spite of a linear relation between *a*<sub>0</sub> and *u*, M-O and T-O are linearly related and this could be caused by a certain degree of inversion.

#### *(Mg, Fe<sup>2+</sup>)Cr<sub>2</sub>O<sub>4</sub> series*

During these runs it was noticed that the amount of spinels is more or less constant, even if it happens that the crystal size decrease. To obtain samples appropriate for single-crystals

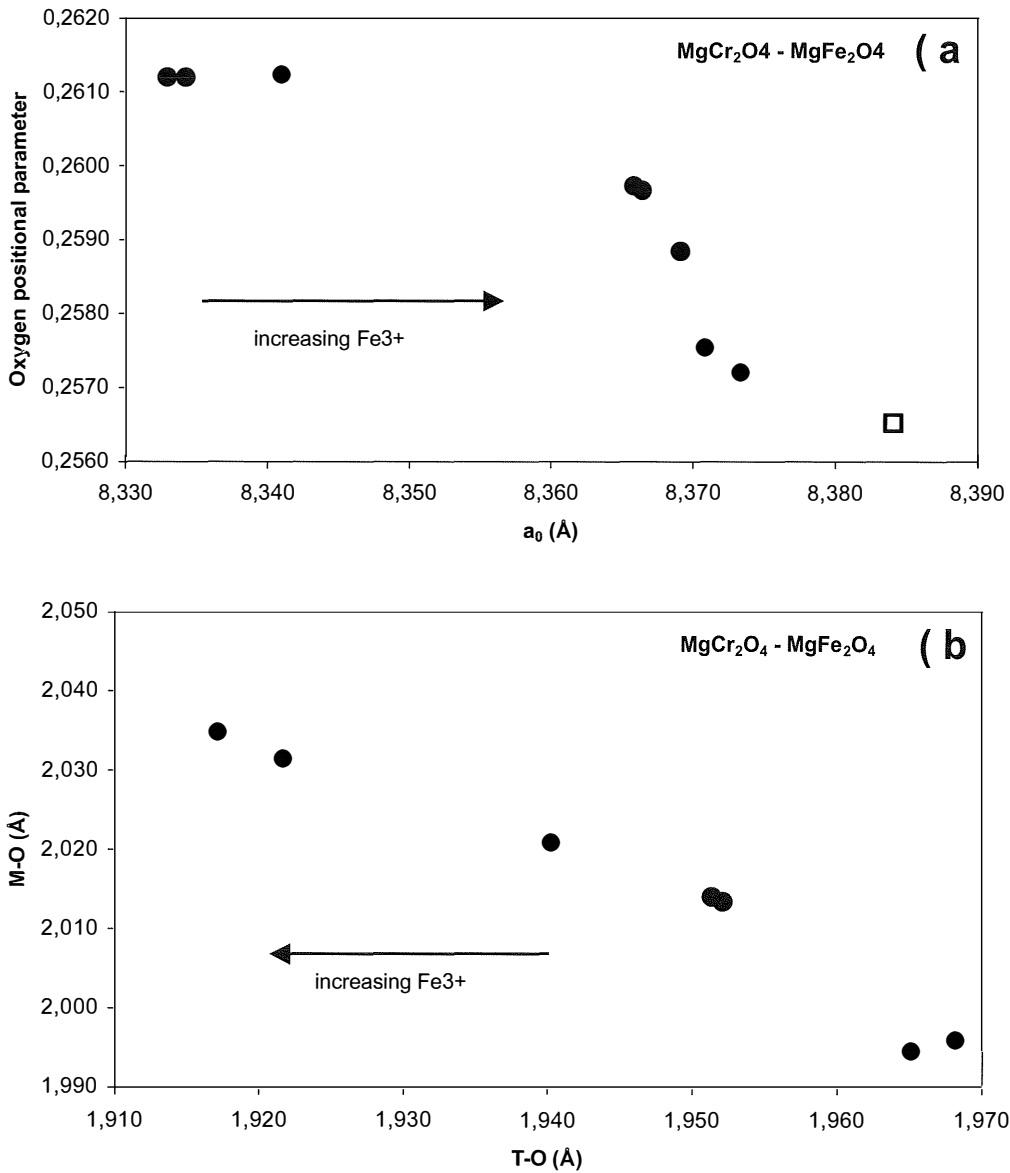


Fig. 2 – Structural parameters in  $MgCr_2O_4 - MgFe_2O_4$  series: a)  $a_0$  vs oxygen positional parameter diagram. Full dots: this study; open square: magnesioferrite endmember (Andreozzi *et al.*, 2001); b) T-O vs M-O distances diagram.

TABLE 2

*Flux grown (Mg, Fe<sup>2+</sup>)Cr<sub>2</sub>O<sub>4</sub> spinels. Runs in controlled atmosphere: molar proportions of starting oxide mixture, flux/compound ratio (N) and resulting amount of spinel (mg). All runs were performed between 1200 and 900°C, cooling rates 4°C/h.*

Runs	Fe2-5	Fe2-10B	Fe2-20	Fe2-20B	Fe2-30	Fe2-40	Fe2-45
MgO	0.95	0.90	0.80	0.80	0.70	0.60	0.55
Cr <sub>2</sub> O <sub>3</sub>	1.00	1.00	0.80	0.80	0.80	0.80	0.80
FeO	0.05	0.10	0.20	0.20	0.30	0.40	0.45
N	2.20	2.40	2.20	2.35	2.35	2.35	2.60
Quantity	430	500	410	150	440	300	300
Runs	Fe2-50	Fe2-55	Fe2-60	Fe2-70	Fe2-80	Fe2-90	Fe2-100
MgO	0.50	0.45	0.40	0.30	0.20	0.10	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.80	0.80	0.80	0.80	0.80	0.80	0.80
FeO	0.50	0.55	0.60	0.70	0.80	0.90	1.00
N	2.50	2.6	2.6	2.60	2.80	3.00	3.20
Quantity	570	120	240	500	230	100	280

methods, the flux/nutrient ratio had to be increased for the Fe-rich compositions (Table 2). <sup>57</sup>Fe Mössbauer spectra were measured at room temperature on the Fe-containing samples using a conventional spectrometer system. With few exceptions, the spectra contain an absorption line centred at 0.92 mm/s, assigned to Fe<sup>2+</sup> in the tetrahedral position (Fig. 3). For compositions close to the Mg-chromite end-member the line is narrow, however, for intermediate compositions the line broadens progressively. Towards the chromite end-member the peak becomes narrow again.

The peak was fitted as a doublet with a small quadrupole splitting, which showed to vary continuously over the solid solution series. The pronounced increase in dq observed at intermediate compositions is interpreted to be caused by the variation in occupancy (Mg or Fe<sup>2+</sup>) in the neighbouring tetrahedral sites. For the samples with the lowest chromite contents (~ 6% Chr), an additional doublet assigned to Fe<sup>3+</sup> was also observed.

Single crystal X-ray diffraction shows that

there is a continuous increase of  $a_0$  from 8.3329 (1) Å for Mg-Cr end-member to 8.3765 (2) Å for Fe-Cr end-member (Fig. 4a). As concerns the oxygen positional parameter  $u$  there is an increase from 0.2612 to 0.2626. T-O bond distance increases with chromite content from 1.965 to 1.996, while M-O remains rather constant ( $1.995 \pm 1$ ), suggesting a Fe<sup>2+</sup>-Mg substitution in T site and a full occupancy by Cr of M site (Fig. 4b). It is to notice that chromite endmember shows T-O bond distance equal to 1.996 very close to the value of 1.995 calculated for Fe<sup>2+</sup> by O'Neill and Navrotsky (1983), but slightly different from those by Shannon (1976) and Lavina *et al.* (2002), equal to 2.000 and 2.001, respectively.

## CONCLUSIONS

Because of the chemical complexity frequently observed in natural spinels and the difficulties in precise site assignment of the major cations, synthetic materials of well-

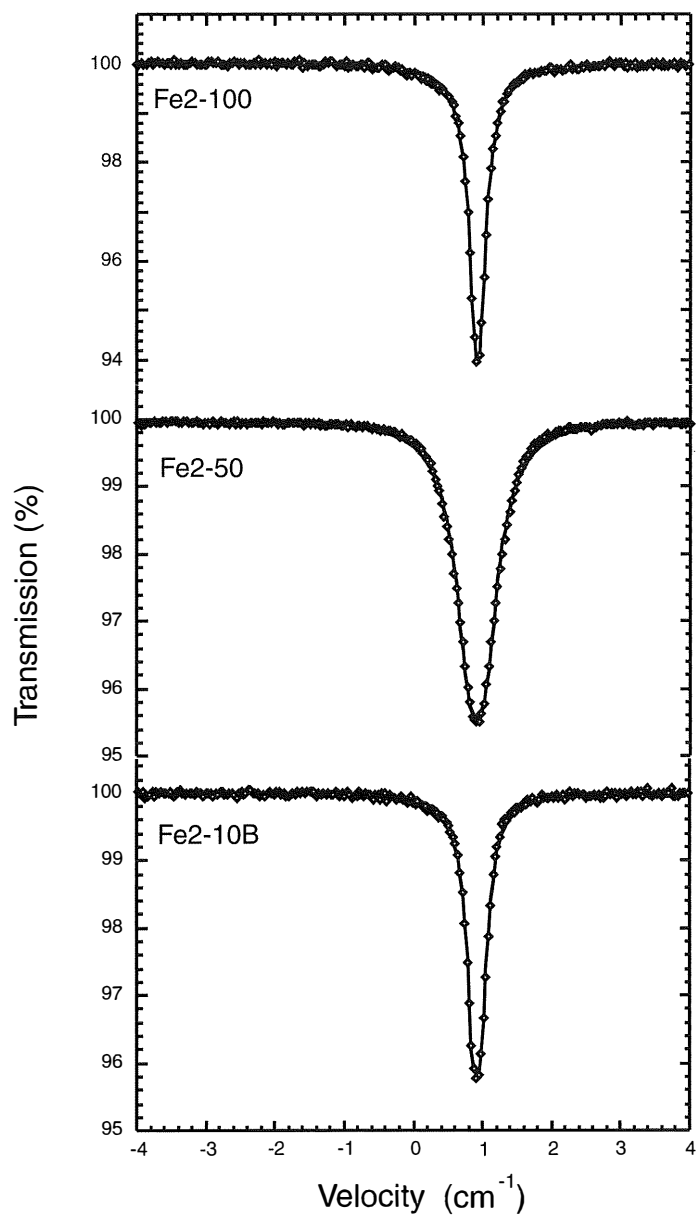


Fig. 3: Room-temperature Mössbauer spectra of three runs from  $MgCr_2O_4 - FeCr_2O_4$  series.

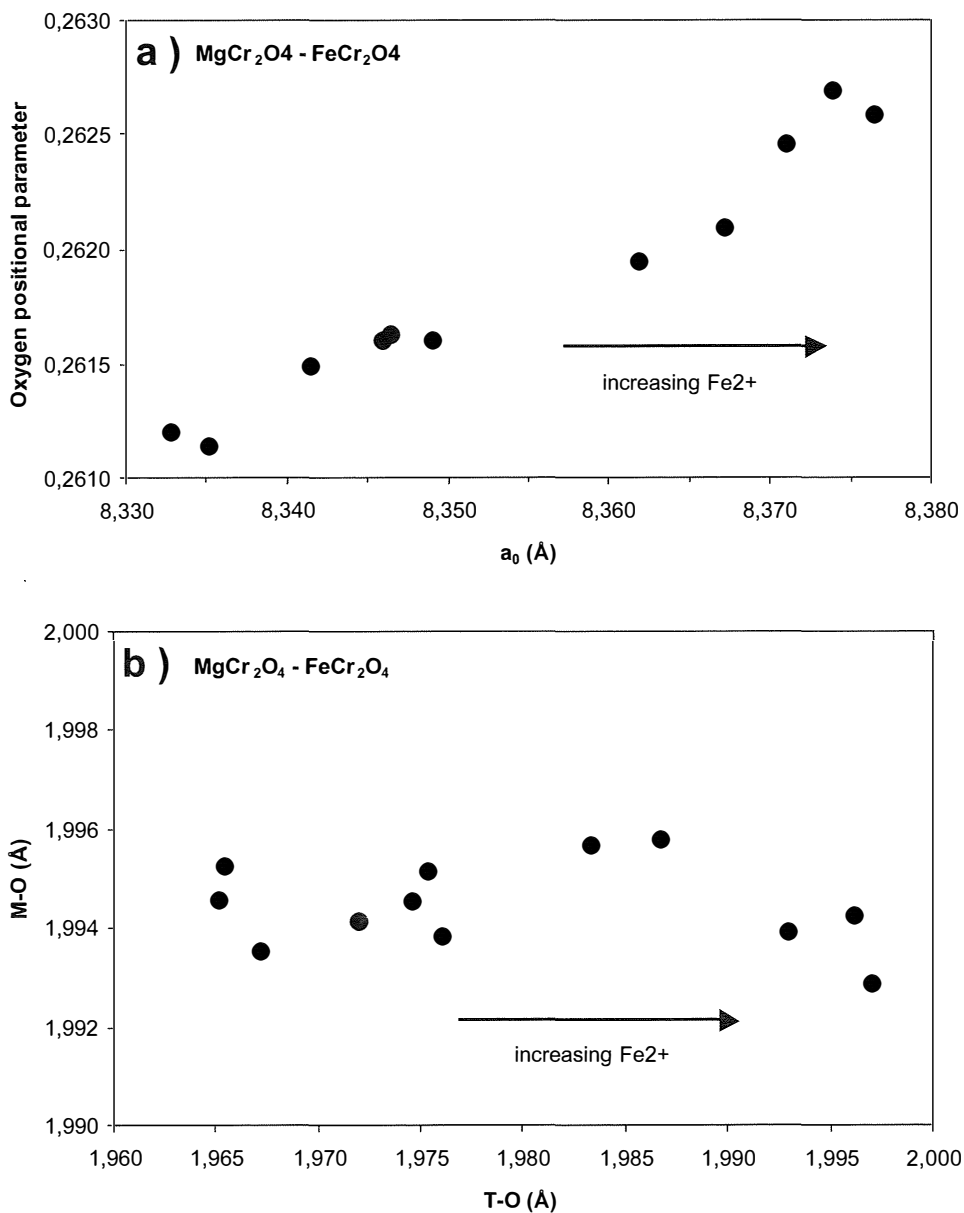


Fig. 4: Structural parameters in  $\text{MgCr}_2\text{O}_4 - \text{FeCr}_2\text{O}_4$  series: a)  $a_0$  vs oxygen positional parameter diagram; b) T-O vs M-O distances diagram.



defined compositions are advantageous to minimise system complexity. In this study spinel single crystals in Mg(Cr, Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> and (Mg, Fe<sup>2+</sup>) Cr<sub>2</sub>O<sub>4</sub> series were synthesised. These spinels allow complementary techniques such as single-crystal X-ray diffraction and microprobe analyses as well as Mössbauer and optical absorption spectroscopy to be utilized in order to achieve a better comprehension of the two series.

## ACKNOWLEDGMENTS

DL thanks the Swedish Museum of Natural History and the financial support through HIGH LAT resources (project number HPRI-CT-2001.00125) within the European Community – Access to Research Infrastructure Action of the Improving Human Potential Programme and COFIN 2001 (F. Princivalle resp.: Cristallochimica e reazioni di scambio cationico in spinelli, olivine e pirosseni). HS acknowledge support from the Swedish Research Council.

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