

Kinetics of cation ordering in natural $\text{Mg}(\text{Al},\text{Cr}^{3+})_2\text{O}_4$ spinels

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ABSTRACT

The kinetics of cation ordering (quench method) in two natural $\text{Mg}(\text{Al}_{2-y}\text{Cr}_y)\text{O}_4$ spinels ($y \sim 0.03$ – 0.06 and 0.24), highly ordered in terms of Mg–Al, were studied by means of X-ray single-crystal diffraction. The equilibrium distribution of Mg and Al between tetrahedral and octahedral sites was investigated at 650°C (in disordering and ordering) and at 850°C (in ordering), through several time-steps to monitor the rate of cation distribution before equilibrium was achieved. The cation distributions for both disordering and ordering experiments were obtained by measuring the oxygen positional parameter u , which is correlated to the inversion parameter x (Al in T site), and then to the composition of the samples.

The Mueller kinetic model, satisfactorily applied to the experimental data, allowed the calculation of the kinetic ordering constants K , linearly related to temperature by means of Arrhenius equations.

The kinetics of ordering processes are influenced by Cr content. The equilibrium for both the isotherms at 650 and 850°C was reached at different elapsed times by the low- and high-Cr spinels: the time for the low-Cr sample was, in both the ordering experiments, about double that of the high-Cr sample. Consequently, the activation energy (186 and 175 kJ/mol for low- and high-Cr samples, respectively) for the intracrystalline Mg–Al ordering decreases with Cr increase.

Keywords: Kinetics, cation distribution, order-disorder, spinels

INTRODUCTION

The time and temperature evolution of the intracrystalline cation exchange between T and M sites in spinels has been extensively studied and provides a potential method for determining the cooling history of host rocks (Della Giusta et al. 1986; Princivalle et al. 1989; Andreozzi et al. 2000). Most studies concern synthetic samples and only a few ones natural spinels. Recent studies on highly ordered natural spinels belonging to the spinel-magnesiocromite series with Cr^{3+} substituting for Al^{3+} have been performed by means of single-crystal X-ray diffraction and in situ heating (Carbonin et al. 2002; Martignago et al. 2003). These works show how Cr^{3+} content influences the relationships between the Mg–Al order-disorder reaction and the temperature: the samples follow different disordering pathways and the temperature at which a certain degree of disorder is achieved is inversely related to Cr^{3+} content. This therefore implies that Cr limits the rate of Mg–Al exchange. In fact it is well known that the Cr^{3+} cation is completely ordered at the M site (Navrotsky and Kleppa 1967; Burns 1975; O'Neill and Dollase 1994). It should be noted, however, that the temperature at which the Mg–Al exchange begins is about 650°C , independent of Cr^{3+} content.

On the basis of these results, crystals belonging to the same spinel-magnesiocromite series from the Olkhon metamorphic complex (Lake Baikal, Russia; Makrygina and Petrova 1998) were chosen in order to study their kinetic behavior. The selected crystals are characterized by low (Ch) and high (Sc) Cr^{3+} contents, i.e., 0.03 – 0.06 and 0.24 atoms per four O atoms, respectively.

The crystals were first used for heating experiments (quench method) at the isotherm of 650°C in disordering and ordering experiments (reversal technique), in order to monitor the cation exchange patterns. A second series of heating ordering experiments was then performed on the same crystals at the isotherm of 850°C .

This paper aims (1) to determine the Mg–Al cation distribution as a function of temperature, and then to describe the cation order-disorder at high temperature; (2) to define the kinetic constants and activation energies; and (3) to illustrate the relationships between the low-Cr sample and synthetic MgAl_2O_4 spinel (Syn) (Andreozzi et al. 2000; Andreozzi and Princivalle 2002), would have similar chemical composition.

EXPERIMENTAL METHODS

Before the heating experiments, a series of crystals with Cr content close to 0.03 – 0.06 atoms per formula unit (afu) and with Cr content close to 0.25 (afu) were tested on a single-crystal diffractometer and chemically analyzed. Initially, crystals Ch ($\text{Cr} = 0.03$ afu) and Sc ($\text{Cr} = 0.244$ afu) were selected. Sample Ch was chosen to compare its results with the pure synthetic MgAl_2O_4 sample (Andreozzi and Princivalle 2002).

Unfortunately, after annealing at 1000°C and before the 850°C isothermal experimental, sample Ch was lost, so a new low-Cr crystal, Ch₁ ($\text{Cr} = 0.057$ afu), was used for the later experiments.

Heating experiments

The crystals used for this study were sealed in a thin-walled quartz tube and submitted to heating-quenching experiments, which were carried out in a vertical tube furnace, with drop-quenching in cold water (20 cm of free fall). Run temperatures were accurately measured and controlled by means of a calibrated Pt/Pt–Rh thermocouple located near the sample; the uncertainty is estimated to be about $\pm 5^\circ\text{C}$.

At first, each crystal was disordered at 650°C in several time-steps, to achieve equilibrium. After the disordering experiments, the same crystals were disordered

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at 1000 °C with an annealing time of 24 h, and they were then re-ordered at the same temperature of 650 °C, for different isothermal time-steps. Further ordering experiments at 850 °C, with different duration with respect to the isothermal steps, were carried out on the same crystals previously disordered and annealed at 1000 °C for 24 hours and then drop-quenched. Isothermal experiments were performed using several time steps, to achieve equilibrium and to calculate kinetic constants.

After each annealing and quenching experiment, the crystals were mounted on a single-crystal diffractometer for X-ray data collection, and then subjected to the next experimental cycle.

Data collection

X-ray single-crystal data were collected using an automated KUMA-KM4 (K-geometry) diffractometer (MoK α radiation monochromatized by a flat graphite crystal). Intensity data were collected up to $2\theta = 90^\circ$ in the ω - 2θ step-scan mode, with a peak-base width of $2\theta = 1.7^\circ$, which increased with the θ angle, and counting time variable from 20 to 40 s, according to peak standard deviation. Because the psi-scan curves were flat, empirical correction for absorption was not applied. Twenty-four equivalents of the (12 8 4) reflection (ca. $82^\circ 2\theta$) were accurately centered at positive and negative values of 2θ and used for cell parameter determination. Structural refinements were carried out in $Fd\bar{3}m$ with the Shelxl-97 program (Sheldrick 1997), without chemical constraints. No violations of this symmetry were detected. Refined parameters were: scale factor, secondary extinction coefficient, oxygen positional parameter u , and anisotropic displacement parameters $U(O)$, $U(M)$, and $U(T)$. For the low-Cr sample, one scattering curve, for Mg²⁺ and Al^{1.5+}, was assigned to the T and M sites, respectively. For the high-Cr sample Mg²⁺ and two scattering curves, for Al^{1.5+} and Cr^{1.5+}, were assigned to the T and M sites, respectively. In spinels, the mean atomic number (m.a.n.) determined by least-squares refinement of site occupancies is quite sensitive to the ionization level of oxygen (Della Giusta et al. 1986) so, for the O-scattering curve, an ionization level between O^{1.5-} and O²⁻ was chosen to obtain the best values for all conventional agreement factors.

Structural refinement results are listed in Tables 1a–b.

Sample characterization

Chemical analysis was carried out on the polished surface of the same crystal used for the X-ray study, using a Cameca/Camebax Microbeam electron microprobe

at the Istituto di Geoscienze e Georisorse, CNR Padova. Analyses were performed at 15 kV and 15 nA sample current by the wavelength-dispersive method (WDS). X-ray counts were converted into oxide weight percentages using the PAP correction program supplied by CAMECA. Synthetic spinel (MgAl₂O₄) and synthetic oxide standards were used. The microprobe analyses are reported in Table 2.

Inversion parameter x (Al in T site) was calculated according to the bond-length method, following Carbonin et al. (1996) and using the ionic radii from Lavina et al. (2002). This method determines cation distributions by minimizing the following function, which takes into account structural data, using a soft chemical constraint:

$$F(X_i) = 1/n \sum_j \{[O_j - C_j(X_i)]/\sigma_j\}^2 \quad (1)$$

O_j are the observed quantities with their standard deviation σ_j . In particular, O_j are the four observed crystallographic parameters (a , u and m.a.n. of T and M sites) and the chemical atomic proportions (at least two) for a total of n . $C_j(X_i)$ are the corresponding quantities calculated by means of variable cation fractions X_i . $F(X_i)$ values ≤ 1 indicate good agreement between the calculated and observed data. Since the values of the atomic fractions are strongly correlated by crystal chemical constraints, evaluation of their standard deviation is not easy. Nevertheless, the reliability of the resulting distribution can be tested by scanning $F(X_i)$ at fixed values of each atomic fraction X_i in a range around the minimum. The variation of each atomic fraction which leads to doubling of the minimized $F(X_i)$ may be assumed as the uncertainty of its optimized value. Table 1a–b reports the $F(X_i)$ values. Agreement between observed and calculated values was very high, confirming the consistency of the cation distribution obtained.

RESULTS

As the oxygen positional parameter u is order-disorder transformation dependent and closely related to the inversion parameter x (Andreozzi et al. 2000), it was assumed to be a good indicator for monitoring the cation exchange between M and T sites in spinels.

At room temperature, the low- and high-Cr samples with similar u values were highly ordered in terms of Mg-Al but when they were disordered at 650 °C using the same time-steps,

TABLE 1A. Structural refinement results and inversion parameter x for the low-Cr (Ch and Ch₁) spinels

	Time (min)	a (Å)	u	m.a.n. (M)	m.a.n. (T)	m.a.n. tot	M-O (Å)	T-O (Å)	Refl.	R_{all}	wR_2	x	$F(X_i)$
Ch sample	Untreated	8.0889 (2)	0.26333 (4)	13.04 (4)	12.17 (8)	38.26 (12)	1.921 (1)	1.938 (1)	123	2.04	3.91	0.143	0.21
Disordering 650 °C	60	8.0889 (2)	0.26334 (4)	13.04 (4)	12.16 (9)	38.24 (12)	1.920 (1)	1.939 (1)	125	2.14	4.02	0.143	0.22
	180	8.0889 (2)	0.26335 (4)	13.02 (3)	12.04 (7)	38.08 (10)	1.920 (1)	1.938 (1)	124	1.86	3.38	0.142	0.24
	420	8.0889 (2)	0.26332 (4)	13.00 (4)	11.89 (7)	37.89 (11)	1.921 (1)	1.938 (1)	123	1.99	3.98	0.144	0.32
	840	8.0888 (2)	0.26332 (4)	13.09 (3)	12.03 (7)	38.21 (10)	1.921 (1)	1.938 (1)	123	1.91	3.57	0.144	0.29
	2520	8.0889 (1)	0.26326 (4)	12.99 (3)	12.12 (7)	38.10 (10)	1.921 (1)	1.937 (1)	120	1.84	3.49	0.148	0.20
	3960	8.0888 (2)	0.26322 (4)	13.01 (4)	12.02 (8)	38.04 (12)	1.921 (1)	1.937 (1)	122	1.82	3.53	0.151	0.24
	7980	8.0889 (2)	0.26315 (4)	13.03 (5)	11.98 (8)	38.05 (13)	1.922 (1)	1.936 (1)	125	2.23	3.99	0.156	0.25
	15840	8.0887 (1)	0.26312 (4)	12.97 (4)	12.17 (7)	38.10 (10)	1.922 (1)	1.935 (7)	124	1.75	3.42	0.159	0.19
33120	8.0888 (1)	0.26301 (4)	13.01 (4)	12.19 (8)	38.22 (11)	1.923 (1)	1.934 (1)	123	2.26	3.89	0.167	0.15	
1000 °C/24h Ordering 650 °C	0	8.0865 (1)	0.26164 (5)	12.82 (5)	12.41 (9)	38.04 (14)	1.932 (1)	1.914 (1)	119	2.03	3.96	0.271	0.17
	12	8.0862 (1)	0.26173 (5)	12.90 (6)	12.49 (9)	38.30 (15)	1.931 (1)	1.915 (1)	118	1.89	3.73	0.258	0.44
	36	8.0863 (1)	0.26182 (5)	12.93 (4)	12.47 (8)	38.34 (11)	1.931 (1)	1.916 (1)	122	1.97	3.72	0.257	0.21
	120	8.0876 (2)	0.26221 (5)	12.95 (5)	12.30 (9)	38.19 (13)	1.928 (1)	1.922 (1)	121	1.98	3.88	0.226	0.13
	240	8.0881 (1)	0.26247 (5)	12.92 (5)	12.29 (9)	38.13 (13)	1.927 (1)	1.926 (1)	122	1.94	3.89	0.203	0.39
	480	8.0883 (2)	0.26253 (4)	12.94 (5)	12.32 (8)	38.20 (12)	1.926 (1)	1.927 (1)	122	2.01	3.62	0.203	0.14
	960	8.0882 (2)	0.26258 (4)	12.86 (5)	12.24 (8)	37.95 (13)	1.926 (1)	1.927 (1)	122	2.10	3.60	0.200	0.16
	6660	8.0882 (2)	0.26258 (4)	12.97 (4)	12.29 (8)	38.22 (11)	1.926 (1)	1.927 (1)	124	1.85	3.61	0.200	0.13
26820	8.0882 (1)	0.26261 (4)	12.98 (4)	12.38 (8)	38.33 (11)	1.926 (1)	1.928 (1)	125	2.23	3.83	0.198	0.22	
Ch ₁ sample	Untreated	8.0928 (1)	0.26337 (4)	13.21 (4)	12.06 (8)	38.47 (10)	1.921 (1)	1.940 (1)	112	1.76	3.05	0.135	0.23
1000 °C/24h Ordering 850 °C	0	8.0907 (1)	0.26167 (6)	13.03 (4)	12.32 (8)	38.37 (11)	1.933 (1)	1.915 (1)	108	1.70	3.47	0.264	0.06
	0.25	8.0907 (1)	0.26169 (5)	12.91 (4)	12.44 (9)	38.25 (12)	1.932 (1)	1.915 (1)	122	2.08	4.10	0.263	0.22
	0.50	8.0908 (1)	0.26180 (6)	12.90 (5)	12.50 (10)	38.29 (14)	1.931 (1)	1.916 (1)	122	2.23	4.61	0.255	0.32
	1.50	8.0909 (1)	0.26182 (7)	13.00 (6)	12.33 (10)	38.33 (16)	1.932 (1)	1.917 (1)	107	1.76	3.83	0.252	0.09
	15	8.0918 (1)	0.26195 (8)	13.17 (6)	12.26 (7)	38.60 (14)	1.931 (1)	1.919 (1)	92	1.71	2.59	0.242	0.03
	30	8.0919 (1)	0.26200 (8)	13.21 (6)	12.31 (8)	38.73 (14)	1.931 (1)	1.920 (1)	96	1.89	2.62	0.239	0.03
	60	8.0919 (1)	0.26201 (9)	13.10 (6)	12.22 (7)	38.43 (14)	1.931 (1)	1.920 (1)	91	1.74	2.7	0.238	0.03
	1440	8.0919 (1)	0.26206 (5)	13.09 (5)	12.37 (8)	38.54 (12)	1.930 (1)	1.921 (1)	110	1.82	3.37	0.235	0.07

Notes: Estimated standard deviation in brackets; Refl. = Number of independent reflections; R_{all} and wR_2 = agreement factors according to SHELXL97 program package; $F(X_i)$ = Sum of square residuals, (Eq.1).

TABLE 1B. Structural refinement results and inversion parameter x for the high-Cr (Sc) spinel

	Time (min)	a (Å)	u	m.a.n. (M)	m.a.n. (T)	m.a.n. tot	M-O (Å)	T-O (Å)	Refl.	R_{all}	wR_2	x	$F(X_i)$
Untreated		8.1180 (1)	0.26326 (6)	14.25 (40)	12.13 (8)	40.63 (80)	1.928 (1)	1.944 (1)	96	1.55	2.34	0.113	0.04
Disordering													
650 °C	60	8.1176 (1)	0.26323 (6)	14.29 (31)	12.12 (7)	40.70 (63)	1.928 (1)	1.944 (1)	98	1.64	2.22	0.115	0.07
	180	8.1175 (1)	0.26324 (7)	14.20 (42)	12.11 (9)	40.51 (84)	1.928 (1)	1.944 (1)	96	1.63	3.11	0.115	0.05
	420	8.1174 (1)	0.26302 (7)	14.36 (34)	12.23 (8)	40.95 (69)	1.930 (1)	1.941 (1)	95	1.50	2.35	0.127	0.15
	840	8.1175 (1)	0.26303 (7)	14.34 (34)	12.13 (7)	40.82 (68)	1.929 (1)	1.941 (1)	98	1.75	2.26	0.129	0.09
	2520	8.1174 (1)	0.26281 (8)	14.25 (37)	12.16 (9)	40.65 (75)	1.931 (1)	1.938 (1)	97	1.96	2.67	0.143	0.06
	3960	8.1174 (1)	0.26276 (7)	14.24 (33)	12.11 (8)	40.58 (67)	1.931 (1)	1.937 (1)	98	1.90	2.33	0.149	0.06
	7980	8.1173 (1)	0.26279 (7)	14.21 (39)	12.16 (8)	40.57 (79)	1.931 (1)	1.937 (1)	94	1.46	2.28	0.145	0.07
	15840	8.1171 (1)	0.26276 (6)	14.22 (31)	12.17 (7)	40.62 (62)	1.931 (1)	1.937 (1)	95	1.67	1.81	0.149	0.03
	33120	8.1174 (1)	0.26278 (6)	14.33 (35)	12.27 (8)	40.93 (70)	1.931 (1)	1.937 (1)	97	1.62	2.05	0.150	0.02
1000 °C/24h	0	8.1163 (1)	0.26188 (9)	14.29 (41)	12.42 (9)	41.01 (82)	1.938 (1)	1.924 (1)	97	2.29	2.81	0.212	0.05
Ordering	12	8.1162 (2)	0.26197 (8)	14.35 (39)	12.55 (10)	41.24 (79)	1.937 (1)	1.926 (1)	93	1.68	2.72	0.203	0.14
650 °C	36	8.1166 (1)	0.26202 (8)	14.25 (41)	12.46 (9)	40.96 (83)	1.937 (1)	1.926 (1)	92	1.48	2.34	0.190	0.61
	120	8.1174 (1)	0.26262 (7)	14.30 (37)	12.34 (8)	40.94 (74)	1.932 (1)	1.935 (1)	95	1.63	2.45	0.157	0.05
	240	8.1178 (1)	0.26280 (9)	14.34 (43)	12.39 (10)	41.07 (87)	1.931 (1)	1.938 (1)	98	1.91	3.02	0.147	0.02
	480	8.1177 (1)	0.26277 (7)	14.30 (41)	12.28 (9)	40.87 (82)	1.931 (1)	1.937 (1)	96	1.85	2.59	0.142	0.30
	6660	8.1176 (1)	0.26282 (7)	14.26 (38)	12.33 (8)	40.86 (76)	1.931 (1)	1.938 (1)	97	1.85	2.29	0.142	0.12
	26820	8.1176 (1)	0.26279 (7)	14.31 (35)	12.42 (9)	41.03 (71)	1.931 (1)	1.937 (1)	92	1.61	2.53	0.144	0.13
1000 °C/24h	0	8.1166 (1)	0.26184 (8)	14.17 (39)	12.47 (8)	40.80 (79)	1.938 (1)	1.924 (1)	93	1.72	2.56	0.215	0.27
Ordering	0.25	8.1166 (1)	0.26184 (7)	14.18 (36)	12.39 (9)	40.75 (73)	1.938 (1)	1.924 (1)	93	1.51	2.22	0.215	0.12
850 °C	0.50	8.1160 (1)	0.26196 (10)	14.38 (43)	12.42 (11)	41.18 (89)	1.937 (1)	1.925 (1)	87	2.20	2.62	0.211	0.01
	1.5	8.1160 (1)	0.26234 (14)	14.30 (60)	12.32 (16)	40.93 (1.20)	1.934 (1)	1.931 (2)	87	3.07	3.01	0.186	0.03
	1440	8.1160 (1)	0.26237 (16)	14.58 (81)	12.55 (21)	41.70 (1.64)	1.934 (1)	1.931 (2)	80	3.15	3.77	0.177	0.12

Notes: Estimated standard deviation in brackets; Refl. = Number of independent reflections; R_{all} and wR_2 = agreement factors according to SHELXL97 program package; $F(X_i)$ = Sum of square residuals, (Eq.1).

they followed distinct pathways, reaching different u values (Tables 1a–b). The degree of disorder reached at the end of the experiments reflects their different chemical compositions and is higher for the high-Cr crystal.

In the high-Cr sample, after heating for 180 min u remained constant, then began to change; that is it changed in between 180 and 420 min [from 0.26324(7) to 0.26302(7)]; after 2520 min, u remained constant at about 0.2628. For the low-Cr sample, u showed slight differences only after 3960 min [from 0.26333(4) to 0.26322(4)], and then slightly decreased to 33 120 min. After annealing at 1000 °C for 24 h and quenching, the samples showed changed u values, reflecting different Mg-Al disorder related to their different chemistries (i.e., the high-Cr sample was less disordered than the low-Cr one). After 36 min at 650 °C during re-ordering experiments, u increased slightly in both samples, whereas after 120 min it changed significantly. In particular, after 240 min, the high-Cr sample reached the same u values obtained at the end of the disordering experiments, demonstrating the achievement of equilibrium. For the low-Cr sample, u changed significantly up to 960 min and then remained constant at 0.2626. This behavior clearly shows that, during disordering experiments, after 33 120 min the sample was still far from equilibrium; it seems that the time to attain equilibrium would be on the order of thousands of days, too long for most laboratory experiments (Fig.1).

After further annealing at 1000 °C for 24 h and at room temperature, the low- and high-Cr samples showed u values similar to those measured after the first annealing at 1000 °C. The crystals were then ordered at 850 °C in several time steps. In both samples, u began to change even after 0.5 min. In spite of this, the high-Cr sample reached the u value corresponding to equilibrium temperature of 850 °C after 1.5 min, whereas the low-Cr sample needed at least 30 min.

The same behavior shown by u also applies to the inversion

TABLE 2. Electron microprobe mean composition of the low-Cr (Ch and Ch₁) and high-Cr (Sc) spinels

Sample	Ch	Ch ₁	Sc
MgO	28.87 (13)	27.72 (14)	26.47 (14)
Al ₂ O ₃	69.76 (39)	68.45 (25)	59.20 (59)
Cr ₂ O ₃	1.59 (10)	2.99 (10)	12.25 (59)
ZnO	0.27 (3)	0.27 (3)	0.35 (8)
Σ	99.49	99.43	98.27
Cations on basis of 4 O atoms			
Mg	0.995 (5)	0.995 (4)	0.993 (8)
Al	1.970 (5)	1.943 (4)	1.756 (10)
Cr ³⁺	0.030 (2)	0.057 (2)	0.244 (11)
Zn	0.005 (1)	0.005 (5)	0.007 (1)
Σ	3.000	3.000	2.999

Notes: Average of 30 analyses; estimated standard deviation in brackets.

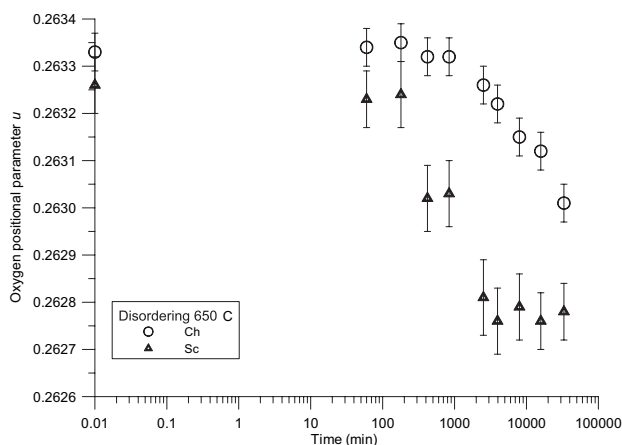


FIGURE 1. Variation of u with time (logarithmic scale) at 650 °C for the Ch (low-Cr) and Sc (high-Cr) samples.

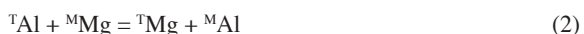
parameter x (Table 1a–b). The initial state of order and the degree of disorder reached at the end of the experiments (in disordering and ordering) were different for the two samples, reflecting their different Al contents.

DISCUSSION

Kinetics of cation ordering

Quantitative analysis of kinetics data is very important in describing the thermal behavior of minerals. Several papers in the literature are devoted to this subject, and the intracrystalline exchange reaction was modelled by Mueller (1967, 1969).

The order disorder process may be described by the following exchange reaction:



in which the forward reaction implies an exchange of Mg with Al at the M site (ordering process), and the backward one an exchange of Al with Mg at the M site (disordering process).

O'Neill (1994) wrote an equation to describe the increase of ordering time with the rate of change of concentration of Al at the T site. This equation, simplified according to Mueller (1967, 1969), assuming ideal mixing in each site, together with the solving integral, is reported in Andreozzi and Princivalle (2002) and

was used here to calculate the rate constant K . The best values for K were found by minimizing the differences of squares between experimental and calculated Δt , for both low- and high-Cr samples. K values of 1.24 ± 0.38 and 2.51 ± 0.25 at 850 °C, and K values of 0.016 ± 0.007 and 0.034 ± 0.015 at 650 °C were calculated for the low- and high-Cr samples, respectively. The “half time of the reaction” $t_{1/2}$, of $0.693 1/K$, is the time required to go halfway from the initial to final inversion degree, and corresponds to 42.3 and 20.3 min at 650 °C, and 0.6 and 0.3 min at 850 °C for the low- and high-Cr samples, respectively. The calculated ordering paths show good fits with experimental data, which are reproduced to within $\pm 2\sigma$, adopting both linear and semi-logarithmic plots (Fig 2a–d).

The fit between experimental and calculated data on both short and long time-scales confirms the validity of the model and the Mueller's assumption that the kinetics of an exchange process follows a second-order rate law, and also that the measured ordering states are highly reliable. The data obtained for the low-Cr sample in terms of $1/K$ are in excellent agreement with those reported by Andreozzi and Princivalle (2002) for the synthetic pure sample.

The temperature dependence of the kinetic constant K , shown in the Arrhenius plot of Figure 3, is expressed as:

$$\ln K = 20.181 - 22425 (1/T) \quad \text{for low-Cr sample} \quad (3)$$

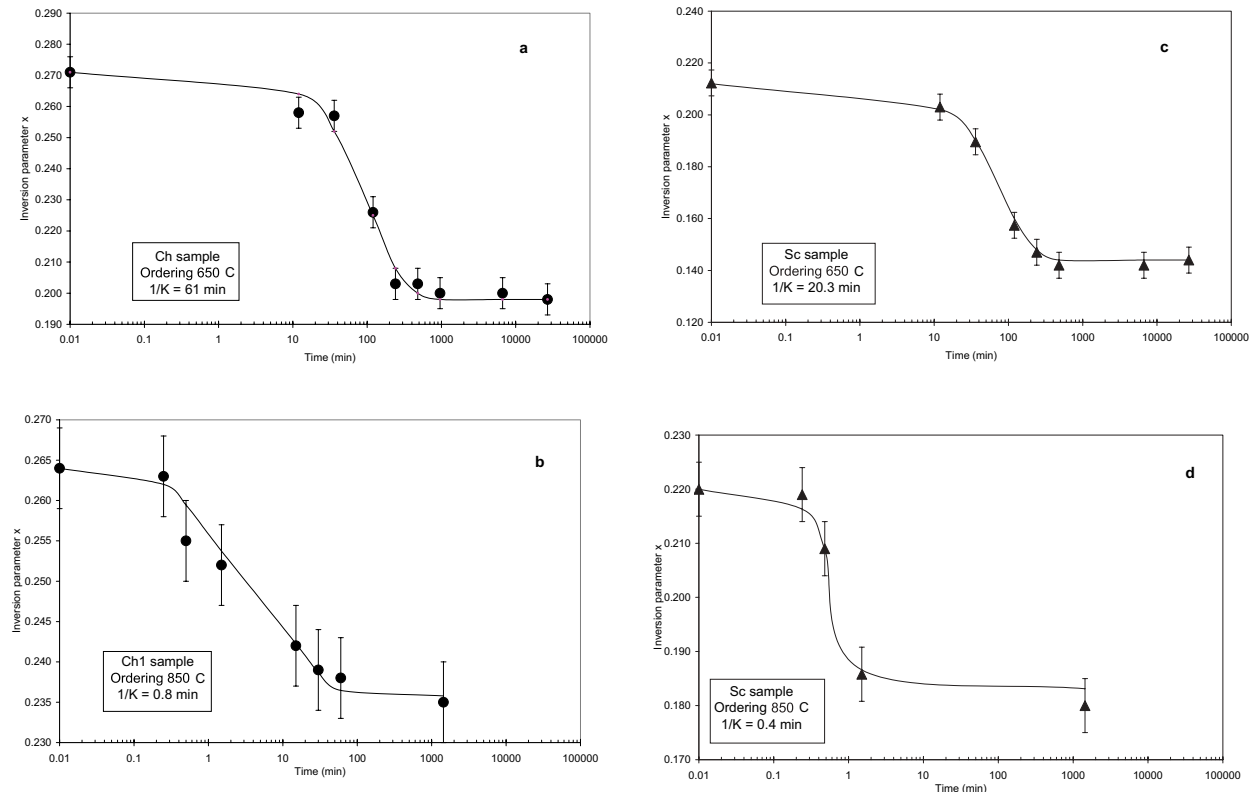


FIGURE 2. (a–d) Time-temperature evolution of the inversion parameter x for the Ch, Ch₁ (low-Cr), and Sc (high-Cr) samples. Experimental data at 650 and 850 °C; error bars correspond to $\pm 2\sigma$ overlap; theoretical curves by Mueller's equation. Kinetic constants are also shown for each temperature.

$$\ln K = 19.500 - 21124 (1/T) \text{ for high-Cr sample} \quad (4)$$

The activation energy (E_a) for Mg-Al ordering, derived from the angular coefficient of these linear relations is 186 and 175 kJ/mol for low- and high-Cr samples, respectively, in the investigated range of temperatures. Figure 3 also shows the data for the synthetic sample (Syn) $MgAl_2O_4$ (Andreozzi and Princivalle 2002). The three spinel compositions show the same behavior, given by three distinct parallel trends, which reflect variable Cr (or Al) content. It follows that the activation energy decreases with Cr increase (or Al decrease). The E_a values are very close to those reported in Andreozzi and Princivalle (2002) for the synthetic $MgAl_2O_4$ spinel (197 ± 22 kJ/mol). In fact, comparing the behavior of the synthetic sample at 700, 800, and 900 °C with that of a low-Cr sample at 650 and 850 °C (Fig.4), the u parameter reveals a similar trend. In particular, the u value of the low-Cr sample at 850 °C plots between those of the Syn sample at 800 and 900 °C.

In conclusion, it is interesting to note that, in highly ordered natural samples with closure temperatures estimated around 500 °C (low grade metamorphism of the host rocks), the Mg-Al exchange between M and T sites in a disordering process begins at 650 °C and requires a lot of time. On the contrary, the time required to reach equilibrium at the same temperature while ordering is faster because the samples were previously annealed at 1000 °C and then quenched. As a consequence, the annealing has likely changed the defect structure of the spinel slightly, enhancing diffusion in all experiments performed subsequently. In addition, the final degree of disorder reached in disordering experiments are also dependant on the chemical composition of the samples.

The kinetics of ordering are different between the Ch and Sc samples, being influenced by the Cr^{3+} content and thus by total Al. In fact, although the Al exchanged between M and T sites at the end of the ordering experiments is quite similar in the two samples, the time required to reach equilibrium in re-ordering at 650 and 850 °C is significantly shorter for the high-Cr sample

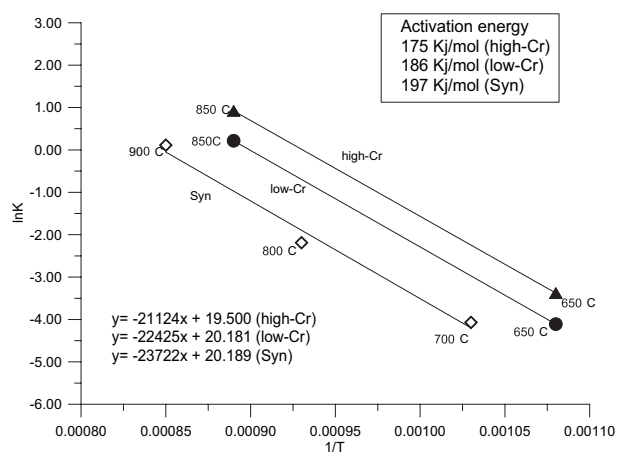


FIGURE 3. Arrhenius plot showing linear dependence of ordering rate constant $\ln K$ with temperature for the low- and high-Cr and Syn (synthetic) samples. Calculated activation energies are also shown.

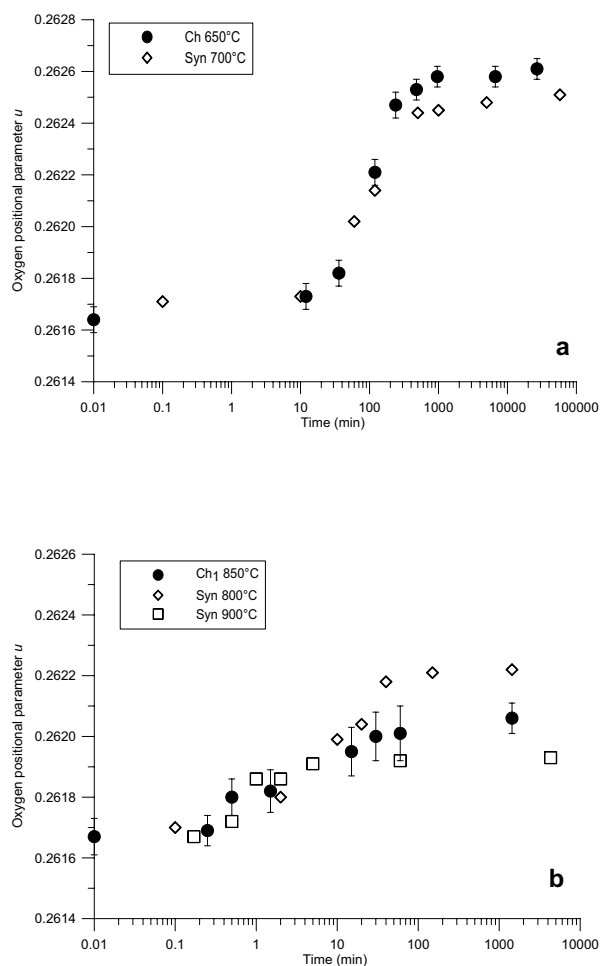


FIGURE 4. (a-b) Comparison of u variation with time (logarithmic scale) for the low-Cr and Syn (synthetic) samples at different temperatures.

than for the low-Cr one. In particular, the results reveal that the differences between the initial and final values of x (Δx) are of about 0.07 and 0.04 for the isothermal experiments of 650 and 850 °C, respectively. This fact shows that the rate of cation exchange increases not only with temperature, but also with Cr^{3+} content because of the concomitant decrease of Mg-Al exchange activation energy.

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