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Kinetics of cation ordering in synthetic $MgAl_2O_4$ spinel

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ABSTRACT

The time and temperature evolution of intracrystalline Mg-Al exchange in synthetic $MgAl_2O_4$ spinel was studied by single-crystal X-ray diffraction of quenched samples, with the aim of contributing to rock cooling-rate estimation. Flux-grown, homogeneous crystals (0.1 mm in size) were annealed at 1000 °C and then were isothermally ordered at 900, 800, and 700 °C for 10 seconds to 40 days. The cation ordering process was investigated by measuring the spinel O atom positional parameter u, which had been previously demonstrated to be closely related to the inversion x at equilibrium by the linear equation ($R^2 = 0.995$):

$$x = 21.396 - 80.714\,u.$$

From $x = 0.27$ after annealing runs, the inversion decreased with time for all of the three ordering runs, and equilibrium was reached after about 4 min at $T = 900$ °C ($x = 0.25$), about 55 min at $T = 800$ °C ($x = 0.23$), and about 700 min at $T = 700$ °C ($x = 0.21$). The Mueller kinetic model was satisfactorily applied to the experimental data. Solution of Mueller's integral gave the kinetic ordering constants $K_{900} = 1.12 \pm 0.57$, $K_{800} = 0.112 \pm 0.047$, and $K_{700} = 0.0171 \pm 0.0045$ min^{-1}, corresponding to $t_{1/2}$ of 0.6, 6.2, and 40.5 min, respectively. The linear dependence of K with temperature ($R^2 = 0.99$) was observed, and may be expressed by the Arrhenius equation:

$$\ln K = 20.189 - 23722/T\ (\mathrm{K})$$

An activation energy of 197 ± 22 kJ/mol was obtained for the intracrystalline Mg-Al ordering reaction, which compares well with the value of 217 kJ/mol reported in the recent literature for Mg-Fe^{3+} exchange in spinels.

INTRODUCTION

Many studies have been done on intersite cation exchange in rock-forming minerals with the aim of quantifying cation ordering as a function of chemical composition, equilibration temperature, and time. This makes it possible to estimate both the closure temperature and the cooling rate of silicates from terrestrial rocks and meteorites (e.g., Ganguly and Stimpfl 2000; Ganguly and Domeneghetti 1996; Redfern et al. 1996; Ganguly and Tazzoli 1994; Molin et al. 1994; Skogby 1992; Seifert and Virgo 1975). Pyroxenes, olivines and amphiboles have been largely investigated for this purpose, whereas spinels—oxides nearly ubiquitous in low crust and upper mantle—have been relatively less carefully examined. As well as the above-mentioned mineral species, spinels show temperature-dependent cation ordering that is non-convergent, i.e., no changes in symmetry are caused by order-disorder reactions.

The spinel structure ($Fd3m$) is formed of an approximately cubic, close-packed array of O atoms. Bivalent A and trivalent B cations—which partially fill the tetrahedral T and octahedral M cavities—undergo continual intersite exchange with temperature. Cation distribution in spinels is described by the following structural formula:

$$^{IV}(A_{1-x}B_x)^{VI}(B_{2-x}A_x)O_4$$

where IV refers to the T site and VI to the M site, and x is the inversion parameter. At low temperatures ($T \rightarrow 0$ K), x tends toward 0 for normal spinels (e.g., $MgAl_2O_4$) and toward 1 for inverse spinels (e.g., $MgFe_2O_4$), both values corresponding to a low-entropy, completely ordered state. At high temperatures ($T \rightarrow \infty$), both normal and inverse spinels are expected to have x tending to 2/3, a fully disordered state corresponding to maximum entropy and random distribution of cations. This is confirmed by experimental data, because high-temperature investigations of cation distribution have shown x up to 0.35 in $MgAl_2O_4$ (Maekawa et al. 1997; Redfern et al. 1999), and up to 0.72 in $MgFe_2O_4$ (O'Neill et al. 1992).

The kinetics of cation ordering in spinels is definitely less well known than the thermodynamics: this is mainly due to the scarcity of experimental data and to difficulties in interpreting non-equilibrium behavior of intracrystalline cation exchange. Ordering kinetics of $MgFe_2O_4$ have been investigated by O'Neill (1994) and Harrison and Putnis (1999), who measured the evo-

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lution of the lattice parameter *a* and in situ magnetic susceptibility, respectively. Although in both cases the samples were synthetic powders quenched from 900 °C, the results are not in agreement, because the sample studied by O'Neill (1994) reached equilibrium at 500 °C after approximately 100 h, whereas that studied by Harrison and Putnis (1999) at 513 °C was only 50% ordered after over 1000 h. Discrepancies in the ordering rate are attributed by the latter authors to a slight MgO excess in their sample. The influence of non-stoichiometry on $MgAl_2O_4$ was investigated by O'Neill (1997) who synthesized various batches with different MgO/Al_2O_3 ratios. The rate constant was found to be extremely sensitive to stoichiometry, because equilibration time increased with the MgO/Al_2O_3 ratio.

The present work focuses on the dependence of cation ordering on both temperature and time in synthetic $MgAl_2O_4$, which is one of the most important components in many natural spinels. Single crystals with stoichiometric $MgAl_2O_4$ composition were investigated by X-ray diffraction after being annealed at 1000 °C, quenched, and then subjected to isothermal ordering at 900, 800, and 700 °C. Because Mg and Al occupancies are not easily discriminated with X-ray diffraction (due to the very similar X-ray scattering power), the O atom coordinate *u* was chosen as the parameter to be monitored, because in spinels *u* is directly related to the inversion parameter *x* (O'Neill et al. 1992; Redfern et al. 1999; Andreozzi et al. 2000), and it has the advantage of being measured routinely with extreme accuracy and precision.

Sample description and experimental details

Sample synthesis and characterization

Colorless, transparent, inclusion-free $MgAl_2O_4$ crystals up to 0.5 mm across were flux-grown between 1200 and 800 °C, after the procedure described by Andreozzi et al. (2000). In the latter study, untreated samples from batch SP3 were confirmed to be in equilibrium at a final temperature of 800 °C. The chemical composition was determined by means of an electron microprobe operating in the WDS mode. The more than one hundred analyses obtained gave average values of 1.006(7) ions per four O atoms for Mg and 1.996(4) for Al, fitting $MgAl_2O_4$ stoichiometry very closely. Deviation from the ideal formula is only within one estimated standard deviation, and is unlikely to be interpreted as an MgO-excess type of non-stoichiometry, because this substitution is generally considered small in spinels (O'Neill et al. 1992). Furthermore, such a substitution—if real—would only cause a 0.2% departure from the ratio MgO/Al_2O_3 = 1, which, in our experience, does not significantly affect the cation ordering reaction. Possible deviation from stoichiometry due to structural vacancies along the $MgAl_2O_4$-$Al_{8/3}O_4$ series was also considered, because it is more frequently observed in synthetic spinels. It is well known that such structural vacancies affect physical properties and cause a linear decrease in the spinel lattice parameter. For vacancy-free $MgAl_2O_4$, the expected *a* dimension is in the range 8.0839–8.0844 Å (Viertel and Seifert 1979; Navrotsky et al. 1986; Lucchesi and Della Giusta 1994). The lattice parameter of our untreated crystals, measured by X-ray single-crystal diffraction, was 8.0844(1) Å. Further discussion about structural characterization of synthetic spinel crystals from the same batch as those examined here may be found in Andreozzi et al. (2000).

On the basis of both chemical and structural results, our crystals do not show any evidence of non-stoichiometry.

Thermal runs

Two gem-quality, octahedral, colorless crystals from the SP3 experiment, each about 0.1 mm across, were used for heating-quenching experiments, one for experiments at 700 and 900 °C (Marocco 1999) and the other for those at 800 °C. Because structural characterization of the two untreated samples gave results coinciding within ±1 standard deviation, they are not distinguished in the discussion and will be considered as a single sample. The crystal was sealed in a thin-wall quartz tube in air and heating-quenching runs were performed at room pressure in air, because oxidation problems were not expected for the composition investigated in the temperature range of interest. No change in crystal color or transparency was observed after heating. At the end of each experiment, the sample was quenched by dropping the quartz tube into cold water (20 cm free fall), with cooling time to 400 °C estimated to be less than 0.5 seconds (Molin et al. 1991; Della Giusta et al. 1996).

Before the three ordering sequences, the sample was annealed at 1000 °C for 12 h and then drop-quenched. Several isothermal ordering experiments were performed for 10 seconds to 40 days at temperatures of 900, 800, and 700 °C (Table 1). The duration of annealing time at 1000 °C was based on a previous study (Andreozzi et al. 2000) to achieve equilibrium at this temperature, whereas variable durations of isothermal steps at the other three temperatures were intended to monitor ordering rate well before the achievement of equilibrium. Temperatures were measured by means of a calibrated Pt/Pt-Rh thermocouple located near the sample; uncertainty was estimated at about ±5 °C.

X-ray diffraction

After quenching, X-ray data were collected from the heat-treated crystal using an automated KUMA-KM4 (K-geometry) diffractometer (Mo$K\alpha$ monochromatized by a flat graphite crystal). Intensity data were collected to 110° 2θ in the continuous ω-2θ scan mode, with a peak-base width of 1.8° 2θ, which increased with the θ angle. Counting times ranged from 30 to 120 s, according to peak standard deviation, with background measured from both sides of the peak for a total of half of the peak collection time. Because the psi-scan curves were flat, an empirical absorption correction was not applied. Twenty-four equivalents of the 12 8 4 reflection (ca. 82° 2θ) were accurately centered at positive and negative values of 2θ and used for cell parameter determination. Tables with structure factors are available from the authors on request.

Structural refinements, performed with the SHELX-93 program (Sheldrick 1993), were carried out in the $Fd3m$ space group with the origin at $\bar{3}m$, without chemical constraints. No violations of this symmetry were detected. Refined parameters were: scale factor, secondary extinction coefficient, O atom positional parameter (*u*), Mg and Al occupancy at the T and M sites, respectively, and anisotropic displacement parameters *U*(O), *U*(M), and *U*(T). The latter were reduced to U_{11}, because

TABLE 1. Isothermal ordering of $MgAl_2O_4$ spinel annealed at 1000 °C: structure refinement data from a single-crystal X-ray diffraction study of the quenched sample

T(°C)	Time (min)	T site m.a.n.	M site m.a.n.	Total m.a.n.	Refl.	$R_{int.}$ (%)	$R1$ (%)	w$R2$ (%)	GooF	Ext.
1000	720	12.3(1)	12.88(6)	38.1(2)	190	7.87	3.21	5.98	1.341	0.52(3)
900	0.17	12.3(1)	12.87(5)	38.1(1)	189	4.48	2.95	5.95	1.430	0.56(3)
900	0.5	12.4(1)	12.79(5)	38.0(1)	188	6.29	2.88	5.20	1.357	0.55(3)
900	1	12.4(1)	12.76(6)	38.0(2)	186	5.92	3.47	5.71	1.329	0.46(3)
900	2	12.2(1)	12.88(6)	38.0(2)	188	5.73	2.86	5.57	1.360	0.55(3)
900	5	12.2(1)	12.92(6)	38.0(2)	186	4.96	3.86	6.76	1.445	0.41(3)
900	60	12.3(1)	12.88(6)	38.1(2)	189	5.95	2.84	4.57	1.365	0.58(3)
900	4320	12.3(1)	12.80(5)	37.9(1)	183	7.29	2.70	5.71	1.397	0.37(2)
1000	720	12.6(1)	12.82(6)	38.2(2)	181	3.86	3.58	6.38	1.347	0.91(6)
800	2	12.4(1)	12.84(5)	38.1(1)	178	5.06	2.40	4.53	1.295	0.64(3)
800	5	12.4(1)	12.84(5)	38.1(1)	180	4.25	2.92	5.32	1.452	0.35(2)
800	10	12.4(1)	12.77(5)	38.0(1)	180	2.88	2.96	5.77	1.410	0.36(2)
800	20	12.4(1)	12.80(5)	38.0(1)	181	3.34	2.75	5.09	1.440	0.38(2)
800	40	12.4(1)	12.82(6)	38.1(2)	179	3.77	3.08	5.60	1.312	0.63(3)
800	150	12.4(1)	12.84(6)	38.1(2)	182	5.38	3.39	5.69	1.292	0.84(5)
800	1440	12.3(1)	12.85(6)	38.0(2)	181	3.59	3.23	6.16	1.421	0.19(1)
800	10080	12.4(1)	12.79(6)	38.0(2)	181	3.59	3.23	6.16	1.421	0.19(1)
1000	720	12.3(1)	12.88(6)	38.1(2)	190	7.87	3.21	5.98	1.341	0.52(3)
700	10	12.3(1)	12.91(6)	38.1(2)	190	7.87	3.22	6.08	1.344	0.51(3)
700	60	12.3(1)	12.86(5)	38.0(1)	170	12.96	3.31	5.61	1.329	0.21(1)
700	120	12.2(1)	12.83(5)	37.9(1)	187	6.24	2.95	5.46	1.334	0.24(1)
700	500	12.1(1)	12.89(6)	37.8(2)	190	4.41	3.83	6.88	1.491	0.59(4)
700	1000	12.1(1)	12.88(5)	37.9(1)	190	7.60	2.90	5.17	1.306	0.61(3)
700	5000	12.2(1)	12.92(5)	38.0(1)	186	4.69	2.20	4.15	1.412	0.57(2)
700	57600	12.3(1)	12.82(5)	37.9 (1)	186	4.74	2.27	3.57	1.138	0.15(1)

Notes: Estimated standard deviation in brackets; m.a.n. = mean atomic number; Refl. = Number of observed reflections; $R_{int.}$, $R1$ and w$R2$ = disagreement factors according to SHELX-93; GooF = goodness of fit; Ext. = Isotropic secondary extinction coefficient.

the out-of-diagonal terms were of the same order as their standard deviations. Values of U_{11} for O, M, and T ranged from 0.0064(1) to 0.0081(1) Å^2, from 0.0037(1) to 0.0044(1) Å^2, and from 0.0038(1) to 0.0046(1) Å^2, respectively. No systematic variations were observed with ordering temperature or time.

Both before and after heating, samples were refined with partially ionized O atom (70%) and neutral cations (see Andreozzi et al. 2000 for details). This gave the best values for $R1$, w$R2$, and GooF in all sin θ/λ shells, as well as a total mean atomic number (m.a.n.) corresponding to that expected from the stoichiometry to within $\pm 1\sigma$ (Table 1).

RESULTS

Results of structural refinements of quenched $MgAl_2O_4$ crystals annealed at 1000 °C and isothermally ordered at 900, 800, and 700 °C through several intervals for increasing times are listed in Table 2. At each annealing temperature, both a and u increase with time, whereas final values at equilibrium are inversely correlated with temperature. To follow cation exchange evolution, the relative change of a may be used, but its value measured by single-crystal X-ray diffraction is affected by various uncertainties (see Andreozzi et al. 2000, for details). Instead, the u parameter may be measured with high accuracy and precision, and its relative variation in our samples is markedly larger than that of a. Moreover, in the spinel structure the position of the O atom is directly influenced by intersite cation exchanges (O'Neill et al. 1992; Redfern et al. 1999; Andreozzi et al. 2000), so that u is definitely more suitable than a for monitoring exchange reactions.

As shown by Andreozzi et al. (2000) for $MgAl_2O_4$ spinel at equilibrium, the inversion parameter x closely correlates with the O atom positional parameter u in the range 600–1100 °C (Fig. 1). The relevant equation is:

$$x = 21.396 - 80.714u \quad (1)$$

In this work, inversion degrees—reported in Table 2—were obtained by using Equation 1.

In the present study a relatively low u value (0.2617) was measured after annealing at 1000 °C, corresponding to a clearly disordered configuration (x about 0.27). At each temperature, during isothermal intervals of increasing duration, the O atom parameter increased, approaching its equilibrium value (Fig. 2). Kinetic paths were characterized by a steep increase in u, followed by sudden flattening at equilibrium. For T = 900 °C, equilibrium corresponded to u = 0.2619 and was reached after about 4 min. At 800 and 700 °C, equilibrium corresponded to u = 0.2622 and 0.2625 and was reached after about 55 min and 700 min, respectively. With respect to the starting annealed state, all three final states are characterized by less intracrystalline disorder, so that inversion of our sample decreased with time from the starting value, x = 0.27 (at 1000 °C) to final x = 0.25, 0.23, and 0.21, corresponding to equilibrium values at 900, 800, and 700 °C, respectively (Table 2). Both final u and corresponding x closely match the equilibrium data of Andreozzi et al. (2000).

When plotted on a logarithmic time scale, kinetic data demonstrate that cation exchange effectively starts after a threshold time that depends on annealing temperature (Fig. 3). Kinetic paths show comparable slopes after the threshold, suggesting

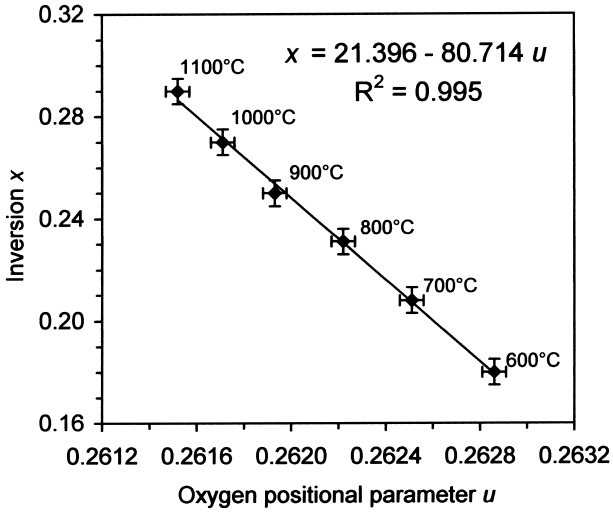

FIGURE 1. Dependence of the O atom positional parameter u on both inversion parameter x and equilibrium temperature in synthetic $MgAl_2O_4$ spinel (data from Andreozzi et al. 2000).

TABLE 2. Isothermal ordering of $MgAl_2O_4$ spinel annealed at 1000 °C: sequence of heating-quenching runs and corresponding structural parameters

T (°C)	Time (min)	Cell parameter a (Å)	Oxygen parameter u	Inversion* x
1000	720	8.0832(2)	0.26171(5)	0.272(5)
900	0.17	8.0832(3)	0.26167(5)	0.275(5)
900	0.5	8.0835(1)	0.26172(4)	0.271(5)
900	1	8.0835(2)	0.26186(5)	0.260(5)
900	2	8.0836(4)	0.26186(5)	0.260(5)
900	5	8.0838(2)	0.26191(6)	0.256(5)
900	60	8.0837(2)	0.26192(4)	0.255(5)
900	4320	8.0838(1)	0.26193(5)	0.254(5)
1000	720	8.0835(1)	0.26171(5)	0.272(5)
800	2	8.0834(1)	0.26178(4)	0.267(5)
800	5	8.0836(1)	0.26181(5)	0.264(5)
800	10	8.0840(1)	0.26198(4)	0.250(5)
800	20	8.0843(1)	0.26205(5)	0.245(5)
800	40	8.0844(1)	0.26220(4)	0.233(5)
800	150	8.0846(1)	0.26221(5)	0.232(5)
800	1440	8.0845(1)	0.26222(6)	0.231(5)
800	10080	8.0846(1)	0.26223(4)	0.230(5)
1000	720	8.0832(2)	0.26171(5)	0.272(5)
700	10	8.0831(3)	0.26173(5)	0.271(5)
700	60	8.0838(3)	0.26202(5)	0.247(5)
700	120	8.0840(3)	0.26214(5)	0.238(5)
700	500	8.0848(3)	0.26244(5)	0.213(5)
700	1000	8.0847(2)	0.26245(4)	0.213(5)
700	5000	8.0848(3)	0.26248(3)	0.210(5)
700	57600	8.0850(1)	0.26251(3)	0.208(5)

Note: Estimated standard deviations in brackets.
* Calculated using Equation 1.

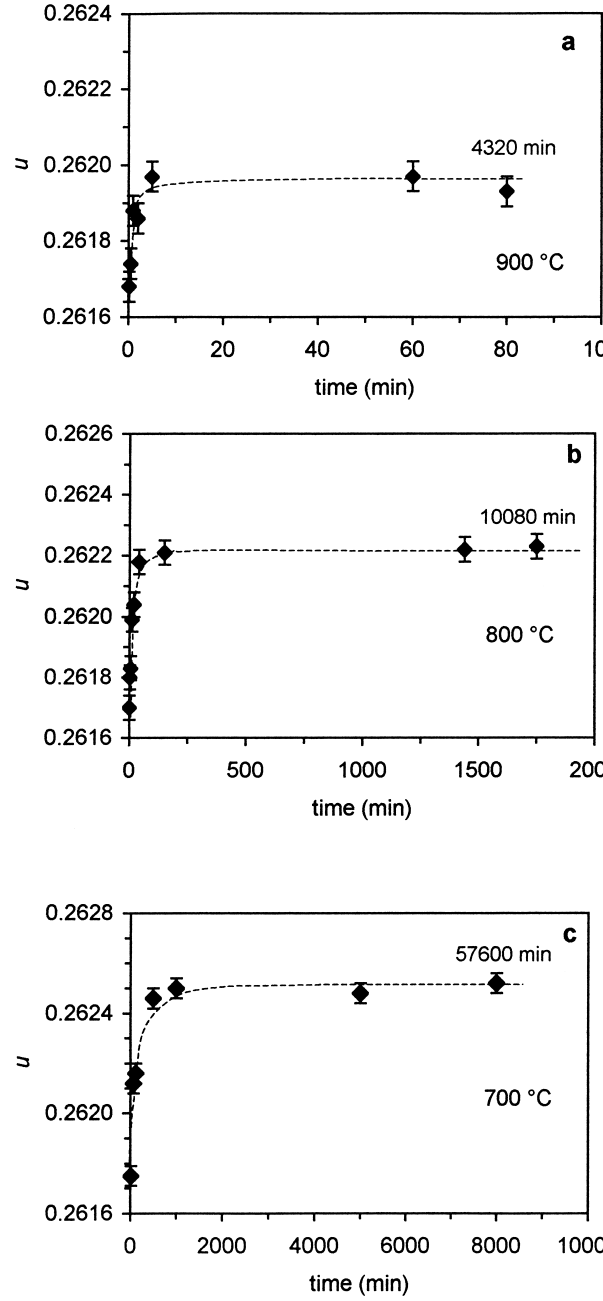

FIGURE 2. Variation of u with time and temperature in synthetic $MgAl_2O_4$ spinel. The value of u at time zero corresponds to a sample annealed at 1000 °C for 12 h. Diagrams (**a**), (**b**), and (**c**) are isothermal runs at 900, 800, and 700 °C, respectively; measurements after 4320, 10080, and 57600 min are plotted out of scale. Dashed lines are guides for the eye, to give a qualitative impression of overall behavior of the ordering process.

that the main ordering mechanisms are probably of the same type in the three cases. Reaction "incubation times" are about 0.5 min at 900 °C, about 2 min at 800 °C, and more than 10 min at 700 °C. Similar behavior has also been observed in orthopyroxenes of terrestrial and meteoritic provenance (Kroll et al. 1997; Heinemann et al. 2000). Provided that the "incubation time" is a true feature of the process (not trivially introduced by the log plot), a heterogeneous mechanism may be invoked to describe spinel order-disorder, and may be tentatively explained by short-range cation ordering as an initial stage, not revealed by X-ray diffraction, followed by long-range ordering. A heterogeneous mechanism of this type, involving

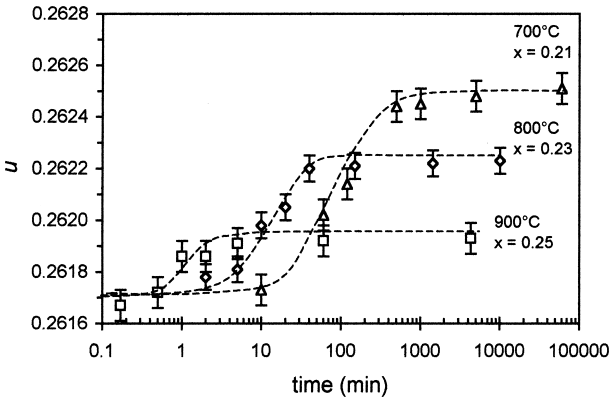

FIGURE 3. Comparisons between time-evolution of u and inversion parameter x in synthetic $MgAl_2O_4$ spinel at different temperatures. A logarithmic scale is chosen for time to highlight differences in the three paths during the first part of the ordering runs. Data for spinel annealed at 1000 °C (u = 0.2617, x = 0.27) are those of the common starting point. Inversion values (far right) correspond to final equilibrium at temperatures of 900, 800, and 700 °C. Dashed lines are guides for the eye, to give a qualitative impression of overall behavior of the ordering process.

nucleation of the ordered phase followed by its growth at the expense of the remaining disordered phase, has also been proposed for the ordering kinetics of $MgFe_2O_4$ (Walters and Wirtz 1971; Harrison and Putnis 1999).

DISCUSSION

Kinetics of cation ordering

Quantitative analysis of kinetic data is an important aspect of the thermal behavior of minerals and has long received detailed attention. The dynamic balance between the rates of forward and backward intracrystalline exchange reactions was modeled by Mueller (1967, 1969) and first applied to the solution of geological problems by Ganguly (1982). Although in some cases this model did not reconcile data from both ordering and disordering experiments (O'Neill 1994; Stimpfl et al. 1997), it is still considered very useful, because it provides a satisfactory phenomenological representation of data (Ganguly and Stimpfl 2000).

The order-disorder process may be described by a chemical exchange reaction as follows:

$$^{T}Al + {}^{M}Mg = {}^{T}Mg + {}^{M}Al \quad (2)$$

the forward reaction accounting for exchange of Al in the T site with Mg in the M site (ordering), and the backward reaction for exchange of Mg in the T site with Al in the M site (disordering). Homogeneous reactions described by Equation 2 are assumed to be second-order chemical reactions, and first-order with respect to the concentration in one site (Ganguly 1982). Following O'Neill (1994), the time rate of change of concentration of Al in the T site $X(^{T}Al)$, which decreases with time on ordering, may be written as:

$$-dX(^{T}Al)/dt = K_1\,\Phi(^{T}Al)\,X(^{T}Al)\,\Phi(^{M}Mg)\,X(^{M}Mg) - K_2\,\Phi(^{T}Mg)\,X(^{T}Mg)\,\Phi(^{M}Al)\,X(^{M}Al) \quad (3)$$

where X values are site fractions, K_1 and K_2 are rate constants for forward and backward reactions, respectively, and Φ values are analogous to activity coefficients and are generally functions of total crystal composition as well as volume and temperature. Assuming ideal mixing in each site, Mueller (1967, 1969) restricted discussion to the case in which $\Phi = 1$, so that Equation 3 simplifies to:

$$-dX(^{T}Al)/dt = K_1\,X(^{T}Al)\,X(^{M}Mg) - K_2\,X(^{T}Mg)\,X(^{M}Al) \quad (4)$$

When equilibrium is attained at any temperature, the net rate of reaction $-dX(^{T}Al)/dt = 0$, which leads to $K_1\,X(^{T}Al)\,X(^{M}Mg) = K_2\,X(^{T}Mg)\,X(^{M}Al)$ and, consequently, to:

$$K_2/K_1 = [X(^{T}Al)\,X(^{M}Mg)]/[X(^{T}Mg)\,X(^{M}Al)] \quad (5)$$

Because in $MgAl_2O_4$ spinel $X(^{T}Al) = x$, $X(^{M}Mg) = x/2$, $X(^{T}Mg) = (1 - x)$, and $X(^{M}Al) = (1 - x/2)$, Equation 5 may be written as:

$$K_2/K_1 = x^2/(1 - x)(2 - x) = K_D \quad (6)$$

where K_D is the equilibrium constant of reaction 2, and is a function of temperature and pressure alone. From Equation 6, $K_2 = K_1K_D$ and substituting into Equation 4, we obtain:

$$-dx/dt = K_1[x^2 - K_D(1 - x)(2 - x)] \quad (7)$$

Equation 7 may be integrated for the case of ordering in isothermal-isobaric conditions, and we thereby obtain the following expression for time intervals Δt:

$$\Delta t = -\frac{1}{K}\int_{x1}^{x2}\frac{dx}{\left[x^2 - K_D(1-x)(2-x)\right]} \quad (8)$$

where the simplified notation K indicates the ordering constant K_1.

The analytical solution of integral 8 only depends on initial ($x1$) and final ($x2$) inversion degree, and on rate constant K. Best values for K were found by minimizing the difference of squares between the experimental and calculated Δt: at 900, 800, and 700 °C, values of $K_{900} = 1.12 \pm 0.57$, $K_{800} = 0.112 \pm 0.047$, and $K_{700} = 0.0171 \pm 0.0045$ min^{-1} were obtained. The "half time of the reaction" $t_{1/2}$, which equals 0.693 $1/K$ and is the time required to go halfway from $x1$ and $x2$, corresponds to 0.6, 6.2, and 40.5 minutes, respectively. 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. 4). The fit between experimental and calculated data on both short and long time-scales confirms the validity of the model. This is further confirmation of Mueller's assumption that the kinetics of exchange processes follows a second-order rate law, and also indicates that the measured ordering states are highly reliable.

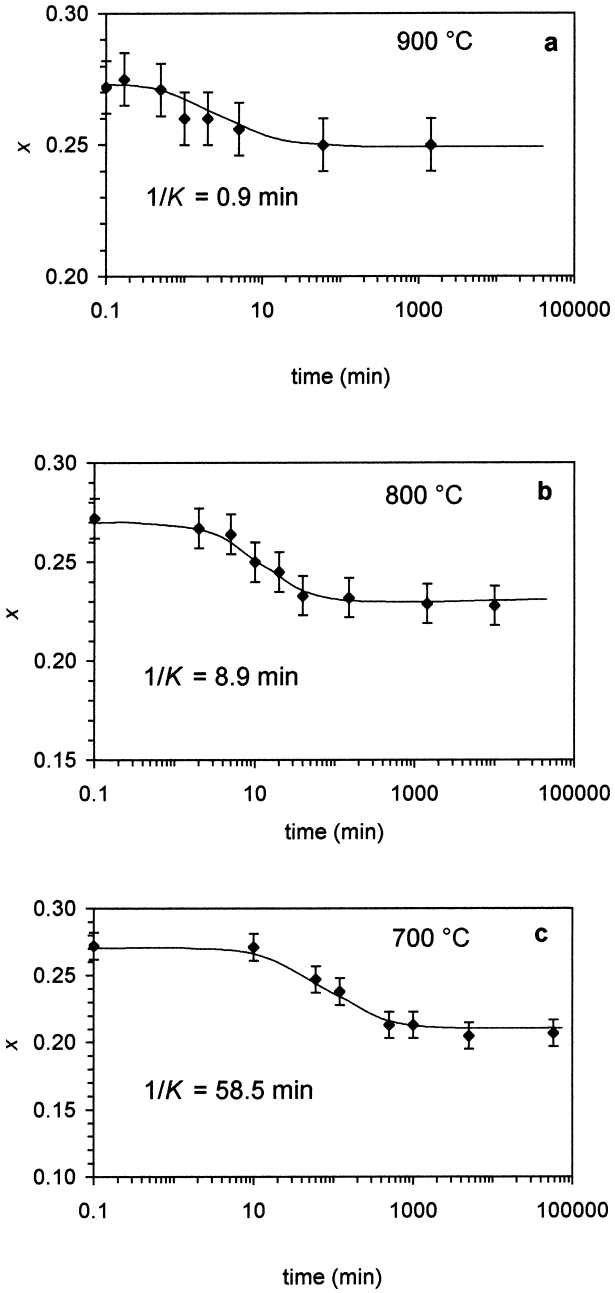

FIGURE 4. Time-temperature evolution of inversion parameter x in synthetic $MgAl_2O_4$ spinel annealed at 1000 °C. Experimental data at 700, 800, and 900 °C with error bars corresponding to $\pm 2\sigma$ overlap theoretical curves calculated by solving Mueller's equation. Kinetic constants are also reported for each temperature. Values for x were obtained from the linear relationship with parameter u (see Fig. 1).

The temperature dependence of the kinetic constant K, shown in the Arrhenius plot of Figure 5, is expressed as:

$$\ln K = -23722\ (1/T) + 20.189 \qquad (9)$$

The angular coefficient of this linear relation is $-E_a/R$, where E_a is the activation energy for Mg-Al ordering in spinel in the range of temperatures investigated. From our ordering data, the value retrieved for E_a is 197 ± 22 kJ/mol, which is in close agreement with the value of E_a = 217 kJ/mol obtained for Mg-Fe^{3+} exchange in $MgFe_2O_4$ by Harrison and Putnis (1999) using O'Neill's (1994) ordering data.

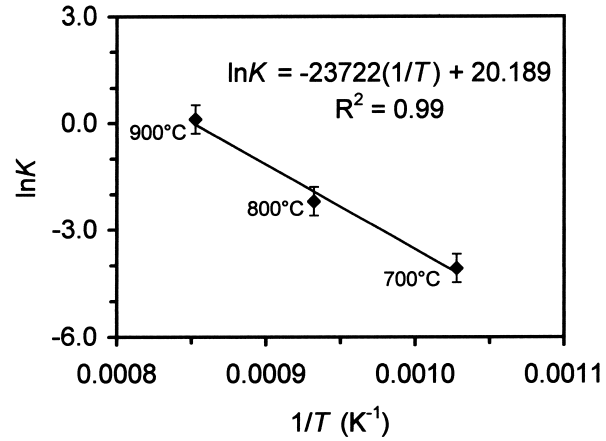

FIGURE 5. Arrhenius plot showing the linear dependence of ordering rate constant K with temperature in synthetic $MgAl_2O_4$ spinel. The activation energy calculated for the Mg-Al exchange reaction in the investigated temperature range is E_a = 197 ± 22 kJ/mol.

Implications

If K is a function of temperature (Eq. 9) and the linearity of ln K with $1/T$ is outside of the temperature interval explored, the time expected for $MgAl_2O_4$ to reach equilibrium at any temperature may be calculated by solving Equation 8 for the T of interest. However, direct application to natural spinels must be discouraged at this stage, because we still do not know the influence of many factors on cation-ordering kinetics; for example, the effect of extra cations other than Mg and Al. Moreover, most existing studies on the kinetics of mineral reactions are based on the (usually unstated) assumption that the time required to attain a certain degree of ordering is the same in conditions of both isothermal and continuous cooling. This is a focal point for geologic applications and might be verified in $MgAl_2O_4$ by comparing data from isothermal ordering with others from a continuous cooling process (work in progress).

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