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Ordering kinetics in synthetic $Mg(Al,Fe^{3+})_2O_4$ spinels: quantitative elucidation of the whole Al-Mg-Fe partitioning, rate constants, activation energies

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Abstract

In this study, we report results of the application of a novel procedure for modeling cation ordering in two synthetic $Mg(Al_{2-y}Fe^{3+}_y)O_4$ spinels (y~ 0.39 and 0.54, samples F39 and F54, respectively). The kinetic profiles suggest a two-stage mechanism, with rapid inter-site exchange of Fe^{3+} with Mg followed by slow exchange of Al with Mg. The trial to apply classical approaches, based on explicit solutions of the differential equations corresponding to single-cation (Sha-Chappel model) or two-cation (Müller model) exchange reactions, proved not feasible in the whole time range, thus implying a lack of information about exchange processes involving the Fe^{3+} cation. Therefore we decided to adopt an alternative methodology where a multistep pathway is simulated by Gepasi modeling. The suggested set of reactions and the simultaneous solving of the related rate laws allowed us to calculate rate constants and corresponding activation energies not only for the Al/Mg cationic interchange (257 and 264 kJ/mol for the F39 and F54 samples, respectively), but also, for the first time in such kind of samples (three cations - two sites), for the Fe/Mg cationic interchange (204 and 234 kJ/mol for low- and high-Fe^{3+} samples, respectively).

The evaluation of the significant effect of the iron content, which actually inhibits Mg-Al exchange between the T and M sites, provided new insights useful for the construction of geothermometers based upon iron-bearing spinels.

Keywords: intersite cation exchange, spinels, kinetics, rate constant, activation energy, geothermometers.

Introduction

The study of intersite cation exchange in rock-forming minerals constitutes a powerful tool for the interpretation of thermodynamic properties and mixing behavior of solid solutions as well as for the retrieval of the thermal history of host rocks (Ganguly 1982; Princivalle et al. 1999; Andreozzi et al. 2000; Ganguly and Stimpfl 2000; Müller et al. 2013). All these applications require a thorough knowledge of both equilibrium distribution and exchange kinetics. Hence, in the last decades, considerable effort has been devoted to the investigation of order-disorder processes in minerals (e.g. Zema et al. 1999; Domeneghetti et al. 2000; Ganguly and Stimpfl 2000; Heinemann et al. 2000; Brizi et al. 2001; Wang et al. 2005) by means of complementary equilibrium and kinetics studies.

In this context the study of cation distribution in spinels is foundamental for constraining the geodynamic processes in which such minerals are involved (Della Giusta et al. 1986; Andreozzi et al. 2000).

It is useful to recall that cation distribution in spinels can be described according to the general scheme:

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

where A and B are bivalent and trivalent cations respectively, IV and VI refer to the coordination of the T and M sites, respectively and x is the inversion parameter.

At low temperature, two ordered configurations of the spinel structure can be adopted: normal configuration (e.g., $MgAl_2O_4$) with x=0, and inverse configuration (e.g., $MgFe_2O_4$), with x=1.

At high temperatures, a completely random distribution of A and B over the T and M sites is expected for normal and inverse spinels (x = 2/3).

A detailed examination of the copious literature reveals that, as a consequence of the difficulties in both gathering and interpreting the non-equilibrium data, the most critical point in obtaining a comprehensive picture of the process, is the determination of the kinetic parameters. This issue has been addressed by several authors with the aim of developing theoretical kinetic models with a wide range of applicability.

Following the pioneering work of Bragg and Williams (1935) and Dienes (1955), Müller (1967, 1969) proposed a model for exchange kinetics based on a two-cation exchange reaction, which can be generally expressed as:

$$A(s1) + B(s2) \underset{k_{-1}}{\overset{k1}{\rightleftarrows}} A(s2) + B(s1)$$

where A and B are different cations, s_1 and s_2 are non-equivalent sites and k_1 and k_{-1} are kinetic rate constants of the forward and backward reactions.

By solving the proper kinetic differential equations the following explicit solution for the site occupancy as a function of time, x(t), can be deduced (Brizi et al. 2001):

$$x_i(t) = \frac{(b^2-4ac)^{1/2}\left(1+\frac{(2ax_1+b)-(b^2-4ac)^{1/2}}{(2ax_1+b)+(b^2-4ac)^{1/2}}e^{-kt(b^2-4ac)^{1/2}}\right)-b\left(1-\frac{(2ax_1+b)-(b^2-4ac)^{1/2}}{(2ax_1+b)+(b^2-4ac)^{1/2}}e^{-kt(b^2-4ac)^{1/2}}\right)}{2a\left(1-\frac{(2ax_1+b)-(b^2-4ac)^{1/2}}{(2ax_1+b)+(b^2-4ac)^{1/2}}e^{-kt(b^2-4ac)^{1/2}}\right)}$$

where x_1 is initial value of the site occupancy and a, b, and c depend on the composition of the crystal and on the equilibrium distribution coefficient K_D.

Müller's model, as developed by Ganguly (1982), has been widely applied to model experimental ordering-disordering data and estimate kinetic parameters (see for example Ganguly 1982; Sykes-Nord and Molin 1993; Andreozzi and Princivalle 2002; Princivalle et al. 2012). However, despite its success, it does not yield explicit general solution for ordering-disordering involving three or more cations between two sites.

This limitation strongly hampers the application of the Müller's method to model experimental data and estimate order-disorder kinetic coefficients, since several minerals have more than two cations that can form solid solutions with ordering-disordering at each sites.

Among the numerous examples, spinels may be mentioned.

In the light of the limitations inherent in the Müller's model, Sha and Chappell (1996a, 1996b, 1997) proposed a kinetic model based on single-cation exchange reactions:

$$ei(s1) \underset{k_{-1}}{\overset{ki}{\rightleftarrows}} ei(s2)$$

where *ei* is any cation involving in the ordering-disordering process.

In the case of a two-site system, the following kinetic equations can be deduced:

$$x_1 = \frac{k_{21} m^0}{k_{12} + k_{21}} + \frac{k_{21} x_2{}^0 - k_{12} x_1{}^0}{k_{21} + k_{12}} e^{\cdot(-k_{12} - k_{21})t}$$

$$x_2 = \frac{k_{12} m^0}{k_{21} + k_{12}} + \frac{k_{12} x1^0 - k_{21} x2^0}{k_{21} + k_{12}} e^{\cdot(-k_{12} - k_{21})t}$$

where x_1 and x_2 are the site occupancies of the cation in the two sites, k_{12} and k_{21} are the direct and inverse kinetic constant and $m^0 = x_1 + x_2$.

It is important to point out that, although this second approach is suitable for both binary and multi-cation ordering-disordering, it does not take into account that the rate of cation exchange reaction at

two non-equivalent sites depends on all the cations involved in the process. In other words, for a three component system the rate constant value for the cation exchange of cation A at sites s1 and s2 depends on whether the cationic exchange occurs with cation B or C, and it will be different in the various cases.

In light of these considerations, in the present work we propose an alternative and highly versatile methodology, based on numerical kinetics simulations. As case study to test the suitability of our approach, we choose to apply it to model experimental ordering-disordering data in two synthetic $Mg(Al_{2-y}Fe^{3+}_{y})O_4$ spinels (y~ 0.39 and 0.54, samples F39 and F54, respectively), already presented by Princivalle et al (2012).

For the purposes of the present work, the system $Mg(Al,Fe^{3+})_2O_4$ is of particular interest, since, although it has been observed that the Fe^{3+} content significantly influences the kinetics of ordering process (Carbonin et al. 2002; Martignago et al. 2003, 2006; Princivalle et al. 2006), the employment of classical methods allowed only the Al/Mg exchange reactions to be considered. As a result, no information about the processes involving the Fe^{3+} cation could be obtained. The procedure here proposed enabled us to evaluate the effect of the Fe^{3+} cation into Mg/Al cation exchange processes, contributing to a closer reconstruction of host rocks thermal history.

Experimental

Set-up and experimental data here treated were presented in Princivalle et al. (2012). The samples used in the present study are two synthetic spinels with the following composition:

$Mg_{1.0}Fe_{0.39}Al_{1.61}O_4$ (**sample F39**) and $Mg_{1.0}Fe_{0.54}Al_{1.46}O_4$ (**sample F54**).

They have been synthetized by flux-growth method and come from the same runs already analyzed by Andreozzi et al. (2001) and Martignago et al. (2006). Synthesis procedure is shown in Andreozzi (1999). Mössbauer and optical absorption spectroscopies performed by Andreozzi et al. (2001)

proved they are stoichiometric. The kinetics of cation ordering has been investigated by means of quench method and X-ray single crystal diffraction. In particular, the distribution of Mg, Al and Fe cations between T and M sites of the spinel structure has been investigated at three different temperatures (550, 650, 750 °C) starting from an equilibrium ordering state corresponding to 1000°C, through several time-steps in order to monitor the rate of cation distribution. In detail, crystals were disordered at 1000°C with an annealing time of 24 hours and then ordered at three temperatures (550, 650, 750 °C), for different isothermal time-steps. After each annealing and quenching experiment, crystals were mounted on a single crystal diffractometer for X-ray data collection, and then subjected to the next experimental cycle by sealing the crystals in a thin-walled quartz tube and putted directly at the wished temperature in the vertical tube furnace.

The modeling process were carried out by adopting a simulation method implemented in the Gepasi software package (Mendes 1993; Mendes 1997; Mendes and Kell 1998). The first step of the modeling procedure consists in building of the kinetic mechanism, which, in the present case, implies the definition of the proposed interaction exchange reactions, their kinetic type (kinetic differential equations describing the rate laws) and initial values of the site occupancies. In a second step, experimental kinetic data (cationic occupancies as a function of time , $x_i(t)$) were fitted on the basis of the proposed model by means of the optimization of the kinetic rate constant values. Numerical Levenberg-Marquardt (LM) (Levemberg 1944; Marquartd 1963) method were applied to simultaneously solve the systems of differential equations associated to each step. It is worth to say that LM method is widely adopted in nonlinear regression problems where explicit form of f(x) ($x_i(t)$ in the present study) is not available (Mendes and Kell 1998)

Results and discussion

Figures 1,2 and 3 report experimental site occupancies of the three cations (Mg, Al, Fe^{3+}) at T and M sites, expressed in atoms per formula unit (a.p.f.u.) as a function of time . At all the experimental temperatures, two different reaction path can be recognized. In the first part of the kinetic profile, we observe an Fe^{3+} increase at the T site balanced by Mg^{2+} increase at the M site, while in the second part the opposite trend can be recognized. As for the Al^{3+} cation, a roughly monotonic increase at the M site is observed. Since, obviously Mg, Fe and Al exchange start simultaneously, the observation of the two distinct trend is due to different rate constants of the involved processes.

Supplementary evidence for the occurrence of the two reaction steps is the trend of the unit-cell parameter (*a*) with time reported in Figure 4, where an initial decrease of *a* followed by a slower increase is recorded.

This behavior can be interpreted by considering that in the first part of the kinetic profile, the two samples are far from equilibrium and mostly behave as inverse spinel magnesioferrite $^{T}(Fe^{3+})^{M}(Mg,Fe^{3+})O_4$. In fact, according to previous studies (Mozzi and Paladino 1963; O'Neill et al. 1992; O'Neill and Dollase 1994; Harrison and Putnis 1999; Andreozzi et al. 2001) the cation distribution of $MgFe_2O_4$ spinel is random at high temperature and becomes gradually more ordered (i.e, inversion increases) at low temperature. Therefore, for both F39 and F54 spinels starting from random distribution, Mg^{2+} cations tend to occupy M site by exchanging with Fe^{3+} ions which tend to fill T site. It is interesting to note that this behavior is particularly evident at the lowest temperature (550 °C).

In the second part of the kinetic profile, approaching the equilibrium pertinent to the experimental isotherm, the two samples behave as normal spinel sensu stricto $^{T}(Mg)^{M}(Al_2)O_4$ and the exchange of Mg vs. Al, become dominant.

As already mentioned in the introduction section, the classical approach to the analysis of such experimental data, based on the Müller's kinetic model, required that only the second part of the isotherm path, where the exchange of Mg vs. Al predominates, would be considered. This way, no information about the first rapid exchange could be obtained.

On the other hand, the trial to apply the model of Sha-Chappel also failed, since in the case of two-site systems, it is not able to reproduce experimental kinetic profiles characterized by the presence of maxima and minima (Sha and Chappell, 1997).

In light of the above considerations, in the present work, we performed the analysis of the experimental kinetic data by means of the Gepasi kinetic simulator, which allows the simultaneous solving of the relevant rate laws (ν) corresponding to the proposed reactions steps.

In particular, we propose the following multistep reaction scheme (Scheme 1)

R1 $Fe_M^{3+} + Mg_T^{2+} \underset{k_{-1}}{\overset{k1}{\rightleftarrows}} Fe_T^{3+} + Mg_M^{2+}$ $v_1 = \frac{dX_{Fe}^T}{dt} = \frac{dX_{Mg}^M}{dt} = -\frac{dX_{Fe}^M}{dt} = -\frac{dX_{Mge}^T}{dt} = k_1 X_{Fe}^T X_{Mg}^M - k_{-1} X_{Fe}^M X_{Mg}^T$

R2 $Al_T^{3+} + Mg_M^{2+} \underset{k_{-2}}{\overset{k2}{\rightleftarrows}} Al_M^{3+} + Mg_T^{2+}$ $v_2 = \frac{dX_{Mg}^T}{dt} = \frac{dX_{Al}^M}{dt} = -\frac{dX_{Mg}^M}{dt} = -\frac{dX_{Al}^T}{dt} = k_2 X_{Al}^M X_{Mg}^T - k_{-2} X_{Al}^T X_{Mg}^M$

R3 $Al_T^{3+} + Fe_M^{3+} \underset{k_{-3}}{\overset{k3}{\rightleftarrows}} Al_M^{3+} + Fe_T^{3+}$ $v_3 = \frac{dX_{Fe}^T}{dt} = \frac{dX_{Al}^M}{dt} = -\frac{dX_{Fe}^M}{dt} = -\frac{dX_{Al}^T}{dt} = k_3 X_{Al}^M X_{Fe}^T - k_{-3} X_{Al}^T X_{Fe}^M$

Scheme 1. Proposed reaction path and corresponding rate laws. k1, k2, k3 stand for ordering, and k_{-1}, k_{-2} and k_{-3} stand for disordering processes.

In order to obtain the rate constant values, we applied the Levemberg-Merquartd method, as implemented in the Gepasi software, to solve the rate laws.

First of all, it has been observed that the best fit of the experimental data is obtained when the kinetic rate constants associated with reaction R3 (forward and backward) reduce close to zero, which can be reasonably interpreted by assuming that the direct exchange between Al and Fe does not occur or is negligible in comparison with the other two cationic exchanges. Therefore the following contracted reaction scheme (Scheme 2) has been tested, where the faster Fe/Mg intersite exchange reaction (R1) is followed by the slower intersite Al/Mg exchange reaction (R2):

R1 $Fe_M^{3+} + Mg_T^{2+} \underset{k_{-1}}{\overset{k1}{\rightleftarrows}} Fe_T^{3+} + Mg_M^{2+}$ $\quad v_1 = \frac{dX^T_{Fe}}{dt} = \frac{dX^M_{Mg}}{dt} = -\frac{dX^M_{Fe}}{dt} = -\frac{dX^T_{Mge}}{dt} = k_1 X^T_{Fe} X^M_{Mg} - k_{-1} X^M_{Fe} X^T_{Mg}$

R2 $Al_T^{3+} + Mg_M^{2+} \underset{k_{-2}}{\overset{k2}{\rightleftarrows}} Al_M^{3+} + Mg_T^{2+}$ $\quad v_2 = \frac{dX^T_{Mg}}{dt} = \frac{dX^M_{Al}}{dt} = -\frac{dX^M_{Mg}}{dt} = -\frac{dX^T_{Al}}{dt} = k_2 X^M_{Al} X^T_{Mg} - k_{-2} X^T_{Al} X^M_{Mg}$

Scheme 2. Proposed reaction path and corresponding rate laws. k1, k2 stand for ordering, and k_{-1}, k_{-2} stand for disordering processes.

The proposed two-stage kinetic mechanism was hypothesized by Harrison et al. (1999), Martignago et al. (2003, 2006) and Marinoni et al. (2011) for both natural and synthetic Mg(Al,Fe)2O4 with different iron content, and by Princivalle et al. (2012) for present samples.

This two-steps model completely reproduces the kinetic data (site occupancies versus time) in the whole compositional and time range as can be easily observed in Figures 1-3 and in Figures S3 and S4 in support of the manuscript, where the experimental kinetic profiles are reported together with the simulated data in linear and logarithmic scale, respectively.

According to Merli et al. (2010) and to Merli and Sciascia (2011) the goodness of fit of the simulation process is confirmed not only by the low values of the Residual Sum of Squares (mean value ~ 0.0001) and Root Mean Squares Error (mean value ~ 0.001) but also by the negligible time trend exhibited by residuals plots (Figures S5-S6 in support of the manuscript).

The simultaneous solution of the rate laws associated with the two steps of the Scheme 2 allowed us to estimate the kinetic constants reported in Table 1, which support the hypothesis that the fastest

reaction step involves the Fe/Mg ionic couple (R1), while the step involving the Al/Mg ionic exchange (R2) is slightly slower. On the other hand it can be observed that the differences between k1 and k2 at the three investigated temperature is not so high, suggesting that the two processes does not occurs on different time scale.

However, despite the probable correlation between the two processes, a quite good accordance between the values here obtained for the kinetic rate constants relative to the Al/Mg exchange and those previously reported by Princivalle et al.(2012), where this correlation is neglected, has to be noticed.

As for the effect of the iron content in the two samples, it can be noted that the kinetic rate constants are always higher for sample F54, indicating that the presence of the Fe^{3+} triggers the ionic exchange between Mg and Al over T and M (Martignago et al. 2006).

In order to further corroborate the validity of the proposed model, the behavior of the a-parameter, calculated according to the procedure described in Lavina et al. (2002), has been also successfully simulated (see Fig.4).

In a second step of the present work, the temperature dependence of the kinetic constant k_i has been employed to construct the Arrhenius plot reported in Figure 5.

The slope of the Arrhenius plot allowed us to calculate the activation energy values reported in Table 2.

First of all, we can observe that, according to the trend of the kinetic rate constants and keeping with the proposed model, the activation energy values corresponding to Fe-Mg ordering (Ea1) are lower than those corresponding to Al-Mg ordering process (Ea2).

The higher activation energy corresponding to Al-Mg exchange agrees with the results of Marinoni et al. (2011) who found that Al^{3+} is involved in the intra-crystalline cation partitioning only at high temperatures, which means that the activation energy associated with the aluminium diffusion is quite high. Intriguingly, this "retarding" effect is observed only when Fe^{3+} is present, which can be

taken as an indication of the reliability of the proposed kinetic mechanism which predicts that ferric ions tend to keep the Mg ions in the M site, thus hampering cationic exchange with the Al cations.

With regards to Fe-Mg cation ordering, it can be observed that the obtained activation energy values increase with increasing Fe^{3+} content in both samples. In the light of the decreased Al content, this trend can be interpreted as follows:

1- the higher Fe^{3+} content implies a lower Al amount due to the substitution Fe^{3+} for Al;
2- as Al shows a site preference for M site, Mg accommodates at T site facilitating the occurrence of the Mg/Fe cationic interchange (R1);
3- the higher is the Al content (F39 sample) the lower is the activation energy for the R1 process.

However, a comparison with the Ea values reported in literature for the synthetic $MgFe_2O_4$ end-member (Harrison and Putnis 1999) indicates that the influence of Al on the Mg/Fe exchange is quite limited. For example Ea1 is lowered of only 6% with respect to $MgFe_2O_4$ at more than 80% of substitution (see Figure 6A, where the activation energy is reported as a function of the Al content, for a clearer view of this data)

As for the Mg-Al exchange reaction, perusal of the data reported in Table 2 indicates that the activation energy values (Ea2) obtained in present study for the F39 and F54 samples are higher than those reported in literature for the $MgAl_2O_4$ end-member and, also in this case, they increase on increasing the iron content. Again, this result is a further proof of the inhibition of the Al/Mg cationic interchange due to the presence of the Fe^{3+} ions. It is interesting to note (see Figure 6B) that the presence of ferric ions has a very strong influence in the Mg-Al exchange process(Ea2 is increased of 34% with respect to $MgAl_2O_4$ at only 27% of substitution).

As already observed for the kinetic rate constant values, the accordance with the results of Princivalle et al. (2012) is reasonably high. However the trend of the Ea values as a function of iron content obtained in the present work is more in line with the activation energy previously obtained

for the corresponding end-member. This can be taken as a proof of the higher capability of the model here proposed to take into account the significant effect of the third cation.

This result could have important petrological implications in the construction of geothermometers based upon the distribution of Mg and Al between the T and M sites of spinels containing Fe^{3+} (see below).

Implications

Spinels are important accessory minerals of several mafic and ultramafic rocks mainly constituted by olivines ± pyroxenes. These silicate minerals can be usually subjected to different degrees of alteration and weathering so that spinel may be present as the sole-surviving primary mineral (Lenaz et al. 2014).

As seen above, the Mg and Al ordering may give information on the thermal history of the host rock. The importance of these minerals as petrogenetic indicators is therefore straightforward (Irvine 1965 and Perinelli et al. 2014).

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Because the question of whether the presence of additional major cations, usually present in natural spinels (especially chromium and iron), affects, to a significant extent, the Mg-Al ordering, Princivalle et al. (1999) introduced a geothermometer for intra-crystalline equilibration temperatures based upon the distribution of Mg and Al between the T and M sites in Cr-spinel, considering in the thermometer equation some coefficients taking into consideration the presence of minor amount of other cations. A review of the recent literature seems to suggest that for low Fe-Cr containing samples the investigation of the partitioning of Mg and Al cations still yield reliable values for the closure temperatures. In fact this model has been successfully used in spinels in which the total iron content is less than 0.25 a.p.f.u. and the chromium content is less than 1 a.p.f.u.

(Uchida et al. 2005; Lenaz et al. 2010, 2014; Princivalle et al. 2014 among the others). Anyway, in natural spinels, very high Fe^{3+} contents yield unreliable temperatures in the range 1400-1900°C (Lenaz et al. 2011; Derbyshire et al. 2013). In the light of the above considerations, the relevance of the results obtained in the present study can be evaluated under different perspectives. First, the acquired data reveal that the high amount of Fe^{3+}, tending to remain in the T site, affects the kinetic parameters of Mg/Al exchange processes by hampering the Mg-Al exchange between the T and M sites. This is a further evidence that geothermometers constructed by neglecting the processes involving the iron ions (see for example the above discussed geothermometer by Princivalle et al., 1999) should be carefully considered, especially when there is a high amount of Fe^{3+} in the studied spinels. In this view, the present study represents a novelty, since the kinetic parameters here provided are not affected by a priori assumptions and can be employed for the construction of reliable geothermometers.

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List of figure captions

Figure 1. Time evolution of the site occupancies of the Al^{3+} ion in the F39 (◊) and in the F54 (■) sample annealed at 1000°C. Symbols denote experimental points, while the curves represent data calculated according to Scheme 2.

Figure 2. Time evolution of the site occupancies of the Mg^{2+} ion in the F39 (◊) and in the F54 (■) sample annealed at 1000°C. Symbols denote experimental points, while the curves represent data calculated according to Scheme 2.

Figure 3. Time evolution of the site occupancies of the Fe^{3+} ion in the F39 (◊) and in the F54 (■) sample annealed at 1000°C. Symbols denote experimental points, while the curves represent data calculated according to Scheme 2.

Figure 4. Variation of cell parameter with time for the F39 (◊) and the F54 (■) samples. Symbols denote experimental points, while the curves represent data calculated according to Scheme 2.

Figure 5. Arrhenius plots showing linear dependence of the logarithm of the rate constants, $\ln k_i$, with inverse temperature, 1/T, for sample F39 and F54; error bars correspond to the standard deviation of the values obtained by simulating the kinetic profiles of the three cations according to Scheme 2.

Figure 6. Activation energy values for Fe-Mg (A) and Mg-Al (B) as a function of Al and Fe content, respectively. The symbols ■ and □ denote the direct and inverse process, respectively.

Tables

	F39			F54		
	550°C	650°C	750°C	550°C	650°C	750°C
$k_1(min^{-1})$	$(7.5\pm0.8)\cdot10^{-4}$	$(1.5\pm0.3)\cdot10^{-2}$	0.25±0.04	$(7.0\pm0.9)\cdot10^{-4}$	$(2.7\pm0.8)\cdot10^{-2}$	0.57±0.09
$k_1(min^{-1})$	$(3.6\pm0.5)\cdot10^{-4}$	$(1.0\pm0.2)\cdot10^{-2}$	0.15±0.04	$(1.8\pm0.6)\cdot10^{-4}$	$(1.6\pm0.6)\cdot10^{-2}$	0.47±0.05

$k_2(min^{-1})$	$(9.0\pm0.8)\cdot10^{-5}$	$(5.0\pm1.0)\cdot10^{-3}$	0.14±0.02	$(2.2\pm0.6)\cdot10^{-4}$	$(1.7\pm0.2)\cdot10^{-2}$	0.42±0.02
$k_{-2}(min^{-1})$	$(9.4\pm0.2)\cdot10^{-6}$	$(3.6\pm0.5)\cdot10^{-4}$	0.011±0.003	$(2.0\pm0.4)\cdot10^{-4}$	$(1.4\pm0.5)\cdot10^{-2}$	0.32±0.02

Table 1. Average values of the rate constants obtained by fitting the time-course profiles reported in figures 1-3.

	Ea_1/Kj mol^{-1} $Fe_M^{3+} + Mg_T^{2+} \xrightarrow{k_1} Fe_T^{3+} + Mg_M^{2+}$	**Ea_{-1}/Kj mol^{-1}** $Fe_T^{3+} + Mg_M^{2+} \xrightarrow{k_{-1}} Fe_M^{3+} + Mg_T^{2+}$	**Ea_2/Kj mol^{-1}** $Al_T^{3+} + Mg_M^{2+} \xrightarrow{k_2} Al_M^{3+} + Mg_T^{2+}$	**Ea_{-2}/Kj mol^{-1}** $Al_M^{3+} + Mg_T^{2+} \xrightarrow{k_{-2}} Al_T^{3+} + Mg_M^{2+}$	**References**
F39	204 ± 9	212 ± 2	257 ± 3	260 ±10	This study
			274		Princivalle et al., (2012)
F54	234 ± 2	274 ± 5	264 ± 7	258 ± 6	This study
			265		Princivalle et al., 2012
$MgFe_2O_4$	217	265			Harrison and Putnis (1999)
$MgAl_2O_4$			197 ± 22		Andreozzi and Princivalle (2002)
			230		Redfern et al., (1999)

Table 2. Activation energy values for Fe-Mg (Ea_1 and Ea_{-1}) and Mg-Al (Ea_2 and Ea_{-2}) ionic exchange reactions obtained in the present study for the F39 and F54 samples compared with the values previously obtained for the same samples and for the end-members $MgFe_2O_4$ and $MgAl_2O_4$. For the sake of clarity the processes relative to each activation energy are also reported in the table.