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Time–temperature-dependent M-site ordering in olivines from high-temperature neutron time-of-flight diffraction

Simon A.T. Redfern*

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

Abstract

The application of neutron diffraction to the study of non-convergent cation order/disorder in minerals is illustrated with the behaviour of M cations in Mn-bearing olivines. The results may be described using a Landau expression for the free-energy change due to ordering. Non-convergent ordering kinetics of the M-site cations at the 50 : 50 composition in tephroite–olivine solid solutions have been analysed using the Ginzburg–Landau model, giving an activation energy for Fe–Mn exchange between M1 and M2 of 193 ± 3 kJ/mol and for Mg–Mn exchange of 172 ± 3 kJ/mol. The order–disorder process is more rapid than the similar phenomenon observed in orthopyroxenes. The M-site occupancy observed at room temperature is a function of the cooling rate of the olivine, raising the possibility that olivine might be useful as a geospeedometer for relatively rapid cooling events. These results show the utility of probing mineral structure in situ by techniques such as neutron TOF powder diffraction, where strong scattering contrast between target nuclei, combined with the ability to control sample environment, provide a unique route to investigating the behaviour of minerals under the conditions of their formation in the Earth.

Keywords: Cation ordering; High-temperature diffraction; Phase transition

1. Introduction

Understanding the time–temperature dependence of cation exchange between crystallographic sites in rock-forming minerals has been a goal for mineralogists for many years now. Not only do such intracrystalline exchange processes have potential influence on the thermodynamic, transport and other physical properties of the solid, they may also be employed as indicators of the pressure/temperature conditions of formation of rocks within the Earth. Very often, changes in inter-site partitioning and ordering are also of fundamental crystal chemical interest. Recent neutron studies of order–disorder phenomena in olivines and spinels illustrate the importance of probing atomic-scale structure in situ, and the utility of pulsed neutron radiation sources in doing so. Pulsed neutron spallation allows time-of-flight diffraction patterns to be collected on rapid time scales, and the kinetics of mineral processes such as cation ordering may now readily be studied in situ at high temperature (T), with the future possibility of simultaneous high pressure (P) and T studies. The penetrating power

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* Fax: + 44 1223 333450; e-mail: satr@esc.cam.ac.uk.

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of neutrons has been exploited to hold samples under controlled T and fO_2 environments. Experiments may be conducted from which it is possible to refine site occupancies accurately and precisely, especially compared with those obtainable by X-ray scattering, since the cations of interest may often have strongly contrasting neutron-scattering lengths. Finally, of course, the variation of neutron scattering length with scattering vector is negligible, unlike the rapid fall-off of X-ray scattering at small d-spacings, so that important information about site occupancies at high temperature can readily be refined from neutron powder diffraction data.

Many of the earlier studies of cation order–disorder in olivine involved the analysis of samples quenched from high-T and/or high-P treatments, with the implicit assumption that the equilibrium high-P/T states could indeed be preserved during the quench to room T and P [1–6]. However, when one considers the crystal structure of olivine (Fig. 1), it can easily be appreciated that the exchange between M1 and M2, given the proximity of the sites, the shared edge between the two octahedra, and the existence of a vacant tetrahedral and octahedral interstices between the two adjacent faces, could have a relatively low activation energy. Indeed, Akamatsu and Kumazawa [7] suggested that the cation redistribution in olivine at modest Ts may be so fast as to render the high-T states unquenchable. Recent in situ high-T neutron diffraction studies of olivine [8–12] confirm this supposition. These results have shed light on the discrepancies between earlier "anneal and quench" studies, which are now seen to have failed to capture the high-temperature equilibrium. The picture has emerged that high-T M1–M2 cation exchange within the olivine structure is rather rapid. While this makes olivine relatively useless as a geothermometer, it may open a way to using the intracrystalline partitioning in olivine as a form of geospeedometer to measure rapid cooling events.

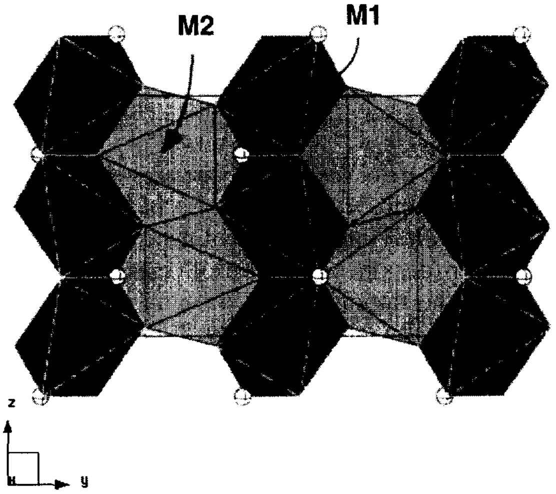

Fig. 1. The crystal structure of olivine projected on (1 0 0) showing the M1 and M2 octahedra.

Non-convergent M-site disorder in $(A,B)_2SiO_4$ olivines has been investigated in olivines with M-site cations A = Fe, Mg, Ni and B = Mn, Mg as a function of T from room T up to 1100°C using time-of-flight neutron diffraction [8–12]. In all cases the kinetics and thermodynamics of cation ordering can been determined from a single heating and cooling run by analysing the M-site partitioning with a Landau model for the excess free energy of non-convergent ordering. For Fe–Mn, Mg–Mn, and Ni–Mg olivines the ordering is dominated by size effects between the cation pairs, and a simple "1–2–4" expansion of the degree of order, Q, adequately represents the order–disorder behaviour, with T-dependence entering the Q^2 term alone. For Mg–Fe olivines the behaviour is rather more complex, and vibrational entropy plays an important role, so that the linear field term in the Landau expansion for the Gibbs free energy has a strong T-dependence.

Similar experiments on AB_2O_4 spinels with A = Mg, Ti and B = Al, Mg have allowed the modelling of the kinetics and thermodynamics of non-convergent ordering between the tetrahedral and octahedral sites of stoichiometric and non-stoichiometric normal and inverse spinels [13]. Here, the degree of cation order is strongly coupled with "A" deficiency (effectively solid solution of γ-alumina in $MgAl_2O_4$ spinel), with apparent re-adjustment of vacancy ordering in response to changes in A–B ordering. A complete thermodynamic and kinetic description of the order–disorder process may be obtained from a single time-temperature diffraction experiment, heating and cooling the sample during the in situ study. The thermodynamics of non-convergent order–disorder have been modelled in terms of a "1–2–6" Landau potential, with the kinetics explained by the related Ginzburg–Landau expression.

In this paper, the implications of the development of an understanding of intramineral cation partitioning over M-sites in the olivine structure are focused upon, showing the way in which neutron diffraction can open the way to the development of novel geochemical and petrological indicators for determining the natural history of rocks. Specifically, by taking recent neutron diffraction results on Mn-containing olivines as an example, it will be shown that M-site cation partitioning in olivine provides a means to measure the cooling rates of olivine-bearing rocks, in a similar way as was earlier shown for Mg/Fe ordering in amphiboles [14] and pyroxenes [15,16] as well as Al/Si ordering in alkali feldspars [17]. It seems M-site ordering in olivine might provide a better geospeedometer than minerals that are structurally more complex because of the relative structural simplicity of olivine. This means that no structural phase transitions, exsolution, or Tschermaks-type substitutions arise to complicate the high-temperature behaviour beyond the simple M1–M2 exchange process. The application of Landau–Ginzburg models to neutron-derived time–temperature-dependent ordering in tephroite–olivine solid solutions is described and its possible use as a geospeedometer is discussed.

The two M-sites in olivine are crystallographically distinct: even when two different cations are mixed completely randomly between them, these two octahedral cation sites are always symmetrically distinct, and any change from an ordered distribution of cations to a disordered one is not accompanied by a symmetry-changing phase transition. This type of disordering is termed non-convergent to distinguish it from convergent (symmetry-breaking) order/disorder phenomena which occur in other structures (e.g. Al/Si ordering in cordierite and albite). The factors controlling the site preferences of particular metal atoms in each of the two sites in olivine are the subject of continuing research. Some of the non-convergent ordering effects in the olivine structure can be rationalised in terms of simple crystal-chemical considerations such as relative ionic radii: because M2 is larger than M1, large cations such as Mn and Ca tend to prefer M2 while Fe^{2+}, Ni and Zn tend to order onto M1. Crystal field stabilisation energies may also control preferential ordering patterns acting in competition with size and covalency effects [18,19].

2. Recent results on the tephroite [Mn_2SiO_4]–olivine [$(Fe,Mg)_2SiO_4$] solid solution

The essential feature of the temperature-dependent structural response of olivine of interest to us is the exchange of metal cations between the M1 and M2 sites. The details of the experiments and the results for the high-*T* behaviour of 50 : 50 tephroite–fayalite and tephroite–forsterite are reported elsewhere [10,11]. The site occupancies of Mn and Fe or Mn and Mg may be related to a distribution coefficient, K_D, for intracrystalline partitioning of the relevant cations over the two M-sites. Alternatively, they may be expressed in terms of an order parameter, Q, describing the degree of cationic order/disorder over the two sites. For samples which are 50 : 50 mixtures of two elements (Fe^{2+} and Mn, or Mg and Mn) on two sites, the formulation of both K_D and Q is particularly simple and they may be related:

$$K_D = \frac{X^{M2}_{Mn}(1 - X^{M1}_{Mn})}{(1 - X^{M2}_{Mn})X^{M1}_{Mn}} = \left[\frac{X^{M2}_{Mn}}{(1 - X^{M2}_{Mn})}\right]^2, \qquad (1)$$
$$Q = X^{M2}_{Mn} - X^{M1}_{Mn} = 2(X^{M2}_{Mn} - 0.5),$$

where X^{M2}_{Mn} is the atomic fraction of Mn in site M2 and similarly X^{M1}_{Mn} for the M1 site. The completely disordered crystal is represented by $K_D = 1$ and $Q = 0$ while completely ordered or antiordered states have $Q = 1$ or -1, respectively. The experimentally observed variations of site occupancy with temperature for 50 : 50 tephroite : fayalite and tephroite : forsterite are shown in Fig. 2, with the corresponding K_D and Q scales indicated. At first, the amount of Mn in M2 remains constant with temperature, but subsequently increases to a maximum, before then decreasing with increasing temperature, corresponding to the high-temperature non-convergent disordering over M1 and M2. The initial increase in Mn in M2 arises because the

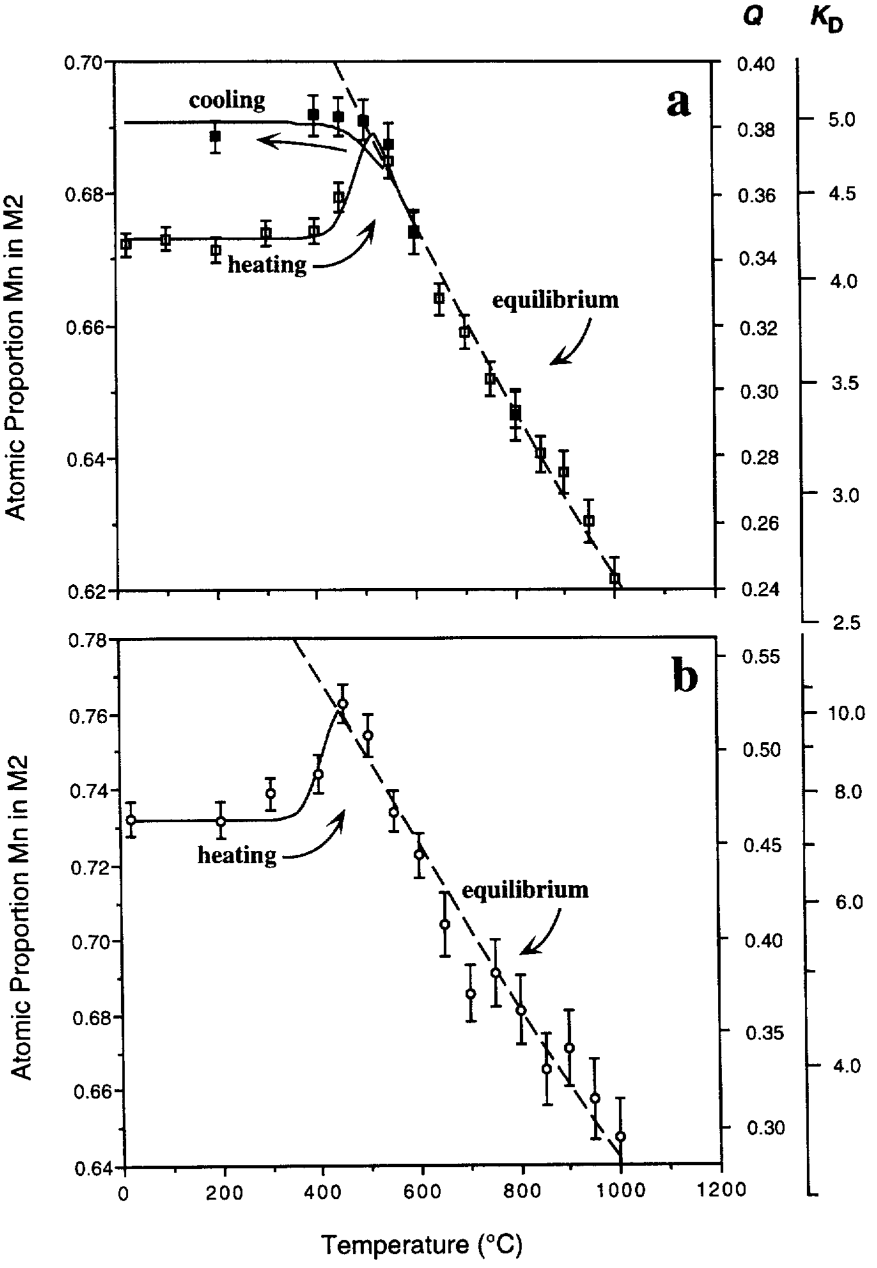

Fig. 2. Temperature dependence of the Mn occupancy of the M2 sites in (a) $FeMnSiO_4$ and (b) $MgMnSiO_4$ tephroite–olivines (after Henderson et al. [10]). The correspondence between the Mn occupancy of M2, the order parameter Q, and the intracrystalline distribution coefficient K_D is indicated at the right-hand side. Solid lines indicate the fit to Eq. (4) using the known heating and cooling rates of the experiments. The dashed lines show the high-temperature equilibrium non-convergent disordering behaviour obtained from the Landau expression for free energy (Eq. (2)).

starting value at room temperature is lower than the equilibrium value. As the temperature increases the thermally activated M1–M2 exchange commences (on the time scale of the experiment), and the occupancy of Mn in M2 begins to increase towards the equilibrium order–disorder line. The states at 550°C and above can be assumed to represent equilibrium and can therefore be used to constrain an expression for the temperature dependence of the equilibrium free energy due to ordering, *G*. The particular form of potential function that should be used to describe the equilibrium non-convergent ordering in olivine can be either based upon the reciprocal solution model or a phenomenological Landau model. At lowest order these two approaches are formally equivalent, although the manner in which free energy is partitioned between entropy and enthalpy differs between them [16,20]. One may adopt a Landau model for the free energy of non-convergent ordering by following the approach of Carpenter et al. [20]. The free energy difference between an olivine with some degree of order Q, and one which is completely disordered, is, therefore, given by

$$\Delta G = -hQ + \frac{a}{2}(T - T_C)Q^2 + \frac{b}{4}Q^4, \qquad (2)$$

where h, a, b and T_c are material-dependent parameters. This Landau formulation essentially treats entropy as vibrational rather than configurational. Essentially, it represents the excess free energy due to non-convergent ordering as a Taylor expansion to second order in Q, with the Q^4 term representing all higher-order powers. This expression is found to be sufficient to fit the high-temperature equilibrium disordering pathways of the Mn-olivines shown in Fig. 2 (indeed, it is preferred in this case to the expression to sixth order suggested by Carpenter et al., 1994 in their examples). Kroll et al. [16] have shown that the addition of a configurational entropy term to expression (2) models the entropy at high Q more accurately. This is particularly important for the non-convergent ordering behaviour of Mg and Fe on M-sites in pyroxene, where the M1 and M2 sites are structurally more distinctive than in olivine, where high degrees of order may arise, and where configurational entropy appears to dominate the ordering process. In olivine, however, the M1 and M2 sites are much more similar to one another. Indeed, Walsh et al. [18] consider the effect of the crystal field stabilisation and vibrational entropy on M-site partitioning in both structure types, and they conclude that vibrational entropy is likely to be of far more importance in olivine than in pyroxene. Artioli et al. [8] also hint at the importance of vibrational entropy rather than configurational entropy in controlling the high-temperature behaviour of M-site ordering in olivine. This gives further justification to adopting a Landau model for the order–disorder behaviour rather than a reciprocal solution approach. In any case, it turns out that by varying the "*a*" parameter in the Landau expansion any discrepancy between Landau entropy and configurational entropy can be minimised for low values of Q (less than around 0.8). Since the highest value of $Q_{\text{equilibrium}}$ expected for Mn-bearing olivines is around 0.7 (the value for $MgMnSiO_4$ at 273 K) significant errors cannot be expected to arise from adopting a Landau formulation of the free energy.

The equilibrium temperature dependence of Q is given by the condition $(G)/Q = 0$, allowing the calculation of the constants in expression (2). The linear term, h, in Eq. (2) corresponds to the difference in site energy between the M1 and M2 sites: if this term is zero the sites become degenerate and the ordering is thermodynamically equivalent to a convergent process. Henderson et al. [10] determined the M1–M2 site exchange energies of these $FeMnSiO_4$ and $MgMnSiO_4$ samples, arriving at an exchange energy of 10.1 ± 0.3 kJ/mol for Fe–Mn exchange and 15.7 ± 0.9 kJ/mol for Mg–Mn exchange. The lower value of b/h (10.9) for $MgMnSiO_4$ compared to that for $FeMnSiO_4$ (13.4) reflects, therefore, the increased difference between the site energies for Mg–Mn partitioning on M1 and M2 compared to Fe–Mn partitioning. The relative strengths of the linear field term, h, which forces non-convergent order/disorder, and the normal driving energy of a convergent process (aT_c) is given by the ratio $h : aT_c$. In these olivines this ratio is around 0.2, as against, for example, 1.77 for Fe–Mg ordering in $En_{50}Fs_{50}$ orthopyroxene [21]. Since the activation energies for site exchange in these Mn-bearing olivines is also lower than that for M1–M2 ordering in Fe–Mg orthopyroxenes, this provides the first indication that M-site ordering in olivine is faster than in orthopyroxene, and may be applicable to the measurement of relatively rapid cooling events.

The degree of order observed below around 500°C is controlled by kinetic effects. The low initial value of K_D (or Mn in M2) is that which was frozen in from the rapid quench of the samples from the synthesis T (approximately 1450°C). The lower-temperature kinetically controlled Q–T–time(t) pathways can be understood in terms of the Ginzburg–Landau equation, which relates the rate at which M1–M2 order/disorder occurs to the thermodynamic potential. The driving force for ordering is proportional to the negative gradient of the $G(Q)$ function multiplied by an attempt frequency (γ) and a Boltzmann-type probability (dependent on the activation energy G^*)

$$\frac{dQ}{dt} = -\frac{\gamma \exp(-\Delta G^*/RT)}{2RT}\frac{\partial G}{\partial Q}. \tag{3}$$

Substituting Eq. (2) into Eq. (3) and integrating one obtains

$$t - t_0 = \int_{Q_0}^{Q} \frac{-2RT}{\gamma h \exp(-\Delta G^*/RT)(-1 + (a/h)(T - T_c)Q + (b/h)Q^3)}\, dQ, \tag{4}$$

which can be solved numerically to obtain the time dependence of ordering behaviour away from equilibrium on both heating and cooling. The fit of this function to the low-T non-equilibrium data shown by solid curves (non-equilibrium heating and cooling) in Fig. 2, and gives an activation energy of Mn–Fe exchange on M1 and M2 of 193 ± 3 kJ/mol and for Mn–Mg exchange an activation energy for exchange of 172 ± 3 kJ/mol (assuming $\log(\gamma h) = 13.1 \pm 0.5$, following the arguments of [22]). Changing the activation energy modifies the temperature at which the maximum of the $Q(T)$ curve occurs on heating.

Eq. (4) may be used to compute cooling paths of olivines from high temperature. If one assumes that cooling starts from a temperature higher than that at which Q first deviates from the equilibrium curve then one obtains typical Q–T cooling curves of the type shown for $FeMnSiO_4$ in Fig. 3, where predicted cooling curves are calculated over 13 decades of cooling rate under conditions of constant cooling. It becomes clear that the room-temperature value of Q (or equivalently K_D or Mn in M2) reflects the rate at which the sample was cooled from high temperature. It does not provide information on the equilibrium properties at the conditions of a high-temperature anneal. This explains discrepancies between the interpretations of various early "anneal and quench" studies conducted on olivines: low-temperature measurement of K_D cannot be used to infer high-temperature equilibrium states, and differences in the values of K_D obtained by the various studies simply reflect differences in quench rates in different labs. Various measurements of K_D reported for a range of heat-treated and synthetic samples in the literature can now be used to calculate the cooling rates of those samples, as can be seen from Ref. [11]. This also provides the first evidence that M-site ordering in olivine might be employed as a practical geospeedometer. However, it is clear that more complex cooling paths may reset the degree of order on, say, re-heating, and it would then be difficult to trace back a complex cooling history from a single measurement of Q at room temperature. In the case of these more complex cooling histories, M-site ordering would have to be carried out in conjunction with other measurements using additional speedometers.

On a non-equilibrium cooling path, the degree of order saturates at some value, Q_{sat}, which remains constant on further cooling and is determined by the rate at which the sample was cooled. The variation of Q_{sat} (the room-temperature measured value of degree of order) with cooling rate is shown for $FeMnSiO_4$ in Fig. 4. As the cooling rate decreases, Q_{sat} increases. However, the rate of increase is not linear in log(cooling rate). This probably results

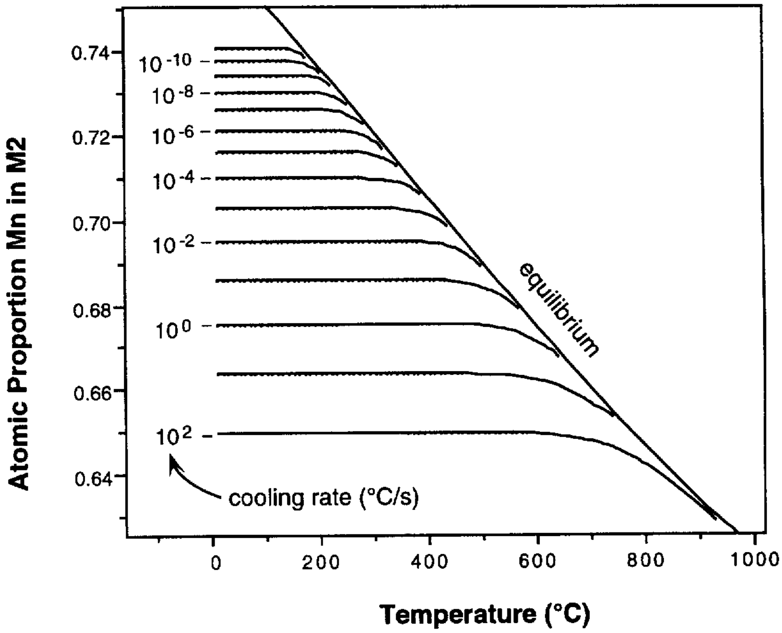

Fig. 3. Calculated cooling paths over thirteen decades of cooling rates showing the dependence of the low-temperature site occupancies in $FeMnSiO_4$ on cooling rate. The room temperature site occupancy is a direct measure of the cooling rate of the sample.

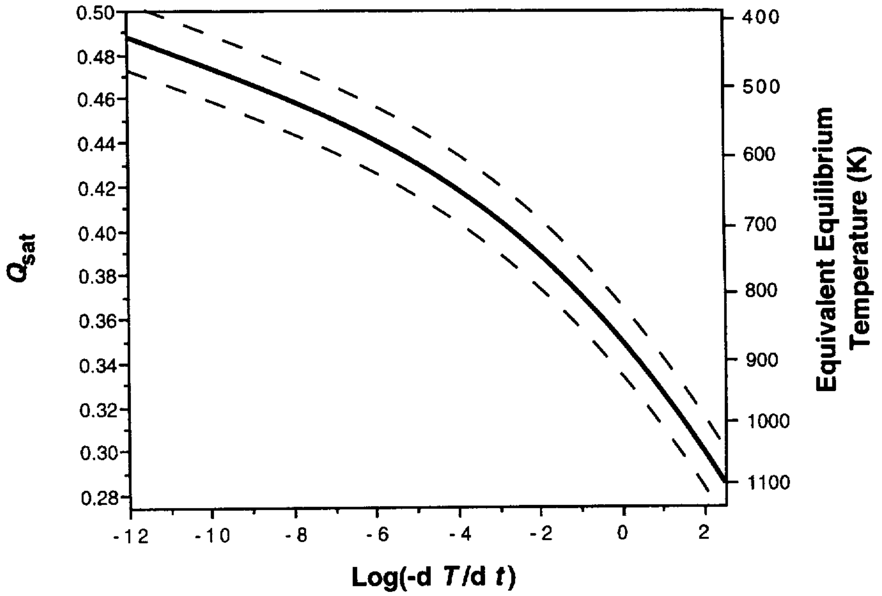

Fig. 4. Dependence of the low-temperature saturation value of degree of M-site order on the cooling rate of an $FeMnSiO_4$ olivine (solid line, log of rate in °C s^{-1}). The dashed curves represent the error limits for the determination of Q by neutron diffraction, and demonstrate that the errors in determination of cooling rate become proportionately greater at faster cooling rates.

from the combined effects of the temperature dependence of the Boltzmann factor, as the temperature falls below the activation temperature for site exchange, and the reduction in dG/dQ as states close to equilibrium are approached. While these calculations are based on cooling at constant dT/dt, other T–t cooling paths could be calculated with ease (to reflect, for example, Newtonian cooling). Using this approach, the initial frozen-in degrees of order in each of the Mn-bearing samples measured by Henderson et al. [10] correspond to the cooling rate experienced in their quench from the conditions of synthesis, amounting to an average cooling rate over the whole temperature interval (down to room temperature) of some $1.5\ \mathrm{K\,s^{-1}}$.

In conclusion, recent neutron diffraction results on the t–T dependence of intracrystalline M-site partitioning suggest that K_D may be a useful determinative tool for pinning down the cooling rates of fayalite–tephroite and forsterite–tephroite olivines. The new data from Mn-bearing samples have enabled the first elucidation of the T–t dependence of M-site ordering in the olivine structure. The application of these methods to the investigation of cation ordering in other important Fe–Mg-containing minerals is now underway and promises to be a most productive step in forming a new view of the behaviour of rock-forming minerals in nature.

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