The diffusion coefficient controlling crystal growth in a silicate glass-former

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Abstract
One of the most relevant open issues in glass science refers to our ignorance concerning the nature of the diffusing entities that control crystal nucleation and growth in non-crystalline materials. This information is very relevant because all the existing nucleation and growth equations account for the diffusion coefficient (DU) of these unknown entities. In this article, we measured the shear viscosity (η) and the crystal growth rates of a supercooled diopside liquid (CaMgSi2O6) in a wide temperature range. The well-known decoupling of viscosity and crystal growth rates at deep supercoolings was detected. We tested and analyzed 4 different approaches to compute DU, three existing and one proposed here. As expected, the classical approach (DU ~ η⁻¹) and the fractional viscosity approach (DU ~ η⁻⁵) were not able to describe the crystal growth rates near the glass transition temperature. However, our proposed expression to calculate DU—gradually changing from a viscosity-controlled to an Arrhenian-controlled process—was able to describe the available data in the whole temperature range and yielded the lowest uncertainty for the adjustable parameters. Our results suggest that viscous flow ceases to control the crystal growth process below the so-called decoupling temperature, corroborating some previous studies.

KEYWORDS
Crystal growth, diffusion, glass forming melts, phase transition, theory, viscosity

1 INTRODUCTION

Understanding and controlling crystal nucleation and growth in glass-forming liquids is a key issue either to avert crystallization¹ to produce a glass or for the development and production of glass-ceramics.² Crystallization is such an important feature of glass-forming liquids that it has been the most frequently used keyword in the past 200 years of glass science,³⁴ and crystal growth is a key part of the crystallization process.

However, one faces some adversities when studying the physics of crystal growth. One of the most relevant is our ignorance of what the diffusing entities (or structural entities)⁵ are that control this phenomenon.⁶ The glass research community does not know if crystal growth kinetics is controlled by 1 chemical element (e.g. silicon, the network former) or a set of atoms (e.g. one or more silica tetrahedral) in the case of silicate glasses. We also do not know if the controlling entity is temperature-, pressure-, and/or structure-dependent. This information is relevant because the current crystal growth equations take into account the effective diffusion coefficient (DU) of these unknown units.

What seems to be a consensus⁷-¹⁴ is that viscous flow is an adequate property to estimate DU in a limited...
temperature range, which spans from the melting point down to the so-called decoupling temperature \( T_d \). This temperature has been reported for different substances\(^{11,12}\) to exceed the laboratory glass transition temperature by a factor of about 1.10-1.25.

In this article, we tested 4 different approaches to estimate \( D_U \), one of them is proposed here for the first time. The test was carried out for a glass with diopside composition (CaMgSi\(_2\)O\(_6\)), for which we report a new dataset of viscosity and crystal growth rates. This particular composition was chosen because it has a plethora of available kinetic and thermodynamic data that were necessary to carry out the present analysis, and thus can be considered a “model” glass-former, similarly to what has been proposed for lithium disilicate.\(^{13}\)

2 | LITERATURE REVIEW AND GOVERNING EQUATIONS

2.1 | Crystal growth kinetics

Crystal growth rates in oxide glass-forming systems are usually analyzed by one of the 3 classical models: normal growth, screw dislocation growth or 2D secondary nucleation growth.\(^{15}\) Here, we focus on the screw dislocation growth model because it satisfactorily describes the experimental crystal growth data in supercooled diopside liquid in a wide temperature range.\(^{14}\) Readers are invited to study Gutzow & Schmelzer’s book\(^1\) for more detailed information on the different crystal growth mechanisms, and Cassar’s thesis\(^{16}\) for an in-depth analysis of the normal and 2D secondary nucleation growth for diopside (briefly, these equations did not perform as well as the screw dislocation growth for this material).

The normal and screw dislocation growth modes are described by the same expression, Equation 1. The difference between these 2 growth mechanisms is the fraction of sites \( f \) on the crystal interface available for atomic attachment. Normal growth prevails if this parameter is temperature independent and approximately unity (as proposed by Wilson\(^{17}\) in 1900). Otherwise, if \( 0 < f < 1 \) and \( f \) is temperature dependent, the screw dislocation mechanism governs growth. This parameter can be estimated by Equation 2 if 1 considers screw dislocations that form Archimedean spirals\(^{18}\) at the liquid-crystal interface.

\[
U = f \frac{D_U}{d_0} \left[ 1 - \exp \left( -\frac{\Delta \mu}{RT} \right) \right] \\
\]

\[ f = \frac{d_0 \Delta \mu}{4\pi \sigma V_m} \]

In the above equations, \( U \) is the crystal growth rate, \( D_U \) is the effective diffusion coefficient controlling crystal growth, \( d_0 \) is the jump distance that some (unknown) diffusing entities or “structural units” must travel through the liquid to attach onto a growing crystal, \( \sigma \) is the crystal-liquid interfacial energy, \( R \) is the universal gas constant and \( V_m \) is the molar volume. The driving force for crystallization, \( \Delta \mu \), for a closed system in an isobaric condition can be calculated\(^{19,20}\) using heat capacity data:

\[
\Delta \mu(T) = \Delta H_m \left( 1 - \frac{T}{T_m} \right) - \int_{T}^{T_m} \left( C_{p,l}(T) - C_{p,c}(T) \right) \frac{dT}{T} \\
\]

\[
dT + T \int_{T}^{T_m} \frac{C_{p,l}(T) - C_{p,c}(T)}{T} dT \\
\]

where \( \Delta H_m \) is the enthalpy of melting, \( C_{p,l} \) is the heat capacity of the supercooled liquid, \( C_{p,c} \) is the heat capacity of the crystal and \( T \) is the absolute temperature.

Finally, the latent heat released at the liquid-crystal interface during crystal growth can significantly increase the interface temperature if it is not dissipated fast enough (oxide liquids are poor heat conductors). Fortunately, Herron & Bergeron\(^{21}\) measured the temperature increase at the liquid-crystal interface during the crystal growth process in several oxide glass-formers. Cassar\(^{16}\) reanalyzed their data and obtained the following empirical expression:

\[
\Delta T_i(T) = 10^{0.64(U(T)\Delta H_m)^{0.58}} \]

where \( \Delta T_i \) is the liquid-crystal interface temperature increase at temperature \( T \). In this expression, \( U \) is given in \( \text{m/s} \) and \( \Delta H_m \) in \( \text{J/mol} \). In this article, we corrected all the analyzed data for this increased interface temperature using Equation 4.

2.2 | The diffusion coefficient for crystal growth

As already stated, the mobility of the diffusing entities that control crystal growth is of major importance for crystal growth. The effective diffusion coefficient \( D_U \) represents the magnitude of this mobility, but the nature of the moving units in oxide glasses is not known. Authors\(^{9-14,22-24}\) have approached this problem differently, but our analysis indicates that they all use the following general phenomenological equation for \( D_U \):

\[
D_U = \left[ x^0 \left( C \frac{T}{\eta^2} \right) \right] + \left[ 1 - x^0 \right] \left[ D_0 \exp \left( -\frac{E_a}{RT} \right) \right] \]

In the above equation, \( x \) is usually set to one (which makes the rightmost term of Equation 5 equal to zero) or set to be temperature dependent (see Subsection 2.2.3 below), \( \eta \) is the viscosity and \( C, D_0, E_a, \xi, n, \) and \( q \) are constants. Please note that \( C = C_\xi \) when Eyring’s diffusion equation\(^{25}\) is considered.
\[ C_E = \frac{k_B}{d} \]  

In the above equation, \( k_B \) is the Boltzmann constant and \( d \) is the diameter of the moving entity that controls viscous flow, usually assumed to be equal to \( d_0 \).

This complex form of \( D_U \) (Equation 5, proposed in this article) results from many attempts to describe \( D_U \) in the literature. These attempts will be described below, case by case. In this article, we test 4 possible expressions of \( D_U \): 3 published approaches (Cases 1-3) and a new method (Case 4) suggested here. These \( D_U \) expressions will be used to fit Equation 1 to experimental crystal growth rate data measured for a supercooled liquid with diopside composition (CaMgSi2O6), the 4 \( D_U \) expressions can be derived from the general Equation 5.

2.2.1 | Case 1: classical \( D_U \) approach

In what we term the “classical” approach,\(^9\)\(^-\)\(^11\)\(^-\)\(^14\)\(^-\)\(^22\)\(^-\)\(^23\) the mobility of the diffusional units controlling crystal growth is linked to the equilibrium viscosity at all temperatures from the melting temperature (\( T_m \)) down to the laboratory glass transition temperature (\( T_g \)) and below. This is the simplest assumption from all the cases studied here, and it effectively considers that \( n = \xi = x = q = 1 \), and \( \eta = \eta_{eq} \) in Equation 5 (where \( \eta_{eq} \) is the equilibrium viscosity). The final expression for \( D_U \) in this case reads:

\[ D_U = C \frac{T}{\eta_{eq}} \]  

(7)

Turnbull and Cohen\(^22\) were some the first to propose and use this method. More recently, however, several reports\(^11\)\(^-\)\(^13\) indicated that the viscosity is indeed a good parameter to calculate \( D_U \) for temperatures near \( T_m \) but does not correctly describe the transport part of crystal growth rates at deep supercoolings, i.e., temperatures near \( T_g \). This observation is the basis of the so-called “decoupling” or “breakdown” of the Stokes-Einstein/Eyring equation that has been extensively discussed elsewhere.\(^11\)\(^-\)\(^13\)\(^-\)\(^23\)

Various equations describe the temperature dependence of the equilibrium viscosity of oxide glass-formers between \( T_m \) and \( T_g \) well. Here, we use the MYEGA\(^26\) expression:

\[ \log_{10}(\eta_{eq}(T)) = a + \frac{T_g}{T} \log_{10}(\eta_{\infty}) \]  

(8)

where \( \eta_{\infty} \), \( T_g \), and \( m \) are taken as adjustable parameters with the following definitions:

\[ \eta_{\infty} = \lim_{T \to \infty} \eta_{eq}(T) \]  

(9)

\[ \eta_{eq}(T_g) = 10^{12} \text{Pa.s} \]  

(10)

\[ m = \frac{d(\log_{10}(\eta_{eq}(T)))}{d\left(\frac{T}{T_g}\right)} \]  

(11)

where \( m \) is known as the liquid fragility.\(^27\)

2.2.2 | Case 2: \( D_U \) with fractional viscosity

In the fractional viscosity approach, Ediger et al\(^24\) considered a parameter \( \xi \) in the \( D_U \) expression that leads to a different temperature dependence of \( D_U \) on viscosity (Equation 12). Their aim was to restore the agreement between crystal growth kinetics and viscous flow in the whole temperature range from \( T_m \) down to \( T_g \). According to their approach, there is no decoupling of the Stokes-Einstein/Eyring equation, as observed in the classical approach (Case 1). They found that the higher the fragility of the liquid, the higher the deviation of \( \xi \) from unity is. This approach was recently re-tested for some oxide liquids and challenged by Schmelzer et al.\(^12\)

Based on the assumptions of this approach,\(^24\) we have that \( n = x = q = 1 \), \( \eta = \eta_{eq} \), and \( \xi \) becomes an adjustable parameter in Equation 5. The final expression for \( D_U \) reads:

\[ D_U = C \frac{T}{\eta_{eq}} \]  

(12)

2.2.3 | Case 3: \( D_U \) with viscosity plus an Arrhenian contribution

Schmelzer et al\(^12\) proposed another approach to calculate \( D_U \) by adding an additional Arrhenian diffusion term \( D_0 \exp(-E_a/RT) \) in the “classical” \( D_U \) equation. This is equivalent to setting \( n = 0, \xi = q = 1 \), and \( \eta = \eta_{eq} \) in Equation 5. With these approximations, the final expression for \( D_U \) is:

\[ D_U = \left[ C \frac{T}{\eta_{eq}} \right] + [1 - x] \left[ D_0 \exp\left(-\frac{E_a}{RT}\right) \right] \]  

(13)

In their manuscript, Schmelzer et al\(^12\) used a hyperbolic tangent function for \( x \):

\[ x = \frac{1 + \tanh(\alpha)}{2} \]  

(14)

with

\[ \alpha = \frac{T - T_d}{\phi T_d} \]  

(15)

In Equation 15, \( \phi \) is a dimensionless parameter that controls the smoothness of \( x \) and \( T_d \) is the decoupling
A relevant property of Equation 13 is that the equilibrium viscosity is used to evaluate $D_U$ at all temperatures. That is, no matter how deep a material is cooled below its $T_g$, the equilibrium viscosity will still be an important parameter to calculate $D_U$. It will be clearer later on that this is the main difference between this approach and the one that we propose in this manuscript.

3 | MATERIALS AND METHODS

3.1 | Experimental

The diopside glass used in this research was obtained by the melt-quenching route. Melting was carried out in a bottom-loaded superkanthal electric furnace, model CM Bloomfield. The diopside batch used in this study is the same used by Reis.28,29 The chemical reagents used were CaCO$_3$ (J. T. Baker 99.9%, lot E06348), MgO (J. T. Baker 99.9%, lot E25597) and colloidal silica (Aldrich 99.8%, lot MKAA0249). The powders were heated at 673 K (CaCO$_3$ and MgO) and at 1173 K (SiO$_2$) for twelve hours for drying before weighing, and the mixture was homogenized in a Fritsch Pulverisette 6 low rotation mill with 8 agate balls. The homogeneous mixture was heated at 1473 K for 48 hours prior to melting to produce the diopside crystal phase via solid state reaction, and the diopside crystal was indeed confirmed by XRD.28 (JCP2 card 75-1577). Four hundred grams of this polycrystalline mass were melted in a platinum crucible at 1823 K for 15 minutes, cast into a metallic mold and annealed at 998 K ($-T_g$) for 240 minutes. The analyzed composition of the glass28,29 was 25.8 CaO, 18.6 MgO, and 55.4 wt% SiO$_2$ (with 0.2 wt% impurities). This result is very close to the nominal composition of stoichiometric diopside.

The viscosity and the crystal growth rates were measured isothermally at various temperatures using glass samples of the same batch. The viscosity of our glass near the glass transition temperature was measured at the Institute of Silicate Chemistry, Russian Federation, using a penetration viscometer, which is described elsewhere.30 We measured the viscosity using samples of the same batch near the melting point using a Brookfield Model DV-III rotational rheometer (Middleboro, MA).

We measured the advancement rates of the surface crystallized layer using cubic samples of polished faces having an edge size of approximately 2 mm. We used 3 cubes for each studied temperature and all of them revealed a linear increment of the crystal layer depth $l$ as a function of heat treatment time (this particular glass only shows surface nucleation in laboratory time/size scales). The slopes of $l \times t$ yielded the crystal growth rates, and for each temperature, we took the average values measured for the 3 cubes. For the isothermal heat treatments, the samples were dropped inside a vertical furnace already stabilized at the desired temperature. This results in the fastest possible heating rate between room temperature and the treatment temperature.

We confirmed that a wollastonite-like phase (WL) appeared after a certain crystallized layer depth of diopside was reached, as shown and discussed by Fokin et al.31,32 Therefore, in this study, we only measured the growth of the diopside crystal layer before this WL phase appeared. The wollastonite-like phase nucleates in the sample interior, just underneath the diopside crystal-liquid interface when a certain level of elastic stress is reached due to the different densities between the crystalline and liquid phases.31,32

3.2 | Calculations and data analysis

We analyzed our crystal growth data near and above $T_g$ alongside data measured by Reis et al.29 (using samples from this same diopside glass batch) and by Kirkpatrick et al.33 Fortunately, the data from Kirkpatrick et al are well above the temperature where the wollastonite-like phase transforms to diopside.

We calculated the thermodynamic driving force via Equation 3, for which we used 334.57 J/K mol for $C_p$,34 137.7 kJ/mol for $\Delta H_m$,34 1670 K for $T_m$34 and Equation 16 for $C_p$ (with $C_p$ in J/K mol and $T$ in Kelvin):

$$C_p = 470 - 0.17T + \frac{2.45}{T^2} - 4820\sqrt{T} + 2.81 \times 10^{-5}T^2$$

(16)

We adopted the expression used by Reinsch et al.23 Equation 17 for the calculation of the jumping distance $d_0$ from the liquid to the growing crystal interface. We obtained an equation for the molar volume of the liquid phase (Equation 18, with $V_m$ in m$^3$/mol and $T$ in Kelvin) by a linear regression of the data reported by Lange36 and Gottsmann & Dingwell.37 We assume that $d = d_0$ and $C = C_E$ throughout this manuscript, in agreement with similarly published research.11-13,23

$$d_0 = \left(\frac{V_m}{N_A}\right)^{1/3}$$

(17)

$$V_m(T) = 7.01 \times 10^{-5} + 7.21 \times 10^{-9}T$$

(18)

We carried out all numerical analyses using the Python programming language with the Jupyter Notebook.38
interactive computational environment equipped with the free and open-source NumPy and SciPy modules. All nonlinear regressions were performed using the module LMFIT using the Levenberg-Marquardt method. The plots were also generated using Python with the aid of the free and open-source matplotlib module. All the uncertainties reported in this manuscript are 1 SD.

3.3 | New approach to calculate $D_U$ (Case 4)

Here, we propose a new method to compute the effective diffusion coefficient, considering that $D_U$ gradually changes from viscosity-controlled to Arrhenian-controlled.

As already mentioned, 1 important consideration of the approach of ref. (Case 3) is that the equilibrium viscosity (or whatever mass transport mechanism that controls viscous flow) always takes some part in the diffusion process controlling crystal growth, even below $T_d$. Here, we propose and test another possibility: that the equilibrium viscosity gradually ceases to control the crystal growth kinetics near and below $T_d$, effectively resulting in a “pure” Arrhenian behavior for temperatures sufficiently below $T_d$.

To account for this behavior, we have set $n = \xi = q = 1$ and $\eta = \eta_{eq}$ in Equation 5. The final expression for $D_U$ in this context is:

$$D_U = \left[x \left\{ C \frac{T}{\eta_{eq}} \right\} + (1 - x) \left\{ D_0 \exp \left( - \frac{E_a}{RT} \right) \right\} \right] (19)$$

We decided to use the same sigmoid function for $x$ as employed in ref. However, after various tests, we settled with a lower value for $\phi$ for this case: 0.02. As already mentioned, $\phi$ controls the smoothness of the sigmoid function used for $x$. Using a lower value of $\phi$ results in a curve that has a sharper transition between viscosity-controlled to Arrhenian-controlled $D_U$. To be clear, we used a value of $\phi = 0.06$ for the Case 3 calculations for 2 reasons: the authors tested other values of $\phi$ and reported this one to be the one that best fitted their data; and to be able to compare our results with those published in ref.

4 | RESULTS AND DISCUSSION

4.1 | Experimental

Figure 1 shows the experimental viscosity data measured for the diopside liquid studied here. The continuous line is the regression of Equation 8, from which we obtained the following values: $T_g = 1000.1(3)$ K, $m = 64.5(3)$, and $\log_{10}(\eta_{eq}) = -1.80(4)$ ($\eta_{eq}$ in Pa.s).

Similarly, Figure 2 shows the experimental crystal growth rates obtained in this study together with data from Kirkpatrick. All the experimental data obtained from this research are reported in Tables S1 and S2.

4.2 | Crystal growth analysis

4.2.1 | Case 1

Figure 3 shows the regression of crystal growth rate data when $D_U$ is given by the considerations in Case 1 (see Subsection 2.2.1). In this approach, we were not expecting a good fit for the data near $T_g$ and this was precisely what we obtained. The regression gives a smaller residual near $T_m$ when only data points to which $T \geq 1.1T_g$ are considered, see Figure 3B in comparison with Figure 3A. The rationale to eliminate the data points below the suspected $T_d$ results from the fact that due to the suspected decoupling, the equilibrium viscosity would no longer describe the growth rates at such deep supercoolings.

Only 1 adjustable parameter is needed in this approach, the surface energy, $\sigma$. From the regressions, we obtained $\sigma = 0.16 (2)$ J/m$^2$ and RMS = 0.42 when all data points were considered (Figure 3A) and $\sigma = 0.22(1)$ J/m$^2$ and RMS = 0.44 when only data points for which $T \geq 1.1T_g$ were considered (Figure 3B). These are reasonable values of surface energy (comparable to values reported from crystal nucleation studies of silicate glasses that undergo homogeneous nucleation).

![Experimental data and regression curve with Equation 8](image-url)
4.2.2 | Case 2

Figure 4 shows the regression curve of crystal growth rate data when $D_U$ is calculated by the considerations of Case 2 (Subsection 2.2.2). Even though the data near $T_m$ are reasonably well described in this approach, all the available data below 1300 K systematically deviate from the regression curve. Our observation is in agreement with recent critiques of this approach. Two adjustable parameters are needed for this approach: $\sigma$ and $\xi$. Our regression yielded $\sigma = 0.20(3)$ J/m$^2$ and $\xi = 0.95(1)$, with RMS = 0.31.

4.2.3 | Case 3

Figure 5 shows the regression curve fitted to crystal growth rate data when $D_U$ is calculated by the considerations in Case 3 (Subsection 2.2.3). It can be readily seen that all crystal growth data are well described by the fit, including the data near $T_g$. Four adjustable parameters are needed for this approach: $\sigma$, $E_a$, $D_0$, and $T_d$. Our regression yielded $\sigma = 0.26(4)$ J/m$^2$, $E_a = 640(60)$ kJ/mol, ln ($D_0$) = 31(7), and $T_d = 1040(140)$ K, with RMS = 0.11 ($D_0$ in m$^2$/s).

4.2.4 | Case 4

Figure 6 shows the overall results of the new approach suggested here, i.e., the regression of crystal growth rate data when $D_U$ is calculated following the considerations of Case 4 (Subsection 3.3). Similarly, as in the previous case, all available data are well described by the regression. The same 4 adjustable parameters are needed for this approach: $\sigma$, $E_a$, $D_0$, and $T_d$. Our regression yielded $\sigma = 0.223(9)$ J/m$^2$, $E_a = 650(50)$ kJ/mol, ln ($D_0$) = 31(6), and $T_d = 1100(30)$ K, with RMS = 0.11 ($D_0$ in m$^2$/s).

4.3 | Comparison of $D_U$ expressions

From the 4 different expressions for $D_U$ studied here, 2 were unable to describe crystal growth data near the glass transition temperature: the classical approach (Case 1) and the fractional viscosity approach (Case 2). These are
expected results due to the breakdown of the Stokes-Einstein/Eyring equation at $T_d$, in agreement with former publications in the field.\textsuperscript{11,13} Both cases had a similar performance for fitting data near the melting temperature, but Case 1 has fewer adjustable parameters. Our results for Case 1 show that viscosity can indeed describe the kinetic part of crystal growth at relatively low supercoolings for $T > T_d$ and it may be used when the available or studied data is above the decoupling temperature.

We repeated the analysis for the approach of Schmelzer et al.\textsuperscript{12} i.e., $D_U$ expression with viscosity plus an Arrhenian contribution (Case 3). As far as we know, this is the first independent study to use this expression after its publication, making this a consistency test. Within this framework, we obtained a $T_d$ value of 1040 (140) K which is statistically equal to the value (1100 K) reported in their manuscript (they the notation $\bar{T}_d$ for this parameter). However, we obtained a value of 640(60) kJ/mol for $E_a$, which is higher than the reported\textsuperscript{12} value of 480 kJ/mol. Unfortunately, they did not report the uncertainty for these 2 parameters. It is possible that both $E_a$ values are statistically equal within the uncertainty, but we cannot be sure. $D_0$ and $\sigma$ were not reported.

We also proposed and tested a new approach to this same problem: $D_U$ undergoing a gradual change from viscosity-controlled to Arrhenian-controlled (Case 4). This approach fitted well all the available data, with very similar residuals and RMS as in Case 3. This approach also has the same 4 adjustable parameters as Case 3: $\sigma$, $D_0$, $T_d$, and $E_a$. However, we observed that Case 4 has a
avoided measuring the crystallization rates of the (spurious) wollastonite-like phase.

The well-known decoupling between viscosity and crystal growth rates at deep supercoolings was detected. We tested and thoroughly analyzed 4 different approaches to compute the effective diffusion coefficient controlling crystal growth, a key parameter controlling the crystallization kinetics that cannot be measured experimentally. As expected, the classical approach and the fractional viscosity approach were not able to describe the crystal growth rates at deep supercoolings near the glass transition temperature. Overall, the approach proposed here (Case 4)—which assumes that \( D_U \) gradually changes from a viscosity-controlled to an Arrhenian-controlled process—was able to describe the available crystal growth rate data in the whole temperature range and yielded the lowest uncertainty among the 4 cases. This result supports the concept that viscous flow ceases to control the crystal growth process below the decoupling temperature.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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