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1 # Thermal conductivity of molten and glassy NaAlSi$_3$O$_8$,

2 # CaMgSi$_2$O$_6$ and Mg$_2$SiO$_4$ by Non Equilibrium Molecular

3 # Dynamics at elevated Temperature and Pressure: Part 1-

4 # Methods and Results

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Abstract

15   Non Equilibrium Molecular Dynamics (NEMD) simulations are used to compute the

16   phonon thermal conductivity (k) for liquids and glasses of composition Mg_2SiO_4,

17    $CaMgSi_2O_6$ and $NaAlSi_3O_8$ at 2000-4500 K and 0-30 GPa based on classical potentials.

18   These compositions span the range of melt polymerization states in natural systems at

19   ambient pressure. The NEMD results compare well with available laboratory

20   measurements on molten $NaAlSi_3O_8$ and $CaMgSi_2O_6$ at 1-bar. Thermal conductivities

21   decrease with increasing temperature (T), increase with increasing pressure (P) and, at

22   low pressure, increase slightly as the mean coordination number of Si and Al around

23   oxygen increases, in the sequence Mg_2SiO_4, $CaMgSi_2O_6$ and $NaAlSi_3O_8$. At 3500 K, the

24   thermal conductivity of $CaMgSi_2O_6$ at 0, 10, 20 and 30 GPa is 1.1, 2.1, 2.5 and 3 W/m K,

25   respectively. At ambient pressure ($0.2 \pm 0.15\,GPa$), k=1.2 and 0.5 W/m K at 2500 K and

26   4500 K, respectively for $CaMgSi_2O_6$. For $NaAlSi_3O_8$ composition, k varies from 1.7 W/m

27   K to 2.7 W/m K at 3050 K for pressures of 6 and 30 GPa, respectively. Mg_2SiO_4 liquid at

28   ambient pressure ($0.07 \pm 0.16\,GPa$) is found to have thermal conductivities of 1.36 and

29   0.7 W/m K at 2500 K and 4500 K, respectively. Tables giving computed k values for all

30   compositions are included for state points studied. The trade-off between T and P implies

31   that the phonon thermal conductivity of silicate liquids at mantle depths increases

32   substantially (factor of 2-3) along isentropes.

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INTRODUCTION

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35   Knowledge of the phonon thermal conductivity of amorphous silicates (melts and

36   glasses) over the range of composition (X), P and T of the Earth's crust and mantle is

37   essential for analysis of many geophysical and geochemical problems. For example, heat

38   transfer during nucleation and dissolution or growth of a crystal from a melt is a

39   significant factor governing rock texture. Similarly, heat exchange between magma and

40   its surroundings is relevant to rates of magma crystallization, mechanisms of volatile-

41   saturation and the thermodynamics of partial melting. Heat transport from the Earth's

42   core to mantle, possibly modulated by a transient molten or partially molten ultra-low

43   velocity zone (ULVZ), is relevant to the long-term thermal history of Earth, the thickness

44   of thermal boundary layers along the core-mantle boundary and the strength and

45   evolution of the Earth's magnetic field (Wen and Helmberger, 1998; Hernlund and

46   Jellinek, 2010; Idehara, 2011; Anzellini et al, 2013; Olsen, 2013). Accurate values of the

47   thermal diffusivity, $\kappa = k/\rho C_P$, where ρ is the density, C_P is the isobaric specific heat

48   capacity, and k is the phonon thermal conductivity, are needed to calculate transient

49   geotherms and predict conditions for crustal anatexis and metamorphism in orogenic

50   regions (e.g., Whittington et al., 2009). Finally, in ceramic and composite materials

51   processing, knowledge of thermal conductivity is required (Kang and Morita, 2006). Of

52   special concern is the lack of any estimates of the effects of pressure on phonon

53   conduction in silicate liquids. In this study, attention is mainly focused upon equilibrium

54   silicate liquids of petrological significance although a few results relevant to glasses are

55   included. The term amorphous is used here to refer to either glass or liquid when the

56   distinction is not essential.

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57   There are few reliable measurements of the thermal conductivity of molten

58   silicates as a function of X and T at ambient P. We are aware of *no* experimental

59   measurements describing the effect of pressure on k for silicate liquids. Although there

60   are measurements and theory related to the effects of pressure on thermal conductivity in

61   crystalline silicates and oxides, liquids are structurally distinct with essentially no long

62   range structure beyond ~ 0.5 nm (Kittel, 1949). Hence, one might expect some

63   differences in modes of phonon excitation in liquids relative to ordered solids because,

64   unlike solids, liquids undergo gradual changes in structure as P increases. One of the

65   goals of this study is to provide quantitative constraints on the pressure-dependence of

66   the thermal conductivity of silicate liquids at elevated temperature. Very limited

67   experimental data at 1-bar on molten silicates of varying atomic-level structure suggest

68   that at fixed T and P, the more polymerized the melt (e.g., the lower the NBO/T ratio),

69   the higher the thermal conductivity (Kang and Morita, 2006). A second goal of this work

70   is to therefore examine, at fixed temperature and pressure, the correlation of thermal

71   conductivity with NBO/T ratio. Finally, although for crystalline solids at constant

72   pressure, thermal conductivity varies according to 1/T (e.g., see summary in Stackhouse

73   and Stixrude, 2010) the validity of this scaling of conductivity with temperature, $k \propto 1/T$,

74   has not been experimentally or numerically studied for molten silicates in the range 2000-

75   5000 K. The high-T scaling of k at fixed P is therefore also investigated here. In short,

76   current knowledge of the thermal conductivity of silicate liquids is meager. In this study,

77   we study of the effects of P, T and melt composition on the phonon thermal conductivity.

78   Obtaining accurate values for the phonon thermal conductivity proves difficult in

79   the laboratory (e.g., Tritt and Weston, 2004). Many measurements are of restricted value

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80   because: (1) they are contaminated by unwanted radiative (photon) transport, (2) include

81   unwanted interfacial contact effects or (3) are affected by convective heat transport. For

82   example, measurements reported by McBirney and Murase (1973) using the hot-wire

83   method are dominated by radiative effects that act to conceal the smaller phonon

84   contribution. Additionally, in hot-wire and hot-layer methods, thermal losses at contacts

85   introduce significant errors difficult to eliminate without complex deconvolution (Healy

86   et al, 1976; Lee and Hasselman, 1985, Hammerschmidt and Sabuga, 2000). Hofmeister

87   and co-workers (Pertermann and Hofmeister, 2006; Hofmeister, 2007; Hofmeister et al,

88   2009; Pertermann et al, 2008) present measurements of thermal conductivity at ambient

89   pressure for a number of compounds. They note that recent advances in contact-free,

90   laser-flash analysis and better data reduction methods (Degiovanni et al., 1994; Mehling

91   et al., 1998) enable removal of direct radiative transfer effects and losses to the container

92   and hence provide accurate phonon conductivities at ambient P and temperatures just

93   above 1-bar melting points. Unfortunately, these measurements are limited to 1-bar (10^{-4}

94   GPa) pressure. Although these data indicate that k decreases weakly with increasing T in

95   the range ~1300-1600 K for silicate liquids, the behavior at higher temperature has not

96   been studied and there are no data on the effects of pressure. Data on alkali halides and

97   metal liquids (e.g., Beck et al, 2007; Galamba et al, 2004; de Koker et al, 2012) suggests

98   that conductivity increases with pressure along an isotherm but for silicate liquids the

99   effects of pressure are unknown. Consequently, the trade-off between variations in T and

100   P is unknown for liquid silicates. Finally, although studies on $CaO-Al_2O_3-SiO_2$ liquids

101   (Kang and Morita, 2006), as well as molten diopside and molten albite (Hofmeister et al.,

102   2009) suggest that that polymerized or strong 'network' liquids exhibit higher k at similar

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103   T and P compared to less polymerized 'fragile' liquids (Martinez and Angell, 2001), the

104   role of composition and its correlative melt polymerization is not well quantified.

105   Because melt structural states correlate with changes in second order thermodynamic

106   property differences between liquid and glass (e.g., isothermal expansivity, isothermal

107   compressibility, isobaric heat capacity), (Giordano and Dingwell, 2003) one might expect

108   a correlation at fixed T and P between melt composition and phonon conductivity such

109   that more fragile melts possess lower conductivities compared to the network (strong)

110   melts. This conjecture can be addressed using liquid structural states, encapsulated in

111   radial distribution analysis and coordination statistics derived from MD simulations (e.g.,

112   Ghiorso and Spera, 2009; Spera et al, 2009). The compositions chosen in this study span

113   the spectrum of polymerization states relevant to natural magmas (Mysen and Richet,

114   2005; Hendersen et al, 2006; Hofmeister et al, 2009). That is, in forsterite liquid the

115   canonical fraction of bridging oxygen at low pressure, X_{BO} (=$N_{BO}/(N_{BO}+N_{NBO})$,

116   approaches zero whereas albite liquid is fully polymerized with each oxygen being shared

117   between two distinct Si-Al tetrahedra (i.e., X_{BO}=1). Diopside liquid is intermediate in the

118   stoichiometric sense with X_{BO}=1/3 at 1-bar pressure. One of the most significant

119   connections between structure and properties observed in all liquid silicates both

120   experimentally and in Molecular Dynamics simulations is the increasing coordination of

121   cations around oxygen (and of oxygen with itself) as pressure increases (e.g., Daniel et al,

122   1996; Allwardt et al, 2007; Spera et al, 2011). This effect dominates a smaller but

123   opposing temperature effect of lengthening bond distances. As shown below, the higher

124   mean coordination number of metals around oxygen gives rise to an increase in the

125   thermal conductivity as pressure increases along an isotherm for all of the compositions

126   studied here. Hence along a mantle adiabat, the thermal conductivity of a melt is expected

127   to increase with depth. At crustal pressures ~ 0-2 GPa, composition effects will dominate.

128   An important result of this study explored more fully in part II is that at the same

129   temperature and crustal pressure, the thermal conductivity of silicic melt (e. g., a rhyolite)

130   is larger by 25-100 % compared to basaltic melt. In summary, the effects of composition,

131   temperature and pressure on thermal conductivity in silicate liquids are largely unknown

132   over the range of states relevant to the Earth. The main purpose of this study is to address

133   these issues.

METHODS

136   Classical Molecular Dynamics

138   The calculations in this study are based on classical Molecular Dynamics (MD)

139   simulations. In classical MD, an empirical relation describing the potential energy

140   between atom pairs is used to compute forces between atoms. This pairwise additive,

141   radially symmetric potential is derived *a priori* and is not part of the MD simulation.

142   Based on these forces, particles are moved to new positions following the dictates of

143   Newton's second law of motion for several million femtosecond (10^{-15} s) time steps.

144   From the locations and velocities of the particles, various thermodynamic and transport

145   properties are computed using the formalism of macroscopic thermodynamics and

146   statistical mechanics. The potential of Matsui (1998) for the system Na_2O-CaO-MgO-

147   SiO_2-Al_2O_3 was utilized in this study. This potential incorporates Coulombic, Born and

148   van der Waals energies and fractional charges on the atoms. The Matsui potential has

149   been used in previous studies to determine the equation of state, tracer diffusivity and

150   shear viscosity for $CaAl_2Si_2O_8$, $CaMgSi_2O_6$, $MgSiO_3$, Mg_2SiO_4, and 1-bar eutectic

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151   composition (system $CaMgSi_2O_6$-$CaAl_2Si_2O_8$) liquid (Creamer, 2012; Martin et al., 2012;

152   Spera et al., 2011; Ghiorso and Spera, 2009; Spera et al., 2009; Nevins et al., 2009;

153   Martin et al., 2009). The Matsui potential provides a reasonable representation of these

154   liquids up to circa 30 GPa based on comparisons with laboratory data and results from

155   first-principles MD simulations on similar compositions (e.g., Sun et al, 2011; Karki et al,

156   2011; Stixrude et al, 2009). Technical details of the basic MD methodology are described

157   in Spera et al. (2009, 2011) and follow standard MD protocols. The time step used in all

158   simulations is 1 femtosecond (1 fs). All NEMD calculations for the thermal conductivity

159   start from a thermally equilibrated initial state following the methods described in Spera

160   et al. (2011).

161

162   Distinguishing Equilibrium Liquid from Non-equilibrium Glass

163   The pressure-temperature range of state points studied for both $NaAlSi_3O_8$ and

164    $CaMgSi_2O_6$ spans the transition from an equilibrium liquid to a non-equilibrium glass on

165   the timescale of the MD simulation. The simulations for Mg_2SiO_4 composition pertain

166   wholly to the liquid. It is important to make the distinction between glass and liquid

167   (melt) because the properties of a glass depend on its history unlike that of an equilibrium

168   or metastable liquid (Donth, 2001). When temperature is decreased rapidly on a liquid

169   and its intrinsic relaxation time exceeds the laboratory or simulation quenching timescale,

170   the liquid falls out of equilibrium and undergoes a kinetic transition to a glass. The glass

171   transition temperature (T_g) for a given composition depends on both quench rate and

172   pressure (Passaglia and Martin, 1964). The glass transition is not a transition in the

173   thermodynamic sense, but instead a kinetic phenomenon, where the amorphous solid with

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174   crystal-like vibrational properties is dynamically arrested and hence preserves the

175   disorder of the liquid (Roland et al, 2005; Langer, 2014). At typical laboratory cooling

176   rates of ~0.1-1 K/s, the glass transition temperature (T_g) for $NaAlSi_3O_8$ and $CaMgSi_2O_6$

177   liquids are 1036 K and 1023 K, respectively, at 1 bar (Arndt and Häberle, 1973, Reinsch

178   et al, 2008). Because the effective quench rates used in MD simulations are vastly

179   greater, of order ~ 10^2 K/ps (10^{14} K/s), the computer glass transition temperature is

180   significantly higher. For example, the computer T_g of $CaAl_2Si_2O_8$ defined by analysis of

181   the mean square displacement *versus* time (see below) is approximately 2800 K for a

182   quench rate of 70- 200 K/ps (Morgan and Spera, 2001). This is significantly higher than

183   the laboratory value of T_g =1025 K (Arndt and Häberle, 1973).

184   The transition from liquid to glass can be detected in MD simulations by two

185   means. For ergodic liquids an excellent correlation exists between the potential energy

186   (E_{POT}) and $T^{3/5}$ at constant density (Spera et al, 2009; Ghiorso and Spera, 2009; Martin et

187   al, 2012; Creamer, 2012). This scaling relationship, proposed by Rosenfeld and Tarazona

188   (1998), is called RT-scaling. Glasses exhibit imperfect RT scaling; on plots of E_{POT} vs

189    $T^{3/5}$ deviations from linearity along isochores occur around T_g and become more

190   pronounced as T decreases. A dynamical method for detection of the glass transition is

191   based on the mobility of atoms (tracer diffusivity) in Euclidean space. In an ergodic

192   liquid, the mean square displacement (MSD) of an atom is a linear function of time; a

193   plot of MSD vs. t in logarithmic coordinates exhibits a slope of unity after a short (< 100

194   fs) ballistic interval (Morgan and Spera, 2001). In contrast, glassy materials exhibit the

195   phenomena of sub-diffusion; a diffusion process with a non-linear relationship to time, in

196   contrast to a normal diffusion process in which the mean squared displacement (MSD) of

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197   a particle is a linear function of time (Wang et al, 2012). In particular, in the non-ergodic

198   region where sub-diffusion holds, the MSD exhibits power-law behavior with MSD $\sim t^{\delta}$

199   following a short ballistic interval. The exponent δ in a thermally arrested liquid (i.e., a

200   glass) is characterized by $\delta < 1$ (Metzler and Klafter, 2004; Weeks and Weitz, 2002). Sub-

201   diffusion arises when a system possesses memory, the hallmark of a non-equilibrium

202   material such as glass. For $CaMgSi_2O_6$ the computer glass transition in our simulations

203   occurs at $\sim 2630 \pm 50$ K at 1 bar. For $NaAlSi_3O_8$ composition, T_g is approximately 2800

204   K based on the RT scaling and MSD criteria. The glass transition temperature depends on

205   pressure in addition to quench rate. The variation of the computer glass transitions with

206   pressure for $CaMgSi_2O_6$ and $NaAlSi_3O_8$ found here empirically lies in the range 10-30

207   K/GPa. In the Tables below for thermal conductivity, glasses are distinguished from

208   liquids based on the RT and MSD analysis outlined above for compositions $NaAlSi_3O_8$

209   and $CaMgSi_2O_6$. The emphasis in this study is on equilibrium ergodic liquids, although

210   some glass results are included.

211   Non-Equilibrium Molecular Dynamics
212
213   Calculations of thermal conductivity from MD simulations can be performed in

214   two ways: Equilibrium MD (EMD) or NEMD. The Green-Kubo method, an EMD

215   approach, uses heat current fluctuations to compute the thermal conductivity *via* the

216   Kubo relations (Kubo, 1966). The microscopic definition of the heat flux for EMD

217   involves interparticle dynamic correlations requiring evaluation of pair velocities and

218   particle energies that are computationally expensive to evaluate and subject to large

219   fluctuations (Rapaport, 1995). Convergence of the current-current correlation function

220   can be slow. Here we employ a Non Equilibrium Molecular Dynamics (NEMD) method,

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221   which is relatively easy to implement, and has proved to be reliable (e.g., Müller-Plathe,

222   1997; Müller-Plathe and Bordat, 2004). In particular, the NEMD method has been

223   successfully applied to liquids giving excellent results in comparison with laboratory

224   measurements (Cao, 2008; Bedrov et al., 2000; Terao et al., 2007) and Green-Kubo

225   (EMD) calculations (Vogelsang et al., 1987).

226   The essential idea of the NEMD method used to obtain k is to impose a known

227   heat flux on the system by exchange of particle kinetic energies and then determine the

228   resulting steady-state temperature gradient in the direction parallel to the heat flux. The

229   thermal conductivity can then be expressed

230

$$k = \frac{\left\langle \int_{0}^{t_D} q_z(t)\,dt \right\rangle}{2 A t_D (dT/dz)}$$

(1)

231   where the integral is the cumulative heat flow imposed during a simulation of duration t_D

232   in the z direction, A is the cross-sectional area of the plane orthogonal to the z-axis, and

233   the temperature derivative is the observed linear temperature gradient once a stationary

234   thermal profile is achieved in the system. In order to impose a heat flux and compute the

235   temperature profile, the simulation box is divided into N slabs perpendicular to the z

236   direction. In the present work N lies between 20-50; all layers are of identical volume.

237   The heat flux is created by exchanging the barycentric velocities of identical type atoms

238   (e.g., O for O, Ca for Ca, etc) between what becomes a cold layer located in the middle of

239   the simulation box and what becomes a hot layer adjacent to one of the domain

240   boundaries. In particular, the velocity exchange is accomplished by switching an atom

241   with the largest kinetic energy (i.e., the hottest) from the cold slab with an atom of the

242   same type with the lowest kinetic energy (coldest) in the hot layer. Serial application of

243   this procedure induces a temperature gradient for a known quantity of heat exchange

244   based on the kinetic energies of the exchanged atoms. The instantaneous local kinetic

245   temperature $<T_k>$ in the kth slab is given by

246
$$T_k = \frac{1}{3k_B n_k} \sum_{i=1}^{n_k} m_i v_i^2 \qquad (2)$$

247   where the sum extends over all n_k atoms of each type of mass m_i and velocity $\mathbf{v_i}$ in the kth

248   slab. This exchange mechanism produces an energy transfer computed from

249
$$\left\langle \int_0^{t_D} q_z(t)dt \right\rangle = \sum_{transfers} (v_c^2 - v_h^2) \qquad (3)$$

250   The heat transfer leads to a temperature difference between the designated layers and

251   gives rise to a steady-state temperature gradient across each half of the system. This

252   temperature gradient is the desired quantity of the NEMD simulation. Exchanging the

253   velocities of two atoms of equal mass (e.g., an O for an O, a Ca for a Ca, etc) leaves the

254   total linear momentum, total kinetic energy, melt composition and the internal energy

255   unchanged. After reaching the thermal steady state, the energy transfer imposed by the

256   velocity exchange is exactly balanced by the heat flux in the opposite direction effected

257   by the phonon thermal conductivity of the liquid. The thermal conductivity is then

258   computed from the expression

259
$$k = \frac{\displaystyle\sum_{transfers} (v_c^2 - v_h^2)}{2t_D L_x L_y (dT/dz)} \qquad (4)$$

260   The sum is taken over all transfers over the duration t_D of the NEMD simulation starting

261   from an equilibrated initial state. All quantities in Eq. (4) are known exactly except the

262   temperature gradient that is obtained from Eq. (2) applied to each layer. The simulation is

263   terminated after a linear or nearly linear temperature gradient is established.

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264   Representative thermal profiles are given in Tikunoff (2013). Attainment of a linear T

265   profile typically requires simulations of 1-5 ns duration. In this study, tetragonal periodic

266   primary MD 'boxes' with $L_z > L_x = L_y$, as well as cubic boxes are used. When cubic boxes

267   are used, uncertainty in k is smaller, because more atoms are being simulated and

268   uncertainty of state point conditions scales according to $N_T^{-1/2}$ where N_T is the total

269   number of atoms used in the simulation. At each state point studied, simulations are

270   performed for several different simulation cell sizes to take account of finite-size effects

271   (see below). Because of the mirror plane at $z = L_z/2$, each simulation provides 2N

272   temperatures over distance L_z. The thermal gradient is determined by linear regression of

273   these 2N values each at a specific value of z corresponding to the mid-point of the layer.

274   The uncertainty of the thermal conductivity (σ_k) is found by propagation of error of the

275   temperature gradient found by regression of T against z. The value of k computed from

276   Eq (4) corresponds to the thermal conductivity at the mean temperature and pressure of

277   the simulation. Typically, with systems of 8000 atoms the uncertainty in T and P are $\pm$ 30

278   K and $\pm$ 0.25 GPa, respectively. These uncertainties can be made smaller by using more

279   particles since σ_T and σ_P scale according to $N^{-1/2}$. For example, with N=24,000 particles,

280   1σ fluctuations in T and P are $\sigma_T \approx 18$ K and $\sigma_P \approx 0.15$ GPa, respectively. In this study N_T

281   varied from 2500 to 350,000 and weighted regression has been used in all cases to find

282   the best statistical fits.

283

284   Critical NEMD parameters

285   There are two critical parameters in an NEMD simulation used to compute k: the

286   duration between particle swaps (Ω) or its reciprocal, the swap frequency, and the longest

287   dimension of the MD rectangular domain (L_z). Tuning of these parameters insures good

288   precision in k and efficient use of computational resources. In order to find the trade-off,

289   a number of simulations for molten diopside at ambient pressure and high T at various Ω

290   and L_z were conducted. Comparison with the laboratory measurements from Hofmeister

291   et al. (2009) at identical (within uncertainty) state points for $CaMgSi_2O_6$ affords an

292   objective evaluation of the quality of the NEMD simulations (see below). Additional

293   NEMD simulations were run on crystalline and supercritical argon, a benchmark material

294   in MD studies, in an earlier phase of this research; these results are presented elsewhere

295   (Tikunoff, 2013) where additional technical details may be found.

296   *Role of swap period (Ω)*

297   The swap period (Ω) is the period, in units of femtoseconds (fs), between particle

298   velocity swaps during the NEMD calculation. The calculated conductivity of amorphous

299    $CaMgSi_2O_6$ at ambient pressure (10^{-4} GPa) and 1700 K in a box of fixed L_z with its one-

300   sigma error (σ_k) is plotted against Ω in Figure 1. For the limiting value of $\Omega=1$ (not

301   shown on Figure 1), or one swap per 1 fs time step, the system does not have sufficient

302   time between velocity exchanges for thermal relaxation and relatively large statistical

303   fluctuations for the thermal gradient occur that obfuscate determination of the

304   conductivity. In contrast, for low swap periods ($\Omega=100$ or one exchange every 100 fs)

305   long simulation times are required for the system to achieve a steady-state temperature

306   profile since relatively little heat is transferred per swap. In this case, for fixed simulation

307   duration t_D, the uncertainty σ_k is relatively large, roughly 10-15 %, relative due to slow

308   convergence. Values of Ω between 20-40 give σ_k errors in the 2-6 % range, relative. In

309   light of the trade-off between computational burden and desired precision, values for Ω in

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310   this range appear optimal and have been used here. Similar results were found for argon

311   fluid (Tikunoff, 2013). For Ω in this range, k can be found with statistical uncertainty of

312   several percent, approximately equal to or less than experimental uncertainties in k for

313   silicate liquids of ~5% relative (Pertermann et al., 2008).

314   *Role of Simulation Cell Length (L_z)*

315   The thermal conductivity k exhibits a dependence on the size of the simulation

316   cell in the direction of the heat flux L_z when the size of the simulation volume is of the

317   same order as the longest phonon path length. This variation is explained by the increase

318   in the number of active phonon modes available as the system size increases as well as

319   the result of scattering that occurs at the interfaces of the heat source and sink in the

320   NEMD system. The interface scattering effect is well known in MD studies and methods

321   have been developed to account for it and hence obtain values of k appropriate for

322   macroscopic systems (Chantrenne and Barrat, 2004; Varshney et al. 2009; Stackhouse

323   and Stixrude, 2010). Finite-size effects are especially apparent in crystalline materials

324   because the long-range order intrinsic to crystals gives rise to long mean free phonon path

325   lengths that can exceed the size of the MD domain. In liquid and glassy materials, this is

326   less of a problem because phonon mean free path lengths (Λ) are of the same order as the

327   scale of short range order, approximately 0.3-0.6 nm for typical silicate liquids and

328   glasses without a great deal of variation (Kittel, 1949). Since the scale of short range

329   order is considerably less than the size of a typical MD simulation box filled with ~10^4

330   atoms of ~5-10 nm in our simulations, finite-system-size effects are less pronounced

331   compared to crystals. However, for good precision it is still desirable to account for

332   finite-system-size effects since variations in L_z constrain the magnitudes of L_x and L_y,

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333   necessarily, when tetragonal NEMD domains are utilized. The critical issue is the phonon

334   mean free path length in an infinite (macroscopic) system (Λ_∞) relative to the z-

335   dimension of the MD simulation box of length L_z. If the distance between the layers

336   undergoing velocity exchange ($L_z/2$) is comparable to Λ_∞, an effective mean free path Λ_{eff}

337   can be defined (Schelling et al., 2002; Yoon et al., 2004) according to:

$$\frac{1}{\Lambda_{eff}} = \frac{1}{\Lambda_\infty} + \frac{1}{L_z} \tag{5}$$

338

339   From kinetic theory, the phonon mean free path (MFP) is related to the sonic speed and

340   specific isochoric heat capacity of the material by (Bridgman, 1914; Kittel and Kroemer,

341   1980)

$$k = \tfrac{1}{3}\rho C_V c \Lambda_{eff} \tag{6}$$

342

343   where ρ is the melt density (kg/m^3), C_V is the isochoric specific heat capacity (J/ kg K)

344   and c is the sonic velocity (m/s). Substituting Eq. (5) into Eq. (6) gives a relation between

345   k and L_z:

$$\frac{1}{k} = A\left(\frac{1}{\Lambda_\infty} + \frac{1}{L_z}\right) \tag{7}$$

346

347

348   where $A = 3\left(\rho C_V c\right)^{-1}$ is constant at any given state point and composition. Eq. (7) is of

349   the form $1/k = C_1 + C_2/L_z$ where C_1 and C_2 are constants. To account for finite-system-

350   size effects, NEMD conductivities from simulations performed in different sized boxes

351   are plotted in $1/k$-$1/L_z$ coordinates. Extrapolation as $1/L_z \rightarrow 0$ gives the desired value of k

352   applicable to a macroscopic system. All of the thermal conductivity values reported

353   below for Mg_2SiO_4, $CaMgSi_2O_8$ and $NaAlSi_3O_8$ have been analyzed as a function of

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354 simulation cell length as outlined above to obtain the desired macroscopic k from Eq. (7)

355 using an optimal swap rates of $\Omega \sim$ 20-40 fs. Additional details on the NEMD method

356 and statistical treatment of data may be found in Tikunoff (2013).

357
358 # RESULTS
359
360   Values of the thermal conductivity at all state points for all compositions

361 including the fluctuations in T and P and the 1σ uncertainties in k are collected in Tables

362 1, 2 and 3 for $CaMgSi_2O_6$, $NaAlSi_3O_8$ and Mg_2SiO_4, respectively. Figure 2 illustrates the

363 calculation of finite-size effects, where the inverse of the thermal conductivity as a

364 function of simulation cell length is plotted for $CaMgSi_2O_6$ at fixed P and T.

365 Extrapolation of the regression line to an infinite size system gives the phonon thermal

366 conductivity k=1.143 $\pm$ 0.004 (1 σ) W/m K. This compares to the laboratory value at

367 2000 K and ambient pressure of 1.159 $\pm$ 0.058 from Hofmeister et al. (2009) quite well.

368 As another example, the NEMD value of k for diopside composition at 1763 K and 1-bar

369 of 1.186 $\pm$0.019 W/m K, in this case uncorrected for a small finite-size effect, is within 1

370 % of the laboratory value of 1.178 $\pm$0.06 W/m K also from Hofmeister et al. (2009).

371 Finally, extrapolation of the 1800 K (1-bar) laboratory measurement for molten albite

372 from Hofmeister et al (2009) gives a value of 1.55 W/m K that can be compared to the

373 NEMD value at 2091 K and 1-bar (Table 2) of 1.498 W/m K. In conclusion, values

374 computed for $NaAlSi_3O_8$ and $CaMgSi_2O_6$ compositions from NEMD compare well with

375 laboratory results at ambient pressure. Evidently, the Matsui potential can recover

376 accurate thermal conductivities at ambient pressure for these compositions. NEMD

377 simulations for glassy materials, based on the criteria given earlier, are identified

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378   explicitly in the Tables. All others are for equilibrium or metastable liquids. Here we

379   summarize the effects of T, P and composition on the thermal conductivity.

380   *CaMgSi$_2$O$_6$*

381   All calculated k values for CaMgSi$_2$O$_6$ composition (both liquids and glass) are

382   plotted on Figure 3. As T increases, k decreases, at all pressures although the effect is

383   diminished as P increases. Figure 4 illustrates that a T increase from 3000 K to 4500 K

384   decreases k by ~ 25 % from 1.02 W/m K to 0.72 in diopside liquid at ambient pressure.

385   At higher pressure (~10 GPa), the T-dependence of k is substantially weaker. At ~ 20

386   GPa, k depends weakly on temperature and assumes a value of ~2.4 W/m K (Table 1). In

387   diopside liquid at 3500 K, a pressure increase from ambient to ~ 20 GPa increases k from

388   ~1.15 W/m K to 2.5 W/m K, an increase of more than 100%. The increase in k with

389   increasing P along an isotherm only slightly depends upon T. For example, at ~4500 K, k

390   increases from 0.73 W/m K at ambient pressure to 2.28 W/m K at ~20 GPa, an increase

391   by a factor greater than 3 which is comparable to the increase with pressure at lower T.

392   In summary, for CaMgSi$_2$O$_6$ k decreases with increasing temperature along an

393   isobar. The effect of increasing pressure on k along an isotherm is rather significant: a

394   factor of ~ 2-3 as pressure increases from ambient to ~30 GPa. The trade-off between the

395   opposing effects of increasing T and P on thermal conductivity for molten diopside can

396   be evaluated by computing the change in k along the diopside liquid 2000 K isentrope.

397   Temperature along the isentrope is given by $T = T_o \exp(\alpha P / \rho C_P)$, where α is the

398   isobaric expansivity, ρ is the melt density and C_P is the isobaric specific heat capacity.

399   Adopting MD-derived mean values of density, heat capacity and expansivity along the

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400   isentrope for liquid diopside from Creamer (2012), one finds that k increases by a factor

401   of 2.2 as pressure increases to 30 GPa along the 2000 K isentrope.

402   *Liquid albite*

403   Albite liquid exhibits k-P-T dependence that is qualitatively similar to molten

404   diopside; all values are listed in Table 2 and depicted in Figure 5. The thermal

405   conductivity decreases with increasing T along an isobar and strongly increases as

406   pressure increases along an isotherm. For example, at ~ 4000 K, k increases from 0.9 to

407   2.6 W/m K from near ambient pressure to ~30 GPa whereas at ambient P, in the T range

408   2100-4024 K, k decreases from 1.45 W/m K to 0.89 W/m K. Similarly, at ~30 GPa, as T

409   increases in the sequence 2060 K, 3068 K, 4034 K, thermal conductivity decreases in the

410   sequence 2.88 W/m K, 2.72 W/ m K, 2.60 W/m K, respectively. In general, thermal

411   conductivity for albite liquid exceeds that for liquid diopside when compared at identical

412   (or nearly so) T-P conditions, although differences become smaller as P increases.

413   *Liquid forsterite*

414   Liquid forsterite shows the strongest negative correlation of k with T at ambient

415   pressure of the three liquid compositions studied. The conductivity decreases from 1.37

416   W/ m K at 2560 K to 0.68 W/ m K at 4580 K (Figure 6). Similar to the other

417   compositions, along an isotherm, k increases substantially as pressure increases (Figure

418   7). For example, at ~3550 K, k increases from 0.90 W/ m K to 2.12 W/ m K as pressure

419   increases from ambient to from ambient to 11 GPa pressure, an increase by a factor of

420   2.4, similar to the behavior in diopside and albite melts.

421   *Glass*

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422   For $CaMgSi_2O_6$ at 2076 K and 2551 K and for $NaAlSi_3O_8$ at 2070 K and 3056 K,

423 the temperature is below the computer glass transition at all pressures. For glassy

424 diopside at fixed pressure, there is a very slight T-dependence of k such that as T

425 increases, k decreases. In contrast, along an isotherm k increases appreciably as pressure

426 increases. For example, at T=2076 K, k increases from 1.14 W/m K at zero pressure to

427 2.89 W/ m K at ~30 GPa, an increase by a factor of ~ 2.5. Glassy albite exhibits similar

428 behavior: a weak, almost negligible, negative dependence of thermal conductivity with

429 temperature but a rather strong increase in k as pressure increases along an isotherm. The

430 weak isobaric thermal dependence of the thermal conductivity of albite and diopside

431 glass is consistent with the experimental findings of Hofmeister et al (2009) as is the

432 observation that glass k values are larger than values for corresponding liquids when

433 compared at temperatures around the glass transition. Because the properties of a glass

434 depend on its preparation (thermal) history, direct comparison between NEMD values

435 and laboratory results is not meaningful given the enormously different cooling rates

436 during preparation of computer versus laboratory glasses. Additional NEMD simulations

437 on the glasses are needed to quantify the effects of preparation history on glass thermal

438 conductivity. Diopsidic and albitic glasses have thermal conductivities of k=1.14 W/m K

439 and k=1.50 W/m K, respectively, at similar state points (e.g., T=2059 ±12 K, P=-0.04

440 ±0.14 GPa and T=2091 ±20 K, P=0.20 ±0.23 GPa, respectively). The more polymerized

441 $NaAlSi_3O_8$ composition in which, to first order, each oxygen has two nearest neighbors

442 of Si and/or Al (at low pressure) is a better thermal conductor than the less polymerized

443 composition $CaMgSi_2O_6$ in which, to first order, two of the three oxygens of the

444 metasilicate (SiO_3) backbone have one nearest neighbor of Si and the remaining oxygen

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445   is bridging oxygen. The relationship between glass or melt atomic structure and phonon

446   conductivity is discussed more fully in Part II. Here we note that as pressure increases,

447   this effect becomes quantitatively muted since, at high pressures structures approximately

448   converge being dominated by high coordination numbers.

449

450   **IMPLICATIONS**

451   Although quantitative knowledge of the effects of temperature, pressure and

452   composition on the phonon conductivity of silicate liquids is critical for the analysis of

453   many geophysical and petrological problems, very few measurements exist due to

454   experimental difficulties. There are virtually no measurements on the effects of pressure

455   on thermal conductivity of silicate liquids that we are aware of. In this study, we have

456   implemented a Nonequilibrium Molecular Dynamics technique within the context of

457   classical Molecular Dynamics to study the phonon conductivities of amorphous (molten

458   and glassy) Mg_2SiO_4, $CaMgSi_2O_6$ and $NaAlSi_3O_8$ at elevated temperatures (2500-4500

459   K) and pressures (0-30 GPa) and provide estimates of this important geophysical

460   parameter in these liquids. The NEMD method takes account of finite-size effects and

461   faithfully captures experimental thermal conductivities for simple fluids such as Ar and

462   alkali halide liquids. The NEMD results compare very well with ambient pressure

463   experimental values for liquid $CaMgSi_2O_6$ and $NaAlSi_3O_8$ from Hofmeister et al (2009).

464   For example, experimental values at 1-bar for $CaMgSi_2O_6$ and $NaAlSi_3O_8$ at 2000 K of

465   1.15 W/m K and 1.55 W/m K compare well with the NEMD values at the same state

466   point of 1.14 W/m K and 1.45 W/m K, respectively. In the temperature range of this

467   study all compositions exhibit a negative dependence of k with temperature and a strong

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468 positive dependence of k with pressure. There is also a discernable effect at low pressure

469 and identical temperatures such that the thermal conductivity increases as the extent of

470 polymerization increases. For example, molten albite, exhibits a greater thermal

471 conductivity than molten Mg_2SiO_4 when compared at comparable state points. As

472 pressure increases this polymerization effect is damped presumably because the effect of

473 pressure is to increase the coordination number of oxygen around a central Si and

474 likewise the coordination number of Si and other cations around a central oxygen. As

475 pressure increases, all compositions become closer in structure and hence the structural

476 control on thermal conductivity diminishes. In part II of this study, the MD-derived

477 thermal conductivities are related to macroscopic thermodynamic properties and melt

478 structures.

479

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References

Allwardt, J.R., Stebbins, J., Terasaki, H., Du, Lin-Shu, Frost, D.J., Withers, A.C., Hirschmann, M.M., Suzuki, A., and Ohtani, E. (2007) Effect of structural transitions on properties of high-pressure silicate melts; ^{27}Al NMR, glass densities, and melt viscosities. American Mineralogist, 92, 1093-1104.

Anzellini, S., Dewaele, A., Mezouar, M., Loubeyre, P., and Morard, G. (2013) Melting of Iron at Earth's Inner Core Boundary Based on Fast X-ray Diffraction. Science, 340, 464-466.

Arndt, J., and Häberle, F. (1973) Thermal expansion and glass transition temperatures of synthetic glasses of plagioclase-like compositions. Contributions to Mineralogy and Petrology, 39, 175-183.

Beck, P., Goncharov, A.F., Struzhkin, V., Militzer, B., Mao, H.-K., and Hemley, R.J. (2007) Measurement of thermal diffusivity at high pressure using a transient heating technique. Applied Physics Letters, 91, 181914-(1-3).

Bedrov, D., Smith, G.D., and Sewell, T.D. (2000) Thermal conductivity of liquid octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from molecular dynamics simulations. Chemical Physics Letters, 324, 64-68.

Bridgman, P.W. (1914) A complete collection of thermodynamic formulas. Physical Review, 3, 273-281.

Cao, B.Y. (2008) Nonequilibrium molecular dynamics calculation of the thermal conductivity based on an improvised relaxation scheme. The Journal of Chemical Physics, 129, 074106 1-8.

Chantrenne, P., and Barrat, J.-L. (2004) Finite size effects in determination of thermal conductivities: comparing molecular dynamics results with simple models. Journal of Heat Transfer, 126, 577–585.

Creamer, J. (2012) Modeling fluid-rock Interaction, melt-rock interaction, and silicate melt properties at crustal to planetary interior conditions. PhD. thesis, University of California, Santa Barbara, 117 p.

Daniel, I., Gillet, P., McMillan, P.F., and Poe, B.T. (1996) Raman spectroscopic study of structural changes in calcium aluminate ($CaAl_2O_4$) glass at high pressure and high temperature. Chemical Geology, 128, 5-15.

de Koker, N., Steinle-Neumann, G., and Vlcek, V. (2012) Electrical resistivity and thermal conductivity of liquid Fe alloys at high P and T, and heat flux in the Earth's core. Proceedings of the National Academy of Sciences, 109, 4070-4073.

Revision 2

527 Degiovanni A., Andre S., and Maillet D. (1994) Phonic conductivity measurement of a
528 semi - transparent material. In: Tong TW (ed) Thermal conductivity 22. Technomic,
529 Lancaster, PN, pp 623-633.
530
531 Donth, E-J. (2001) Relaxation Dynamics in Liquids and Disordered Materials. Springer
532 Series in Materials Science, 48, 419.
533
534 Galamba, N., Nieto de Castro, C.A., and Ely, J.F. (2004) Thermal conductivity of molten
535 alkali halides from equilibrium molecular dynamics simulations. Journal of Chemical
536 Physics, 120, 8676-8682.
537
538 Ghiorso M., and Spera F. (2009) Large scale simulations. Reviews of Mineralogy and
539 Geochemistry, 71, 437-463 (eds. R. Wentzcovitch and L. Stixrude). Mineralogical
540 Society of America.
541
542 Giordano, D., and Dingwell, D. B. (2003) The kinetic fragility of natural silicate melts.
543 Journal of Physics: Condensed Matter, 15, S945.
544
545 Hammerschmidt, U., and Sabuga, W. (2000) Transient Hot Wire Method (THW):
546 Uncertainty Assessment. International Journal of Thermophysics, 21, 1255-78.
547
548 Healy, J.J, de Groot, J.J, and Kestin, J. (1976) The Theory of the Transient Hot-Wire
549 Method for Measuring Thermal Conductivity. Physica C, 82, 392-408.
550
551 Hernlund, J., and Jellinek, A. (2010) Dynamics and structure of a stirred partially molten
552 ultralow-velocity zone. Earth and Planetary Science Letters, 296, 1-8.
553
554 Hofmeister, A. (2007) Pressure dependence of thermal transport properties. Proceedings
555 of the National Academy of Sciences, 104, 9192-7.
556
557 Hofmeister, A.M., Whittington, A.G., and Pertermann, M. (2009). Transport properties of
558 high albite crystals and near-end member feldspar and pyroxene glasses and melts to high
559 temperature. Contributions to Mineralogy and Petrology, 158, Pp. 381-400.
560
561 Idehara, K. (2011) Structural heterogeneity of an ultra-low-velocity zone beneath the
562 Philippine Islands: Implications for core–mantle chemical interactions induced by
563 massive partial melting at the bottom of the mantle. Physics of the Earth and Planetary
564 Interiors, 184, 80–90.
565
566 Kang, Y., and Morita, K. (2006) Thermal Conductivity of the $CaO-Al_2O_3-SiO_2$ System.
567 Iron and Steel Institute of Japan International, 46, 420-426.
568
569 Karki, B. B., Bohara, B., and Stixrude, L. (2011) First-principles study of diffusion and
570 viscosity of anorthite (CaAl2Si2O8) liquid at high pressure. American Mineralogist, 96,
571 744-751.
572

Revision 2

573   Kittel, C. (1949) Interpretation of the thermal conductivity of glasses. Physical Review
574   Series II, 75, 972-974.
575
576   Kittel, C., and Kroemer, H. (1980) Thermal Physics. W. H. Freeman and Company.
577
578   Kubo, R. (1966) The fluctuation-dissipation theorem. Reports on Progress in Physics, 29,
579   255-284.
580
581   Langer, J.S. (2014) Theories of glass formation and the glass transition. Reports on
582   Progress in Physics, 77, 042501.
583
584   Lee, H. L., and Hasselman, D.P.H. (1985) Comparison of Data for Thermal Diffusivity
585   Obtained by Laser-Flash Method Using Thermocouple and Photodetector. Journal of the
586   American Ceramic Society, 68, C-12–C-13.
587
588   Martin, B., Spera, F.J., Ghiorso, M., and Nevins, D. (2009) Structure, thermodynamic
589   and transport properties of molten Mg_2SiO_4: Molecular dynamics simulations and model
590   EOS. American Mineralogist, 94, 693-703.
591
592   Martin G.B., Ghiorso, M., and Spera, F. (2012) Transport properties and equation of
593   1954state of 1-bar eutectic melt in the system $CaAl_2Si_2O_8$-$CaMgSi_2O_6$ by molecular
594   dynamics simulation. American Mineralogist, 97, 1155-1164.
595
596   Martinez, L.M., and Angell, C.A. (2001) A thermodynamic connection to the fragility of
597   glass-forming liquids. Nature, 410, 663-667.
598
599   Matsui M. (1998) Computational modeling of crystals and liquids in the system Na2O–
600   CaO–MgO–Al2O3–SiO2. In Properties of Earth and Planetary Materials at High Pressure
601   and Temperature (eds. M. H. Manghnani and T. Yagi). AGU, Washington, DC, pp. 145–
602   148.
603
604   McBirney, A., and Murase, T. (1973) Rheological Properties of Magma. Annual Review
605   of Earth and Planetary Sciences, 12, 337-357.
606
607   Mehling, H., Hautzinger, G., Nilsson, O., Fricke, J., Hofmann, R., and Hahn, O. (1998)
608   Thermal Diffusivity of Semitransparent Materials Determined by the Laser-Flash Method
609   Applying a New Analytical Model. International Journal of Thermophysics, 19, 941-949.
610
611   Metzler, R., and Klafter, J. (2004) The restaurant at the end of the random walk: recent
612   developments in the description of anomalous transport by fractional dynamics. Journal
613   of Physics A: Mathematical and General, 37, R161-R208.
614
615   Morgan, N. A., and Spera, F. J. (2001) A molecular dynamics study of the glass transition
616   in $CaAl_2Si_2O_8$: Thermodynamics and tracer diffusion. American Mineralogist, 86, 915-
617   926.
618

Revision 2

619   Müller-Plathe, F. (1997) A simple nonequilibrium molecular dynamics method for
620   calculating the thermal conductivity. Journal of Chemical Physics, 106, 6082-85.
621

622   Müller-Plathe, F., and Bordat, P. (2004) Novel Methods in Soft Matter Simulations,
623   edited by M. Karttunen, I. Vattulainen, and A. Lukkarinen, Lecture Notes in Physics Vol.
624   640. Springer, Heidelberg, Germany.
625

626   Mysen, B.O., and Richet, P. (2005) Silicate Glasses and Melts, Properties and Structure.
627   Elsevier, Amsterdam, Pp. 544.
628

629   Nevins, D., Spera, F.J., and Ghiorso, M. (2009) Shear Viscosity and diffusion in liquid
630   $MgSiO_3$: Transport properties and implications for terrestrial planet magma oceans.
631   American Mineralogist, 94, 975-980.
632

633   Olsen, P. (2013) The geodynamo's unique longevity. Physics Today 66, 11, 30.
634

635   Passaglia, E., and Martin, G.M. (1964) Variation of glass temperature with pressure in
636   polypropylene. The Journal of Research of the National Institute of Standards and
637   Technology, 68A, 273.
638

639   Pertermann, M., and Hofmeister, A. (2006) Thermal diffusivity of Olivine-group
640   minerals at high temperature. American Mineralogist, 91, 1747-1760.
641

642   Pertermann, M., Whittington, A.G., Hofmeister, A.M., Spera, F., and Zayak, J. (2008)
643   Transport properties of low-sanidine single-crystals, glasses and melts at high
644   temperature. Contributions to Minerology and Petrology, 155, 689-702.
645

646   Rapaport D. C. (1995) The Art of Molecular Dynamics Simulation. Cambridge
647   University Press.
648

649   Reinsch, S., Nacimiento, M.L.F., Muller, R., and Zanotto, E.D. (2008) Crystal growth
650   kinetics in cordierite and diopside glasses in wide temperature ranges. Journal of Non-
651   Crystalline Solids, 354, 5386-5394.
652

653   Roland, C.M., Hensel-Bielowka, S., Paluch, M., and Casalini, R. (2005) Supercooled
654   dynamics of glass-forming liquids and polymers under hydrostatic pressure. Reports on
655   Progress in Physics, 68, 140.
656

657   Rosenfeld, Y., and Tarazona, P. (1998) Density functional theory and the asymptotic high
658   density expansion of the free energy of classical solids and fluids. Molecular Physics: An
659   International Journal at the Interface Between Chemistry and Physics, 95, 141-150.
660

661   Schelling, P.K., Phillpot, S.R., and Keblinski, P. (2002) Comparison of atomic-level
662   simulation methods for computing thermal conductivity. Physical Review B, 65, 144306
663   1-12.
664

Revision 2

665

666   Spera, F.J., Nevins, D., Ghiorso, M.S., and Cutler, I. (2009) Structure, thermodynamics
667   and transport properties of $CaAl_2Si_2O_8$ liquid. Part I: Molecular dynamics simulations.
668   Geochimica et Cosmochimica Acta, 73, 6918-6936.
669

670   Spera, F.J., Ghiorso, M. S., and Nevins, D. (2011) Structure, thermodynamic and
671   transport properties of liquid $MgSiO_3$: Comparison of molecular models and laboratory
672   results. Geochimica et Cosmochimica Acta, 75, 1272-1296.
673

674   Stackhouse, S and Stixrude, L. (2010) Theoretical Methods for Calculating the Lattice
675   Thermal Conductivity of Minerals. Reviews in Mineralogy & Geochemistry. 71, 253-
676   269.
677

678   Stixrude, L., de Koker, N., Sun, N., Mookherjee, M., and Karki, B.B. (2009)
679   Thermodynamics of silicate liquids in the deep Earth. Earth and Planetary Science Letters,
680   278, 226-232.
681

682   Sun, N., Stixrude, L., de Koker, N., and Karki, B.B. (2011) First principles molecular
683   dynamics simulations of diopside (CaMgSi2O6) liquid to high pressure. Geochimica et
684   Cosmochimica Acta, 75, 3792-3802.
685

686   Terao, T., Lussetti, E., and Müller-Plathe F. (2007) Nonequilibrium molecular dynamics
687   methods for computing the thermal conductivity: application to amorphous polymers.
688   Physical Review E, 75.
689

690   Tikunoff, D. (2013) Composition, Temperature and Pressure Dependence of the Phonon
691   (Thermal) Conductivity of Silicate Geoliquids. M.S. thesis, University of California,
692   Santa Barbara, 73 p.
693

694   Tritt T.M., and Weston D. (2004) Measurement techniques and considerations for
695   determining thermal conductivity of bulk materials. Tritt T.M., Thermal conductivity
696   theory, properties, and applications, Kluwer Academic/Plenum Publishers, New York,
697   187–203.
698

699   Varshney,V., Patnaik,S., Roy, A., and Farmer, B. (2009) Heat Transport in Epoxy
700   Networks: a Molecular Dynamics Study. Polymer, 50, 3378-3385.
701

702   Vogelsang, R., Hoheisel, C. and Ciccotti, G. (1987) Thermal conductivity of the
703   Lennard-Jones liquid by molecular dynamics calculations. The Journal of Chemical
704   Physics, 86, 6371-6375.
705

706   Wang, B., Kuo, J., Bae, S., and Granick, S. (2012) When Brownian Diffusion is not
707   Gaussian. Nature Materials, 11, 481.
708

709   Weeks, E. R., and Weitz D.A. (2002) Subdiffusion and the cage effect studied near the
710   colloidal glass transition. Journal of Chemical Physics, 284, 361-367.

Revision 2

711
712 Wen, L., and Helmberger, D. (1998) Ultra-Low Velocity Zones Near the Core-Mantle
713 Boundary from Broadband PKP Precursors. Science, 279, 1701-1703.
714
715 Whittington, A., Hofmeister, A., and Nabelek, P. (2009) Temperature Dependent
716 Thermal Diffusivity of the Earth's Crust and Implications for Magmatism. Nature, 458,
717 319-321.
718
719 Yoon, Y.G., Car, R., Srolovitz, D.J., and Scandolo, S. (2004) Thermal conductivity of
720 crystalline quartz from classical simulations. Physical Review B, 70, 012302 1-4.
721
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729   **Figure Legends**

730

731   **Figure 1**: Phonon thermal conductivity of $CaMgSi_2O_6$ (ρ=2569 kg/m^3 at P=0.36 ±0.17

732   GPa and T=1764 ±13 K) versus particle swap time interval Ω in femtoseconds. Aspect

733   ratio of the NEMD box equals unity (i.e., k has not been corrected for finite-system-size

734   effects). For large values of Ω, the uncertainty in k is relatively large although its mean

735   value is not very different from the best estimate of 1.154 ±0.02 W/m K at Ω=20. The

736   laboratory value from Hofmeister et al. (2009) at 1764 K and 1 bar is 1.17 ±0.06 W/m K.

737   Applying a finite-system-size correction increases the value of k whereas the effect of

738   pressure is to increase k from its one-bar value. These effects approximately cancel in

739   this case. In the remainder of this work the duration between swap events is between 10

740   and 30 fs, and the total duration of NEMD simulation is 2 ns.

741

742   **Figure 2**: Inverse phonon thermal conductivity (k^{-1}) *versus* inverse system cell length L_z

743   for $CaMgSi_2O_6$ at T=2060 ±15 K, P= -0.04 ±0.15 GPa and ρ=2392 kg/m^3. Extrapolation

744   in the limit $L_z \rightarrow 0$, the intercept, gives the value k=1.143 ±0.004 W/m K. This can be

745   compared to the laboratory value at 2000 K and ambient pressure of 1.159 ±0.058 from

746   Hofmeister et al. (2009). The number of particles N used in the simulations for L_z = 4.22

747   nm, 8.44 nm, 12.66 nm and 16.88 nm are 5000,10000,15000 and 20000, respectively. In

748   all cases the swap time interval is Ω= 20 fs and the total simulation duration t_D= 2 ns.

749

750   **Figure 3**: Thermal conductivity for amorphous diopside (glass and liquid) *versus*

751   pressure along quasi-isotherms ~2000 K, 2500 K, 3500 K and 4500 K. Raw data is in

752   Table 1. Data at the highest pressure are near the limits of the classical potential used in

753   the simulations and are included for the purposes of completeness.

754

755   **Figure 4:** Variation of thermal conductivity at ambient conditions and at 10 GPa for

756    $CaMgSi_2O_6$ composition. The effect of T on k is muted as pressure increases.

757

758   **Figure 5**: Thermal conductivity for amorphous albite (glass and liquid) *versus* pressure

759   along three quasi-isotherms at ~2000 K, 3000 K and 4000 K. Raw data can be found in

760   Table 2.

761

762   **Figure 5**: Thermal conductivity for amorphous albite (glass and liquid) *versus* pressure

763   along three quasi-isotherms at ~2000 K, 3000 K and 4000 K. Raw data can be found in

764   Table 2.

765

766   **Figure 6:** Thermal conductivity of molten Mg_2SiO_4 at $P = 0.07 \pm 0.16 GPa$ as a function

767   of temperature.

768

769   **Figure7:** Thermal conductivity of molten Mg_2SiO_4 as a function of pressure along the

770    $T = 3548 \pm 18 K$ isotherm.

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TABLES

Table 1: NEMD results for liquid and glassy $CaMgSi_2O_6$. Temperatures in bold are
averages used in the Figures. 1σ fluctuations are reported for T and P of the NEMD run.
1σ errors for k are found by propagation of error of the computed T gradient and the
deviation from linearity in $1/k$ *versus* $1/L_z$.

Density (kg/m^3)	T (K)	σ_T (K)	P (GPa)	σ_P (GPa)	k (W/m K)	σ_k (W/m K)	State
2392.49	2059	12.31	-0.04	0.14	1.143	0.002	*Glass*
2936.33	2067	11.07	5.24	0.16	1.585	0.009	*Glass*
3199.44	2084	11.93	10.09	0.17	2.023	0.067	*Glass*
3593.14	2075	15.85	20.20	0.26	2.262	0.060	*Glass*
3882.94	2096	12.55	31.63	0.15	2.870	0.113	*Glass*
	2076						
2287.70	2519	30.38	0.13	0.33	1.194	0.040	*Glass*
2842.69	2554	18.21	5.27	0.21	1.611	0.087	*Glass*
3115.19	2559	18.47	10.07	0.27	1.914	0.057	*Glass*
3543.53	2561	18.11	21.51	0.27	2.400	0.099	*Glass*
3800.88	2561	22.28	31.30	0.35	2.265	0.067	*Glass*
	2551						
2250.00	2815	13.60	0.37	0.13	1.088	0.022	Liquid
3107.01	2812	17.00	10.80	0.25	1.990	0.004	Liquid
2130.00	3055	14.57	0.18	0.13	1.018	0.003	Liquid
3047.07	3060	19.88	10.39	0.23	1.942	0.022	Liquid
1990.00	3300	15.89	0.03	0.12	0.899	0.006	Liquid
3017.68	3295	21.26	10.51	0.25	1.930	0.002	Liquid
2043.78	3558	22.13	0.43	0.16	0.977	0.007	Liquid
2770.78	3562	12.01	6.82	0.12	1.903	0.005	Liquid
2931.74	3540	22.92	9.59	0.28	1.862	0.014	Liquid
3354.22	3516	31.20	20.24	0.38	2.495	0.099	Liquid
3618.39	3523	28.35	30.10	0.36	3.045	0.110	Liquid
	3540						
1570.00	3814	19.26	-0.13	0.10	0.675	0.012	Liquid
2950.00	3784	17.60	10.69	0.19	1.892	0.002	Liquid
1770.00	4053	20.00	0.23	0.12	0.801	0.001	Liquid
2910.00	4037	18.81	10.64	0.19	1.962	0.005	Liquid
1730.00	4304	20.82	0.35	0.12	0.768	0.011	Liquid

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2870.00	4313	21.92	10.64	0.21	1.850	0.041	Liquid
1625.79	4527	28.72	0.33	0.15	0.717	0.014	Liquid
2506.22	4521	36.77	5.40	0.30	1.437	0.024	Liquid
2824.53	4525	30.94	10.38	0.27	1.847	0.072	Liquid
3199.46	4525	38.37	19.71	0.41	2.280	0.145	Liquid
3494.87	4488	44.71	30.18	0.52	2.292	0.093	Liquid
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Table 2: NEMD results for liquid and glassy $NaAlSi_3O_8$. Temperatures in bold are
averages used in the Figures. 1σ fluctuations are reported for T and P of the NEMD run.
1σ errors for k are found by propagation of error of the computed T gradient and the
deviation from linearity in $1/k$ *versus* $1/L_z$.

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Density (kg/m^3)	T (K)	σ_T (K)	P (GPa)	σ_P (GPa)	k (W/mK)	σ_k (W/mK)	State
2313.68	2091	20.30	0.20	0.23	1.454	0.083	*Glass*
2786.85	2057	23.56	4.96	0.36	1.959	0.028	*Glass*
3072.49	2078	19.75	10.22	0.33	2.161	0.133	*Glass*
3487.10	2064	17.75	21.51	0.31	2.381	0.089	*Glass*
3698.19	2060	19.00	29.61	0.28	2.883	0.152	*Glass*
	2070						
2093.73	3062	19.90	0.04	0.19	0.989	0.036	*Glass*
2737.45	3057	23.72	6.05	0.29	1.768	0.093	*Glass*
2960.77	3047	24.97	10.31	0.30	2.548	0.135	*Glass*
3271.26	3046	23.22	18.65	0.34	2.294	0.059	*Glass*
3578.91	3068	19.05	30.55	0.30	2.716	0.142	*Glass*
	3056						
1841.85	4024	43.56	0.22	0.27	0.888	0.033	Liquid
2550.35	4013	37.82	5.11	0.37	1.652	0.098	Liquid
2803.67	3996	33.72	9.42	0.43	1.884	0.055	Liquid
3250.39	4016	36.07	21.88	0.48	2.417	0.022	Liquid
3464.66	4034	30.61	30.72	0.39	2.597	0.206	Liquid
	4017						

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803   **Table 3**: NEMD results for liquid Mg_2SiO_4 thermal conductivity values. Temperatures
804   and Pressures in bold are averages used in the Figures. 1σ fluctuations are reported for T
805   and P of the NEMD run. 1σ errors for k are found by propagation of error of the
806   computed T gradient and the deviation from linearity in 1/k *versus* $1/L_z$.

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Density (kg/m^3)	T (K)	σ_T (K)	P (GPa)	σ_P (GPa)	k (W/mK)	σ_k (W/mK)
2324.97	2549	12.51	0.02	0.14	1.364	0.009
2163.23	2723	27.75	-0.35	0.26	1.163	0.020
2163.23	3023	30.64	0.09	0.27	1.170	0.038
2031.11	3289	16.77	0.00	0.13	1.056	0.005
1825.22	3555	18.67	-0.16	0.12	0.896	0.002
1939.27	3805	18.60	0.36	0.13	1.043	0.004
1798.12	4062	19.39	0.26	0.12	0.933	0.001
1588.67	4581	30.48	0.34	0.11	0.681	0.001
			0.07			
1825.22	3555	18.67	-0.16	0.12	0.896	0.002
2306.17	3567	19.63	1.79	0.15	1.292	0.008
2503.73	3552	16.96	3.51	0.17	1.629	0.013
2724.53	3528	17.79	6.28	0.18	1.825	0.023
2844.71	3535	18.21	8.32	0.19	1.936	0.023
2972.07	3554	17.97	10.96	0.20	2.114	0.005
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812 **FIGURES**

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814 **Figure 1**
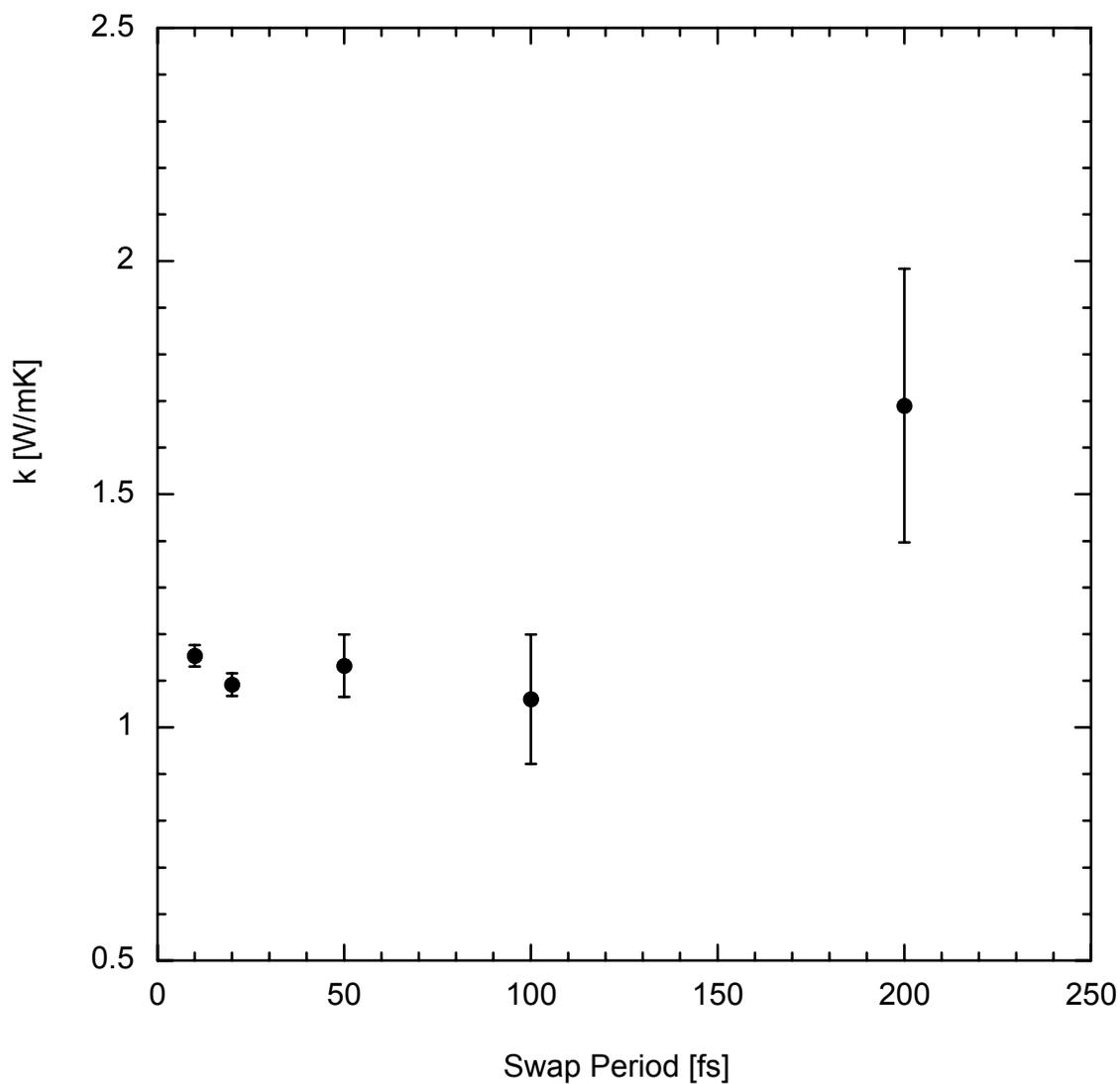
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816   **Figure 2**

The plot shows k^{-1} [W/mK^{-1}] on the y-axis versus L_z^{-1} [Å^{-1}] on the x-axis, with the fit:

$$k^{-1} = 0.88 + 4.30 L_z^{-1}$$

$$R^2 = 0.996$$
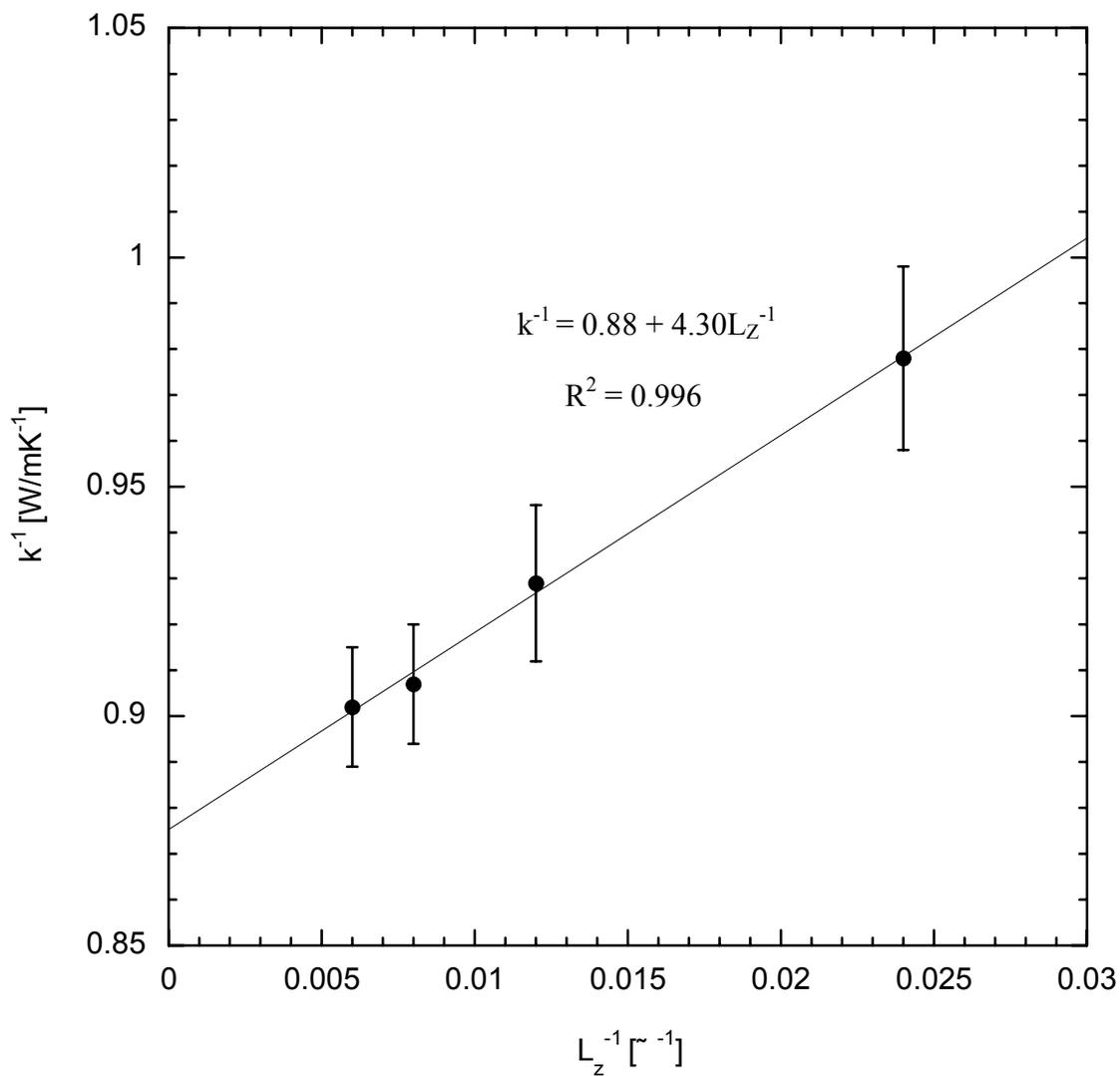
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828   **Figure 3**

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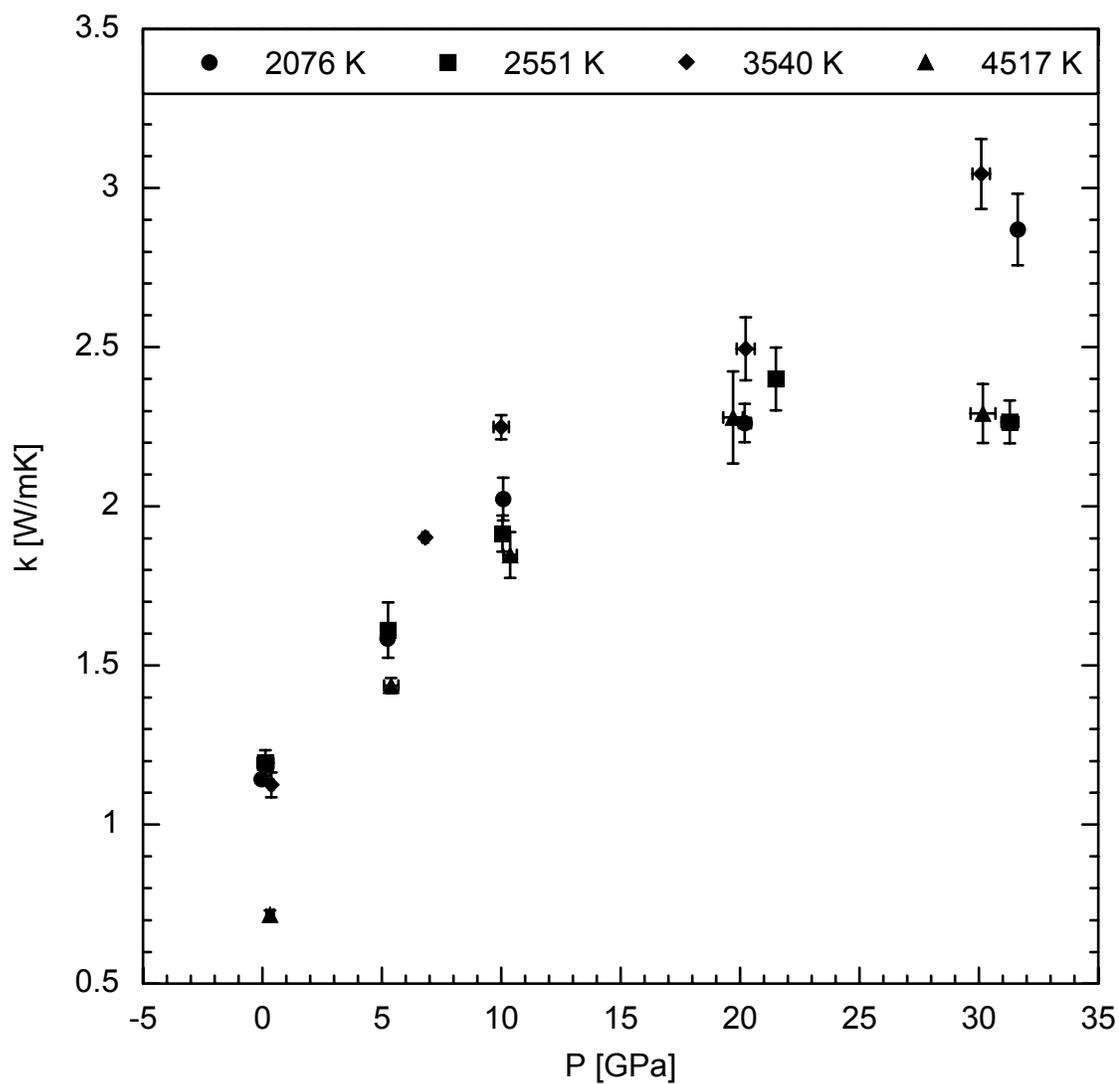
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833 **Figure 4**

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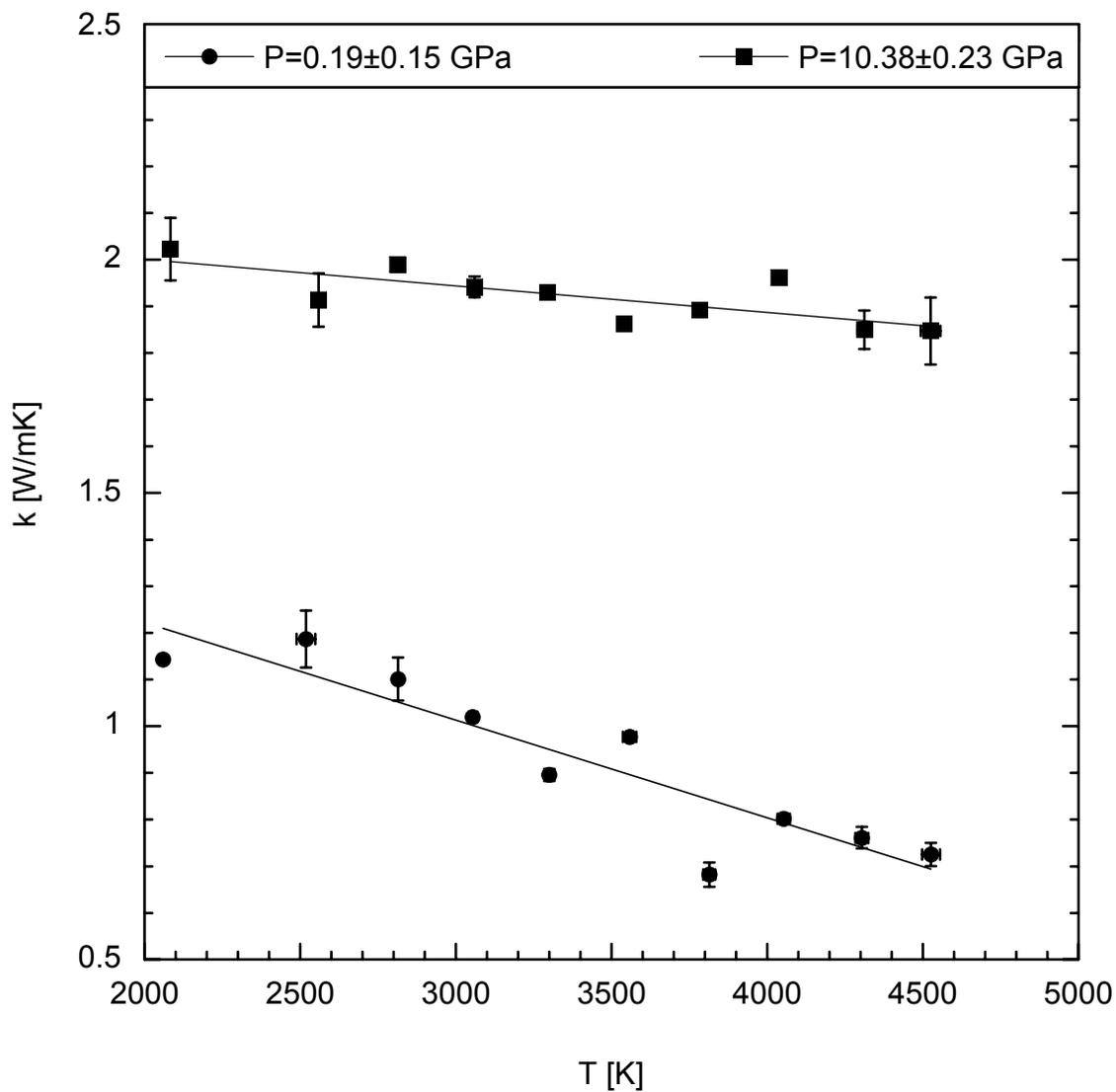
837 **Figure 5**
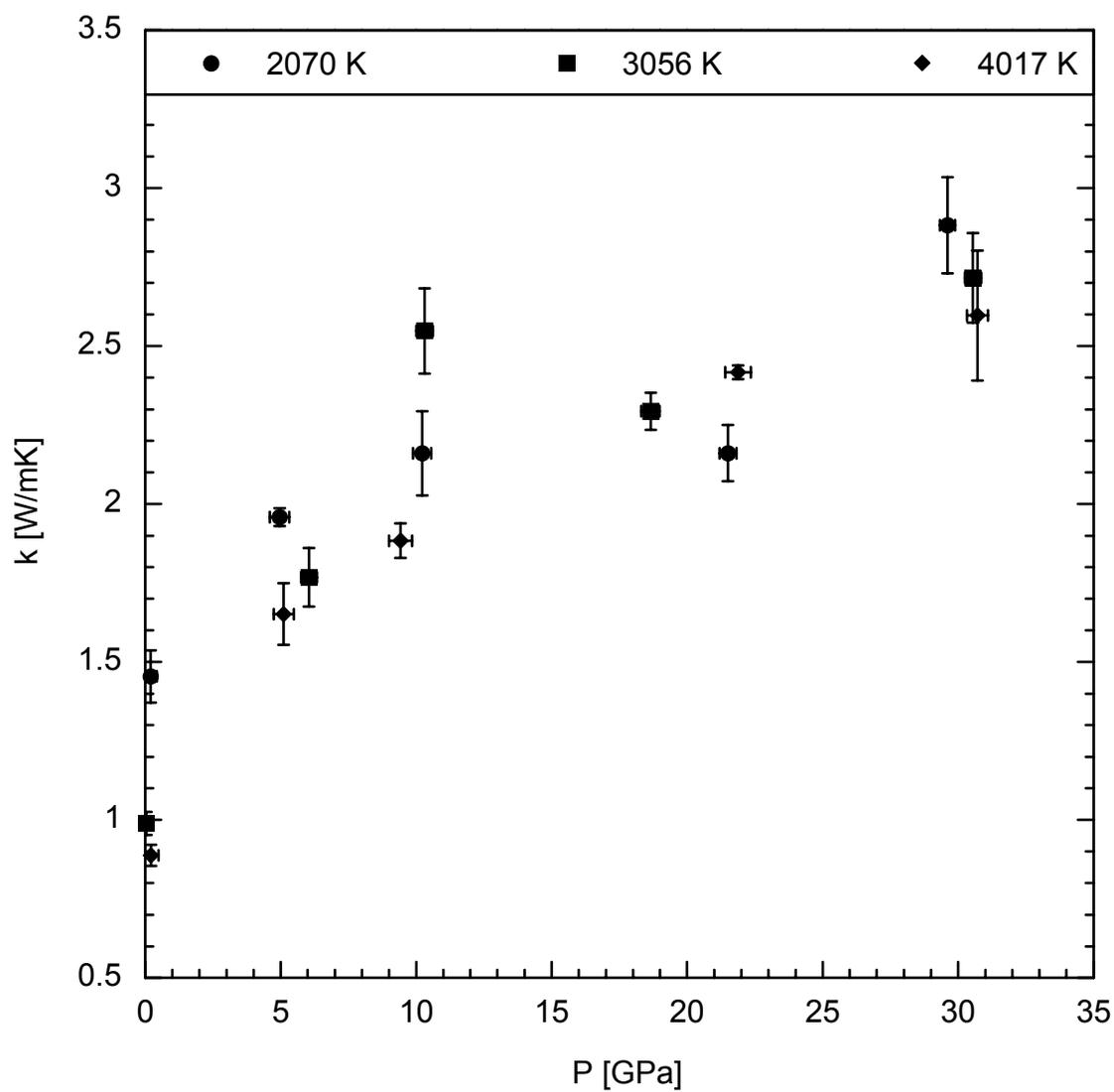
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842   **Figure 6**

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845   **Figure 7**

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