



HAL
open science

Melting behavior of SiO₂ up to 120 GPa

Denis Andrault, G. Morard, G. Garbarino, M. Mezouar, Mohamed Ali M.A.
Bouhifd, T. Kawamoto

► **To cite this version:**

Denis Andrault, G. Morard, G. Garbarino, M. Mezouar, Mohamed Ali M.A. Bouhifd, et al.. Melting behavior of SiO₂ up to 120 GPa. *Physics and Chemistry of Minerals*, 2020, 47 (2), 10.1007/s00269-019-01077-3 . hal-02462133

HAL Id: hal-02462133

<https://uca.hal.science/hal-02462133>

Submitted on 31 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Melting behavior of SiO₂ up to 120 GPa

D. Andrault^{1,*}, G. Morard², G. Garbarino³, M. Mezouar³, M.A. Bouhifd¹, T. Kawamoto⁴

¹ Université Clermont Auvergne, CNRS, IRD, OPGC, LMV, Clermont-Ferrand, France.

² Sorbonne Université, MNHN, CNRS, IRD, IMPMC, Paris, France.

³ European Synchrotron Radiation Facility, ESRF, Grenoble, France.

⁴ Department of Geoscience, Faculty of Science, Shizuoka University, Shizuoka, Japan.

* Corresponding Author: denis.andrault@uca.fr; Tel: 00334 7334 6781

ABSTRACT

The structure of liquid silicates is commonly described as a statistical mixture of various atomic entities with relative abundances that can vary with pressure, temperature and composition. Unfortunately, this view remains largely theoretical due to scarce experimental reports on the silicate melt structure, in particular under pressure. We performed X-ray diffraction of the SiO₂ end-member to probe the melting curve up to ~120 GPa and 7000 K, and the melt structure up to ~80 GPa. We confirm the steep increase of the melting curve above ~14 GPa when stishovite becomes stable over coesite in subsolidus conditions, with a slope of about 80 K/GPa. Then, around 45 GPa and 5400 K, the melting curve flattens significantly, an effect most likely reflecting the densification of the SiO₂ melt structure. The signal of diffuse X-ray scattering is compatible with a change of the Si coordination number from 4 to 6 along the melting curve, in agreement with previous works reporting a similar evolution during the cold compression of SiO₂-glass. Because of the limited pressure range (within 10 to 20 GPa) in which the melting curve changes its slope, we speculate a difficult coexistence of tetrahedral SiO₄ and octahedral SiO₆ units in SiO₂ melt at high pressures.

KEYWORDS

SiO₂-silica, melting diagram, melt structure, lower mantle pressures

ACKNOWLEDGEMENTS

We thank anonymous reviewers for helpful comments. This research was financed by the French Government Laboratory of Excellence initiative n°ANR-10-LABX-0006, the Région Auvergne and the European Regional Development Fund. This is Laboratory of Excellence ClerVolc contribution N°XX.

I. INTRODUCTION

Although SiO_2 is rarely present as a pure phase in mantle rocks, it is a dominant component of terrestrial planets. Because SiO_2 is highly refractory, its melting curve significantly affects the melting diagram of silicates present in the crust and the mantle. At subsolidus conditions, SiO_2 undergoes a major transition from coesite to stishovite, at a pressure of ~ 14 GPa for a temperature of 3000 K (Zhang et al. 1993). The transition involves a change of the Si coordination number from tetrahedral “ SiO_4 ” to octahedral “ SiO_6 ” units, accompanied with a density change of $\sim 30\%$ (Akaogi et al. 2011). This transition occurs in all silicates with a transition pressure that depends on composition. The structural changes are major and induce a divergence of physical and chemical properties between the shallower and deeper parts of planetary mantles.

The change of the Si coordination number is also expected to occur in silicate melts (Sanloup et al. 2013). For SiO_2 , the experimental investigation on the melt is strongly hampered by a steep increase of the melting curve at pressures higher than the coesite to stishovite transition: The melting temperature was reported to increase from 3000 to 3900 K between ~ 14 GPa and ~ 22 GPa (Shen and Lazor 1995). Such a steep Clapeyron slope ($dT/dP = \Delta V/\Delta S$) denotes a large volume of fusion between stishovite and a low density melt (LDM) containing Si in 4-fold coordination. In contrast, the Clapeyron slope of the melting curve is almost flat below ~ 14 GPa, which implies a negligible density contrast between coesite and LDM (Zhang et al. 1993). The brutal change of slope of the melting curve at ~ 14 GPa shows that LDM is maintained at pressures above the Si coordination change in the solid state.

The pressure-induced Si coordination change in amorphous SiO_2 was investigated experimentally at room temperature (Benmore et al. 2010; Lin et al. 2007; Murakami and Bass 2010; Sato and Funamori 2010) and theoretically (Meade et al. 1992; Stixrude and Karki 2005; Takada et al. 2016; Usui and Tsuchiya 2010). In both cases, the transformation to an octahedral-based SiO_2 structure is clearly demonstrated. At high temperatures, the formation of a high-density melt (HDM), with a similar structure to the high-density glass potentially, would induce a smaller density contrast between stishovite and HDM, compared to stishovite and LDM. This would induce the flattening of the Clapeyron slope of the melting curve with increasing pressure. This line of reasoning agrees with the report of a moderate increase of the melting temperature from 5000 K to 5800 K with increasing pressure from 40 to 120 GPa (Usui and Tsuchiya 2010). Still, large inconsistencies remain. For example, the melting temperature was reported from 4400 K (Luo et al. 2002) to 5250 K (Usui and Tsuchiya 2010) at pressures around 50 GPa. In addition, neither the change in Clapeyron slope of the SiO_2 melting curve at increasing pressure, nor the change in Si coordination number in the melt have been properly documented.

II. MATERIALS AND METHODS

75 **2.1 Experimental design**

76 We first refined the melting curve of SiO₂ up to ~120 GPa using the laser-heated diamond anvil
77 cell (LH-DAC) coupled with *in situ* X-ray diffraction. Samples consisted of small shards of pure SiO₂
78 glass, typically of 20-50 μm across and 10-15 μm thick. The glass was loaded in the pressure chamber
79 between two KCl layers of similar thickness. The use of a KCl makes the X-ray analysis more
80 difficult, due to intense KCl peaks; however, a critical advantage is to minimize the axial thermal
81 gradients within the sample. In addition, soft KCl layers favor homogenous sample pressure at high
82 temperature. The amount of water trapped in the pressure chamber was minimized by performing all
83 sample-loading operations under N₂-flux in a glove bag. Samples were heated alternatively using a
84 CO₂ laser on one side or two fiber-lasers on both sides of the DAC. We found that SiO₂ absorbs
85 relatively well the 1 μm radiation of fiber-lasers after the sample is already heated to high
86 temperatures using the CO₂. In all cases, laser spots were more than 20 μm in diameter.

87 In a second series of experiments, we probed the structure of SiO₂ melt at high pressures. We did
88 not use a pressure medium in this case to prevent artifacts that could arise from its diffuse scattering, if
89 the pressure medium eventually melts. Yet, a small grain of KCl was loaded in the gasket hole for the
90 measurement of the nominal pressure. The sample geometry consisted in two thin disks of SiO₂ quartz
91 single crystal in direct contact with the diamonds, between which a little bit of Si-metal powder was
92 distributed. The role of Si-metal is to couple with fiber-lasers in order to initiate the sample heating
93 before the annealed SiO₂ could eventually absorb the laser radiation by itself. We preferred the
94 addition of Si to Pt powder that would have also provided an internal pressure calibrant, because Pt
95 melts at lower temperature than SiO₂ at high pressures; its signal of diffuse scattering would have
96 hampered the study of SiO₂-melt. The presence of a minor excess of Si in SiO₂ melt should not affect
97 significantly the melt structure, nor the mechanism of the pressure-induced Si coordination change.
98 Upon laser heating, SiO₂ eventually melts at mid-distance between the two diamond culets. Then,
99 further increase of the laser power induces a thicker layer of molten SiO₂. In such a sample
100 experiencing large axial temperature gradient, some SiO₂ always remain solid at the contact with cold
101 diamonds. More importantly, the temperature gradient within the molten part of the sample should be
102 minor, due to turbulent convection in the high-pressure melt.

103

104 **2.2 Determination of pressure and temperature in the laser heated diamond anvil cell**

105 We used the equation of state of KCl (Dewaele et al. 2012) to determine the nominal pressure at
106 300K before and after laser heating. Then, the sample pressure at high temperature was determined
107 using two different cross-calibrated methods: (i) the P-V-T equation of state of stishovite (Wang et al.
108 2012) and (ii) the nominal pressure corrected by $X_{Th}\alpha KT$ to account for the increase of pressure in the
109 laser spot (X_{Th} is an adjustable parameter, α and K are thermal expansion and bulk modulus,
110 respectively, of coesite (Akaogi et al. 2011) at nominal pressures below 14 GPa and stishovite (Wang
111 et al. 2012) for pressures above). We used samples loaded in KCl and heated below the melting curve

112 to calibrate the value of X_{Th} . For this sample geometry, the two methods give pressures within +/- 5
113 GPa for X_{Th} values increasing linearly from 35% to 90%, when temperature is increased from 4000 to
114 7000 K, respectively. At the melting temperature, the second method is preferred, because the
115 remaining fraction of stishovite grains may encounter a temperature lower than the SiO₂-melt, because
116 they are located closer to the diamonds. The second method was also used to determine the pressure
117 for DAC loadings without KCl pressure medium.

118 Temperatures up to 7000 K were determined based on spectroradiometric measurements (Fig. 1).
119 To make these measurements accurate, a critical parameter of the optical set-up is the use of reflective
120 Schwarzschild-type telescopes and the absence of any refractive device along the optical path, in order
121 to prevent chromatic aberration (Schultz et al. 2005). Temperature measurements are performed with a
122 precision of ± 100 K and a reproducibility better than ± 30 K. When not using KCl insulating layers in
123 the DAC, the temperature uncertainty could be twice larger, due to steeper axial temperature gradient.
124 We note that the measured temperature corresponds to the hottest part of the sample, where thermal
125 emission is the most intense.

126 The sample behavior was monitored *in situ* using an X-ray beam much smaller than the hot-spot on
127 the sample (see below). The fluorescence (in the visible range of wavelength) of the irradiated KCl
128 pressure medium, or irradiated Re-gasket, was used to adjust the spectrometer position, in order to
129 perform the temperature measurement at the position of the X-ray beam. The spectrometer alignments
130 were carefully checked before and after each melting experiments.

131

132 **2.3 X-ray diffraction measurements**

133 At the ID27 beamline of the ESRF (Grenoble, France), we used a monochromatic X-ray beam of
134 0.3738 Å wavelength focused by two Kirkpatrick-Baez mirrors onto a spot of less than 2x2 μm².
135 Diffraction patterns were recorded using a MAR-160 CCD detector and integrated using DIOPTAS
136 (Prescher and Prakapenka 2015). Acquisition times extended to 10 sec and 300 sec for solid and
137 molten SiO₂ samples, respectively. For experiments dedicated to the determination of the melting
138 curve, volumes and relative abundances of SiO₂ and KCl were refined using the XRDUA code (De
139 Nolf et al. 2014). For experiments dedicated to probe the structure of SiO₂-melt, we inserted Soller
140 slits between the DAC and the CCD detector. These slits filter out a major fraction of the Compton
141 diffusion coming from diamonds (Weck et al. 2013), which results in a significant improvement of the
142 signal of X-ray diffuse scattering coming from the melt. We first recorded the X-ray diffuse scattering
143 of SiO₂ glass under compression up to ~50 GPa, before we performed measurements at high
144 temperatures in SiO₂ melt up to 80 GPa. In both cases, we also recorded the diffuse background
145 coming from diamond anvils (Compton diffusion). For the melt, small diffraction peaks of not-molten
146 stishovite were eventually visible in the Q region between 1 and 8 Å⁻¹. The peaks were carefully fitted
147 by Gaussian functions and subtracted. Then, after subtraction of the diamond Compton diffusion, the
148 scattering signal coming from the sample was normalized to obtain the scattering factor S(Q). Finally,

149 the wavelength position of the first sharp diffraction peak (FSDP) was extracted from the $S(Q)$ using a
150 Gaussian function coupled with a polynomial background.

151

152

III. RESULTS AND DISCUSSION

153

3.1 A steep SiO₂ melting curve up to 45 GPa

154 We first refine the melting curve of SiO₂ up to ~120 GPa using the LH-DAC coupled with *in situ*
155 X-ray diffraction. With increasing temperature, the glass starting material first crystallizes in coesite
156 below 14 GPa, stishovite or in the CaCl₂-form above ~60 GPa (Andrault et al. 1998). The presence of
157 thin and continuous diffraction rings are evidences for fine crystalline SiO₂ powders under a moderate
158 temperature gradient within the X-ray beam (Fig. 2A). At a sample temperature interpreted hereafter
159 as the melting point of SiO₂, several changes occur simultaneously (such as reported in (Andrault et al.
160 2014)): (i) Additional increase of the laser power does not induce an increase of the sample
161 temperature (discussed in (Geballe and Jeanloz 2012)); (ii) texture of diffraction rings becomes
162 spottier; (iii) position of diffraction spots on the image plate changes rapidly at constant temperature;
163 (iv) integrated intensity of the SiO₂ diffraction peaks decreases severely relative to the KCl pressure
164 medium (Fig. 2); (v) upon quenching, intense stishovite peaks reappear, which certifies the presence of
165 non-crystalline (i.e. molten) SiO₂ within the X-ray spot at high temperature. The reason why all
166 diffraction peaks of SiO₂ do not disappear abruptly at the melting temperature is the unavoidable axial
167 temperature gradient between the two diamonds. Also, the SiO₂ melt may absorb the laser radiation
168 less than solid SiO₂, resulting in a relatively lower heating efficiency when the sample is partially
169 molten. This can explain the temperature plateau despite an increase of the laser power.

170 Our measurements confirm the steep increase of the SiO₂ melting temperature above ~14 GPa (Fig.
171 3, Table 1), in agreement with previous experimental (Shen and Lazor 1995) and theoretical
172 (Belonoshko and Dubrovinsky 1995; Usui and Tsuchiya 2010) studies. Within experimental
173 uncertainties, the melting curve appears linear between ~15 and ~45 GPa. The Clapeyron slope of ~80
174 K/GPa remains ~4 times smaller than that reported at ~300 K/GPa for the coesite to stishovite
175 transition (Akaogi et al. 2011). Basic thermodynamic relations apply around the triple point where
176 coesite, stishovite and the LDM of SiO₂ coexist (Table 2). As a consequence, we estimate the volume
177 of fusion of stishovite ($2 \times \Delta V_{\text{Melting}} / (V_{\text{LDM}} + V_{\text{Si}})$) at ~28% from the combination of the volume change
178 of ~28% at the subsolidus transition (Akaogi et al. 2011) and a negligible volume of fusion of coesite
179 derived from the quasi-horizontal melting line between 9 to 14 GPa (Zhang et al. 1993). On the other
180 hand, the entropy of melting of stishovite (ΔS_m) is estimated to ~60 J/molK, a value 4 times larger
181 than the entropy change at the coesite-stishovite transition (Akaogi et al. 2011).

182

3.2 A relatively flat SiO₂ melting curve from 45 to 90 GPa

183

184

185 The response of our samples to laser heating was different below and above a pressure of ~45 GPa.
186 Between ~15 and ~45 GPa, after the onset of sample melting between ~3000 and ~5400 K (Fig. 3),
187 further increase of the laser power always yield to the same pressure-temperature conditions of ~45
188 GPa and ~5400 K. This behavior could result from the very large volume of fusion (~28%, see above).
189 Increasing the amount of melt by LH within a nearly constant sample volume in the DAC would
190 logically result in a significant increase of the sample pressure. Above ~45 GPa, this effect is not
191 observed anymore; full sample melting could be achieved within the X-ray spot at each given
192 experimental pressure.

193 Between ~45 to ~90 GPa, the SiO₂ melting curve presents a Clapeyron slope of ~13 K/GPa, which
194 is ~6 times lower than that observed at lower pressures (Fig. 3). The difference cannot result from
195 subsolidus properties, because the stability field of stishovite extends continuously between ~15 and
196 ~90 GPa below the melting line. Instead, it can be related to the evolution of the structure of the SiO₂
197 melt. A smaller Clapeyron slope (dT/dP) above 45 GPa denotes either a smaller volume of fusion
198 (ΔV_m) and/or a higher entropy of fusion (ΔS_m). A higher ΔS_m above 45 GPa is improbable, because
199 we expect large structural similarities between stishovite and HDM, as they both contain most of the
200 Si in a 6-fold coordination (Benmore et al. 2010; Lin et al. 2007; Meade et al. 1992; San et al. 2016;
201 Sato and Funamori 2010). Instead, their structural similarities suggest a lower ΔS_m . Therefore, the
202 flattening of the melting slope above ~45 GPa is likely to result from a decrease of the volume of
203 fusion due to the presence of a HDM of SiO₂ above the melting curve.

204 Now, if we consider a fictive triple point between LDM, HDM and stishovite at ~45 GPa and 5400
205 K, we can use Clapeyron relations ($\Sigma \Delta V=0$, $\Sigma \Delta S=0$ around triple points, and $dT/dP=\Delta V/\Delta S$) to
206 retrieve the thermodynamical parameters of these three phases. Assuming a negligible entropy
207 difference between LDM and HDM ($\Delta S_{LDM-HDM}$), the stishovite volume of fusion (ΔV_m) is estimated
208 to ~5.3% above ~45 GPa (see details of the calculation below Table 2). ΔV_m becomes 6.6 % or 4.0 %
209 for hypothetical $\Delta S_{LDM-HDM}$ values of e.g. -15 or 15 J/mol.K, respectively. Such range of ΔV_m values
210 is comparable to the density contrast (reported at ~3 %) between stishovite and a glass compressed
211 above 45 GPa at room temperature (Petitgirard et al. 2017). Then, we can estimate a volume difference
212 of ~25% between LDM and HDM melts. This value is marginally affected (+/- 2%) by changing
213 $\Delta S_{LDM-HDM}$ in a range of possible values. Such volume change is comparable to the 28% reported
214 between coesite and stishovite (Akaogi et al. 2011). We finally estimate the SiO₂ LDM and HDM
215 densities at $\sim 3.26 \cdot 10^3$ and $\sim 4.17 \cdot 10^3$ kg/m³, respectively, at 45 GPa and 5400 K (Table 2). Such LDM
216 density is consistent with a previous theoretical report considering less than 10% Si in 6-fold
217 coordination in the melt (Takada et al. 2016).

218

219 **3.3 Melting of the CaCl₂-form of SiO₂ above 90 GPa**

220 Above ~90 GPa, the slope of the SiO₂ melting curve increases slightly to ~35 K/GPa to yield a
221 melting temperature of ~7000 K at ~120 GPa. The progressive increase of the Clapeyron slope could
222 be related to the 2nd order phase transformation from stishovite to the CaCl₂-type polymorph (Fig. 3),
223 even though the location of this phase boundary in the P-T diagram remains controversial (see (Fischer
224 et al. 2018) and references therein). In fact, our X-ray measurements confirm that the subsolidus phase
225 transformation occurs between ~80 and ~100 GPa at ~5400 K (Fig. 4). The change of slope of the
226 melting curve is unlikely to come from a difference of volume between the two SiO₂ polymorphs,
227 because it was reported to be insignificant up to ~120 GPa, at least at 300 K (Andraut et al. 2003). In
228 contrast, the higher entropy of the CaCl₂-form, compared to stishovite, implies a lower entropy of
229 melting (ΔS_m) above the transition pressure and, consequently, a steeper melting curve (because
230 $dT/dP = \Delta V_m / \Delta S_m$). In addition, the strain energy becomes significant with increasing pressure above
231 the transition. The CaCl₂ distortion of the stishovite-based lattice observed at ~107 GPa and 5400 K
232 corresponds to a strain energy of ~2 kJ/mole (Andraut et al. 2003). This value is significant compared
233 to the enthalpy of fusion of quartz of 9.4 kJ/mole (Akaogi et al. 2011). Thus, the stabilization energy
234 associated to the CaCl₂-distortion can modify the Clapeyron slope of the melting curve.

235

236 **3.4 Comparison with previous works**

237 Previous LH-DAC experiments suggested an even steeper Clapeyron slope than ours above ~14
238 GPa (Shen and Lazor 1995). However, after correction of the nominal pressures of the early
239 experiments regarding the pressure increase due to laser heating in the DAC, the two data sets are in
240 fact quite similar to each other. On the other hand, our melting curve plot in relatively good agreement
241 with theoretical calculations, except in a few aspects (Fig. 3). The experimental melting slope remains
242 steep, with little pressure-induced flattening, up to pressures higher than reported in theoretical studies
243 (Belonoshko and Dubrovinsky 1995; Luo et al. 2002; Usui and Tsuchiya 2010). When it eventually
244 flattens around 45 GPa and up to 90 GPa, the SiO₂ experimental melting curve is found parallel, but at
245 200-300 K higher temperatures, compared to the most recent calculation (Usui and Tsuchiya 2010).
246 The significant increase of melting temperature observed experimentally above ~90 GPa is not
247 reported in any theoretical studies yet.

248 We note an important discrepancy, of e.g. ~1000K for the melting temperature at 45 GPa, among
249 the previous theoretical studies (Belonoshko and Dubrovinsky 1995; Luo et al. 2002; Usui and
250 Tsuchiya 2010). It could come from the difficulty to model properly the local structure in SiO₂ melt, in
251 particular the strength of the Si-based structural units in LDM and HDM, respectively. Then,
252 compared to shock compressions, our measurements plot at the upper limit of the Hugoniot plots of
253 (solid) quartz and fused quartz (see (Akins and Ahrens 2002) and references therein). Using this
254 technique, one generally identifies the melting temperature when melting is truly achieved at higher
255 impact energies, rather than in the solid at the highest temperatures, before the solid melts. However,
256 this remains a matter of interpretation and the range of temperature uncertainties is large.

257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293

3.5 Analysis of the SiO₂-melt structure factors

Polyamorphism in liquid SiO₂ has been extensively discussed in the past by theoretical approaches (e.g. (Brazhkin et al. 2011; Lin et al. 2007; San et al. 2016; Takada et al. 2016)). To address experimentally the structural evolution of liquid SiO₂ under high pressures, we performed LH-DAC experiments coupled with the Soller slits system installed at the ID27 beamline (Weck et al. 2013). This maximizes the signal of the SiO₂ melt over the noise from the sample environment. No KCl pressure medium was used for these experiments. First, we collected diffraction patterns for the cold-compression of SiO₂ glass up to ~45 GPa, in order to validate our experimental measurements of the structure factors S(Q). Our results are found in good agreement with previous studies (e.g. (Prescher et al. 2017)). Spectra present a first sharp diffraction peak (FSDP) around 2 Å⁻¹, a second, less intense, around 5 Å⁻¹ and a new contribution growing with increasing the pressure between 3 and 3.5 Å⁻¹ (Fig. 5). These experimental features have been correlated to the gradual compaction of the structure of amorphous SiO₂ (Benmore et al. 2010; Prescher et al. 2017; Sato and Funamori 2010).

We then recorded diffuse patterns of SiO₂ melt between ~25 and ~75 GPa, which we normalized to obtain S(Q) (Fig. 6). In comparison to the glass, the same FSDP position is found at higher pressure in the melt (Figs. 7 and 8). In addition, the new diffraction peak starts growing between 40 and 54 GPa, and 18.5 and 30.5 GPa, for the melt and the glass, respectively (Fig. 5). In the melt, the shift of the FSDP occurs prior to the appearance of the new diffraction peak, a similar behavior as in the glass (Benmore et al. 2010; Prescher et al. 2017; Sato and Funamori 2010). This effect has been associated to the first regime of the compression where the structural changes are dominated by the compaction of the oxygen network (Wu et al. 2012), before Si changes its coordination number at higher pressures. At pressures higher than ~54 GPa, the additional contribution between 3 and 3.5 Å⁻¹ appears clearly in the signal of SiO₂-melt diffuse scattering. At this point, the position of the FSDP is found above 2.2 Å⁻¹ and, at 76 GPa, the melt presents the same FSDP position as the glass at ~45 GPa (Fig. 8). All experimental features are similar to those observed in the glass upon change of Si coordination number from 4 to 6 (Benmore et al. 2010; Inamura et al. 2004; Meade et al. 1992; Prescher et al. 2017; Sato and Funamori 2010).

It appears clear that the structural changes occur at higher pressures in the liquid than in the glass. Regarding the extremely high temperatures considered (between 5250 K and 6200 K, Fig. 6), this could be an effect of thermal pressure; the sequence of structural compaction may take place for similar SiO₂ volumes in the glass and in the melt. However, higher temperature requires higher pressure to achieve a similar SiO₂ volume. This hypothesis is supported by the large similarities between diffraction patterns recorded in the liquid and in the glass.

IV. CONCLUSION

294 The compaction mechanisms of liquid and amorphous SiO₂ are complex and involve various
295 atomic processes. Our experimental measurements suggest a change of the SiO₂ melt structure in a
296 relatively narrow range of pressures, within 10-20 GPa, around 45 GPa. Such evolution is compatible
297 with a previous work investigating the Si coordination change from 4 to 6, e.g. in a SiO₂-glass using
298 transverse acoustic wave velocities (Murakami and Bass 2010). In our experiments, the change in the
299 SiO₂ melt structure is recognized based on (i) a change in the Clapeyron slope of the SiO₂ melting
300 curve and (ii) the occurrence of the new diffraction peak between 3 and 3.5 Å⁻¹. The relative sharpness
301 of the structure change in the melt suggests a dominant role of the covalent character of Si-O bonds in
302 the melt (Lin et al. 2007), which could induce a significant difference in energy between the
303 tetrahedral "SiO₄" and octahedral "SiO₆" electronic configurations as a function of pressure and
304 temperature. The two different melt structures could be relatively incompatible with each other, in
305 agreement with previous reports (Brazhkin et al. 2011; Lin et al. 2007; Takada et al. 2016)).
306
307

308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355

REFERENCES

Akaogi M, Oohata M, Kojitani H, Kawaji H (2011) Thermodynamic properties of stishovite by low-temperature heat capacity measurements and the coesite-stishovite transition boundary *Am Miner* 96:1325-1330

Akins JA, Ahrens TJ (2002) Dynamic compression of SiO₂: A new interpretation *Geophys Res Lett* 29:1394

Andrault D, Angel RJ, Mosenfelder JL, Le Bihan T (2003) Equation of state of stishovite to lower mantle pressures *Am Miner* 88:301-307

Andrault D, Fiquet G, Guyot F, Hanfland M (1998) Pressure-induced landau-type transition in stishovite. *Science* 23:720-724

Andrault D, Pesce G, Bouhifd MA, Bolfan-Casanova N, Henot JM, Mezouar M (2014) Melting of subducted basalt at the core-mantle boundary *Science* 344:892-895

Belonoshko AB, Dubrovinsky LS (1995) Molecular-dynamics of stishovite melting *Geochim Cosmochim Acta* 59:1883-1889

Benmore CJ, Soignard E, Amin SA, Guthrie M, Shastri SD, Lee PL, Yarger JL (2010) Structural and topological changes in silica glass at pressure *Phys Rev B* 81

Brazhkin VV, Lyapin AG, Trachenko K (2011) Atomistic modeling of multiple amorphous-amorphous transitions in SiO₂ and GeO₂ glasses at megabar pressures *Phys Rev B* 83

De Nolf W, Vanmeert F, Janssens K (2014) XRDUA: crystalline phase distribution maps by two-dimensional scanning and tomographic (micro) X-ray powder diffraction *Journal of Applied Crystallography* 47:1107-1117 doi:doi:10.1107/S1600576714008218

Dewaele A, Belonoshko AB, Garbarino G, Occelli F, Bouvier P, Hanfland M, Mezouar M (2012) High-pressure high-temperature equation of state of KCl and KBr *Phys Rev B* 85 doi:10.1103/PhysRevB.85.214105

Fischer RA et al. (2018) Equations of state and phase boundary for stishovite and CaCl₂-type SiO₂ *Am Miner* 103:792-802 doi:10.2138/am-2018-6267

Geballe ZM, Jeanloz R (2012) Origin of temperature plateaus in laser-heated diamond anvil cell experiments *Journal of Applied Physics* 111:123518

Inamura Y, Katayama Y, Utsumi W, Funakoshi K (2004) Transformations in the intermediate-range structure of SiO₂ glass under high pressure and temperature *Phys Rev Lett* 93

Lin JF et al. (2007) Electronic bonding transition in compressed SiO₂ glass *Phys Rev B* 75

Luo SN, Cagin T, Strachan A, Goddard WA, Ahrens TJ (2002) Molecular dynamics modeling of stishovite *Earth Planet Sci Lett* 202:147-157

Meade C, Hemley RJ, Mao HK (1992) High-pressure X-ray diffraction of SiO₂ glass *Phys Rev Lett* 69:1387-1390

Murakami M, Bass JD (2010) Spectroscopic Evidence for Ultrahigh-Pressure Polymorphism in SiO₂ Glass *Phys Rev Lett* 104

Petitgirard S et al. (2017) SiO₂ Glass Density to Lower-Mantle Pressures *Phys Rev Lett* 119

Prescher C, Prakapenka VB (2015) DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration *High Pressure Research* 35:223-230

Prescher C, Prakapenka VB, Stefanski J, Jahn S, Skinner LB, Wang YB (2017) Beyond sixfold coordinated Si in SiO₂ glass at ultrahigh pressures *Proc Natl Acad Sci U S A* 114:10041-10046

San LT, Hong NV, Hung PK (2016) Polyamorphism of liquid silica under compression based on five order-parameters and two-state model: a completed and unified description *High Pressure Research* 36:187-197

356 Sanloup C et al. (2013) Structural change in molten basalt at deep mantle conditions Nature
357 503:104-+

358 Sato T, Funamori N (2010) High-pressure structural transformation of SiO₂ glass up to 100
359 GPa Phys Rev B 82

360 Schultz E et al. (2005) Double-sided laser heating system for in situ high pressure-high
361 temperature monochromatic x-ray diffraction at the ESRF High Pressure Research
362 25:71-83

363 Shen G, Lazor P (1995) Measurement of melting temperatures of some minerals under lower
364 mantle conditions J Geophys Res 100:17699-17713

365 Stixrude L, Karki BB (2005) Structure and freezing of MgSiO₃ liquid in the Earth's lower
366 mantle Science 310:297-299

367 Takada A, Bell RG, Catlow CRA (2016) Molecular dynamics study of liquid silica under high
368 pressure Journal of Non-Crystalline Solids 451:124-130

369 Usui Y, Tsuchiya T (2010) Ab Initio Two-Phase Molecular Dynamics on the Melting Curve
370 of SiO₂ J Earth Sci 21:801-810

371 Wang FL, Tange Y, Irifune T, Funakoshi K (2012) P-V-T equation of state of stishovite up to
372 mid-lower mantle conditions J Geophys Res: Solid Earth 117:B06209

373 Weck G, Garbarino G, Ninet S, Spaulding D, Datchi F, Loubeyre P, Mezouar M (2013) Use
374 of a multichannel collimator for structural investigation of low-Z dense liquids in a
375 diamond anvil cell: Validation on fluid H₂ up to 5 GPa Rev Sci Instr 84

376 Wu M, Liang Y, Jiang J-Z, Tse JS (2012) Structure and Properties of Dense Silica Glass
377 Scientific Reports 2

378 Zhang JZ, Liebermann RC, Gasparik T, Herzberg CT, Fei YW (1993) Melting and subsolidus
379 relations of SiO₂ at 9-14 GPa J Geophys Res: Solid Earth 98:19785-19793
380
381

FIGURES AND TABLES

382

383

384 **Figure 1: Typical temperature measurements.** Thermal emission spectra were recorded at
385 the center of the laser spot for sample temperatures of e.g. 5010 K (left) and 6140 K (right),
386 using the online optical system installed at the ID27 beamline. The raw spectra (upper frames)
387 are corrected by the response of the optical system (itself calibrated with a W-lamp at 2600 K)
388 and fitted using the Wien law (middle frames). The so-called “two-color” methods (lower
389 frames) shows a temperature variation of less than 10% of the mean temperature within a
390 range of wavelength from ~670 to ~870 nm, which establishes the good quality of the thermal
391 emission spectra. Temperature measurements are performed with a precision of ± 100 K and a
392 reproducibility better than ± 30 K.

393

394 **Figure 2A: X-ray evidences for melting of SiO₂ at ~40 GPa.** Time elapses from bottom to
395 top. Temperature uncertainty is ± 100 K. After crystallization of stishovite, continuous rings
396 remain clearly visible up to more than 5000 K. At 5100 K the intensity of SiO₂ diffraction
397 lines is already significantly decreased. At sample temperatures of 5600 and 5400 K, the only
398 remaining diffraction lines come from the KCl pressure medium. Diffraction lines of
399 stishovite reappear when the laser power is decreased to 5050 K, evidencing the SiO₂
400 recrystallization.

401

402 **Figure 2B: X-ray evidence for the melting of SiO₂ at 105 GPa.** Time elapses from top to
403 bottom. For temperatures lower than 6200 K, the set of diffraction lines evidences the
404 presence of the CaCl₂-form of SiO₂ (see Fig. 4) in addition to the KCl pressure medium. The
405 intensity of the SiO₂ peaks decreases severely at 6300-6400 K before they almost disappear at
406 6500 K. The stishovite to KCl ratio of diffraction peaks intensity decreases by a factor of 10
407 around between 6200 and 6500 K.

408

409 **Figure 3: Melting curve of SiO₂ up to ~120 GPa.** We report temperatures of solid (blue) and
410 liquid (red) SiO₂ together with a smooth trend through the data set (grey band). Our
411 temperature and pressure uncertainties are 200 K and 5 GPa, respectively. We also plot
412 previous melting curve determinations based on early experimental works (Shen and Lazor
413 1995; Zhang et al. 1993) (light blue), theoretical calculations (purple (Usui and Tsuchiya
414 2010), blue (Belonoshko and Dubrovinsky 1995) and green (Luo et al. 2002)) and shock wave

415 experiments (orange (Akins and Ahrens 2002)). For the latter, we report Hugoniot plots in
416 solid and molten states for starting materials composed of quartz and fused-quartz.

417

418 **Figure 4: Subsolidus transition from Stishovite to the CaCl₂-form between 75 and 102**

419 **GPa:** The stishovite model fits well the upper diffraction pattern recorded at ~75 GPa and
420 ~4500 K. In contrast, the diffraction pattern recorded at ~102 GPa and ~5400 K is not well
421 fitted with the stishovite model (middle frame), but instead with the CaCl₂-form model (lower
422 pattern). At these conditions, the CaCl₂-form presents (a, b, c) unit cell parameters of
423 (3.831(6), 3.967(5), 2.543(3)). Black, red and blue profiles are experimental data, background
424 and Rietveld fit, respectively.

425

426 **Figure 5: Structure factor of the compressed glass:** As previously noticed (e.g. (Prescher et
427 al. 2017) and references therein), a new contribution around 3-3.5 Å⁻¹ grows above ~20 GPa.

428

429 **Figure 6: Structure factors S(Q) of SiO₂ recorded in the melt between ~38 and ~76 GPa.**

430 Spectra recorded at high temperature in the melt at pressures of 38 GPa (orange), 40 GPa
431 (bleu), 54 GPa (grey) and 76 GPa (yellow) are bracketed between spectra recorded at 300 K
432 in the glass compressed to ~18.5 GPa (green) and ~49.5 GPa (dark blue). The contributions
433 observed for the melt below and above ~45 GPa are comparable to those of the glass at ~18.5
434 GPa and ~49.5 GPa, respectively. It indicates an evolution of the SiO₂ melt structure between
435 40 and 54 GPa comparable to that reported during the compression of the glass (Fig. 5).

436

437 **Figure 7: Diffuse scattering signals of melt and quenched glass.** The quenched glass
438 (orange, recorded at 8 GPa and 300 K) presents a FSDP position significantly sharper and at
439 slightly higher Q position compared to the corresponding melt (blue, recorded at 26 GPa and
440 ~5150 K). This suggests less densification of the local structure of SiO₂ melt at high
441 temperature, compared to the glass. We did not successfully produced a glass at experimental
442 pressures exceeding 45 GPa, because of full sample crystallization.

443

444

445 **Figure 8: Pressure dependence of the first sharp diffraction peak.** Our measurements
446 performed in melts (Red) and in glasses either quenched from high temperature (Blue) or
447 during cold-compression (Green) are compared with previous reports. The shift of the FSDP
448 to high wavenumbers occurs at lower pressures in the glass, compared to the melt.

449

450 **Table 1. Melting temperatures:** Sample temperatures are directly provided by radio-
451 spectrometry (Fig. 1). Sample pressures are derived from cross correlation between two
452 methods: the P-V-T equation of state of stishovite and an empirical model of thermal pressure
453 (see text). Experimental uncertainties are within 5 GPa and 100 K.

454

455 **Table 2. Clapeyron relations:** Volumes and entropies relations calculated around (i) the true
456 triple point where coesite, stishovite and LDM coexist and (ii) the fictive triple point where
457 LDM, HDM and stishovite would coexist (see text). Thermodynamical parameters come from
458 (Akaogi et al. 2011; Wang et al. 2012; Zhang et al. 1993).

459

Fig. 1

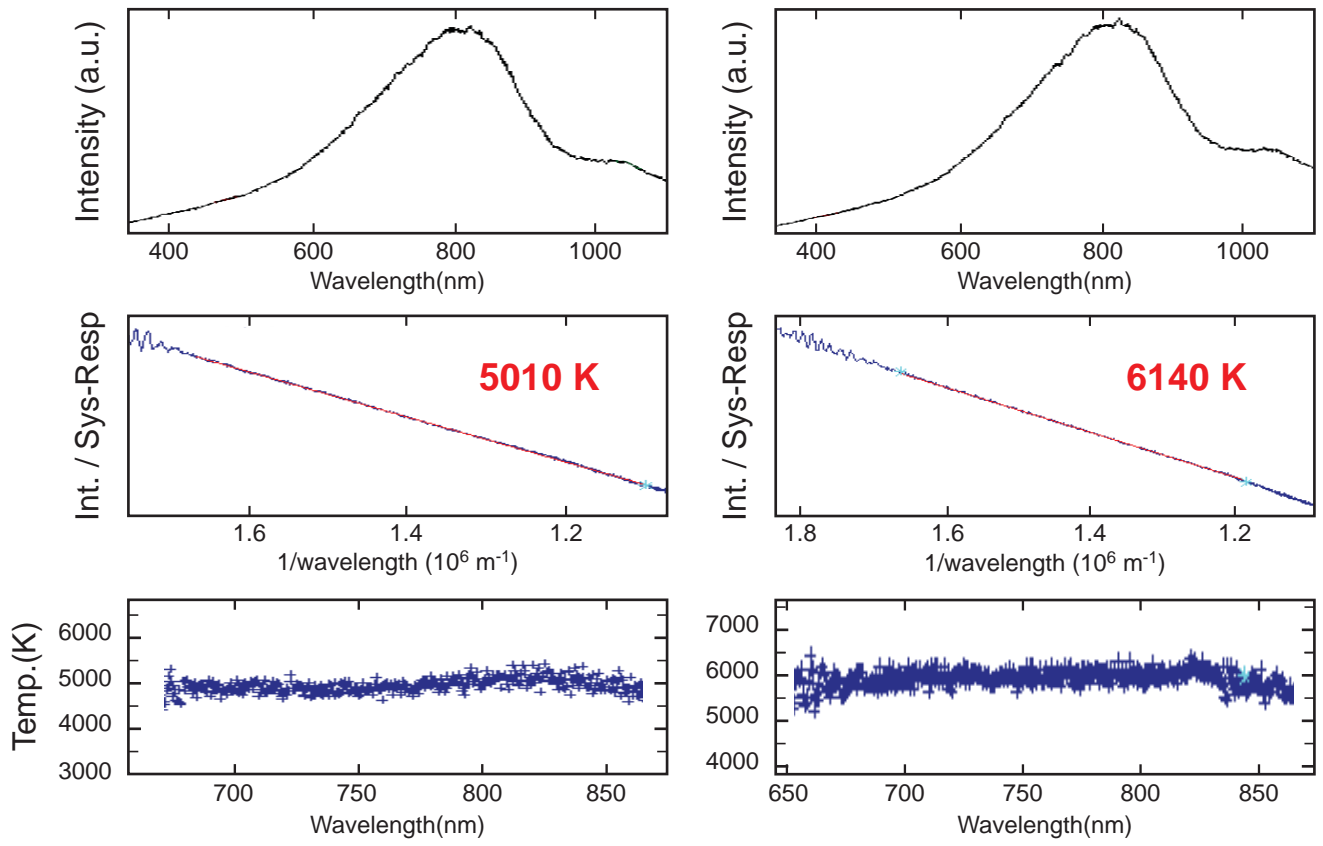


Fig. 2A

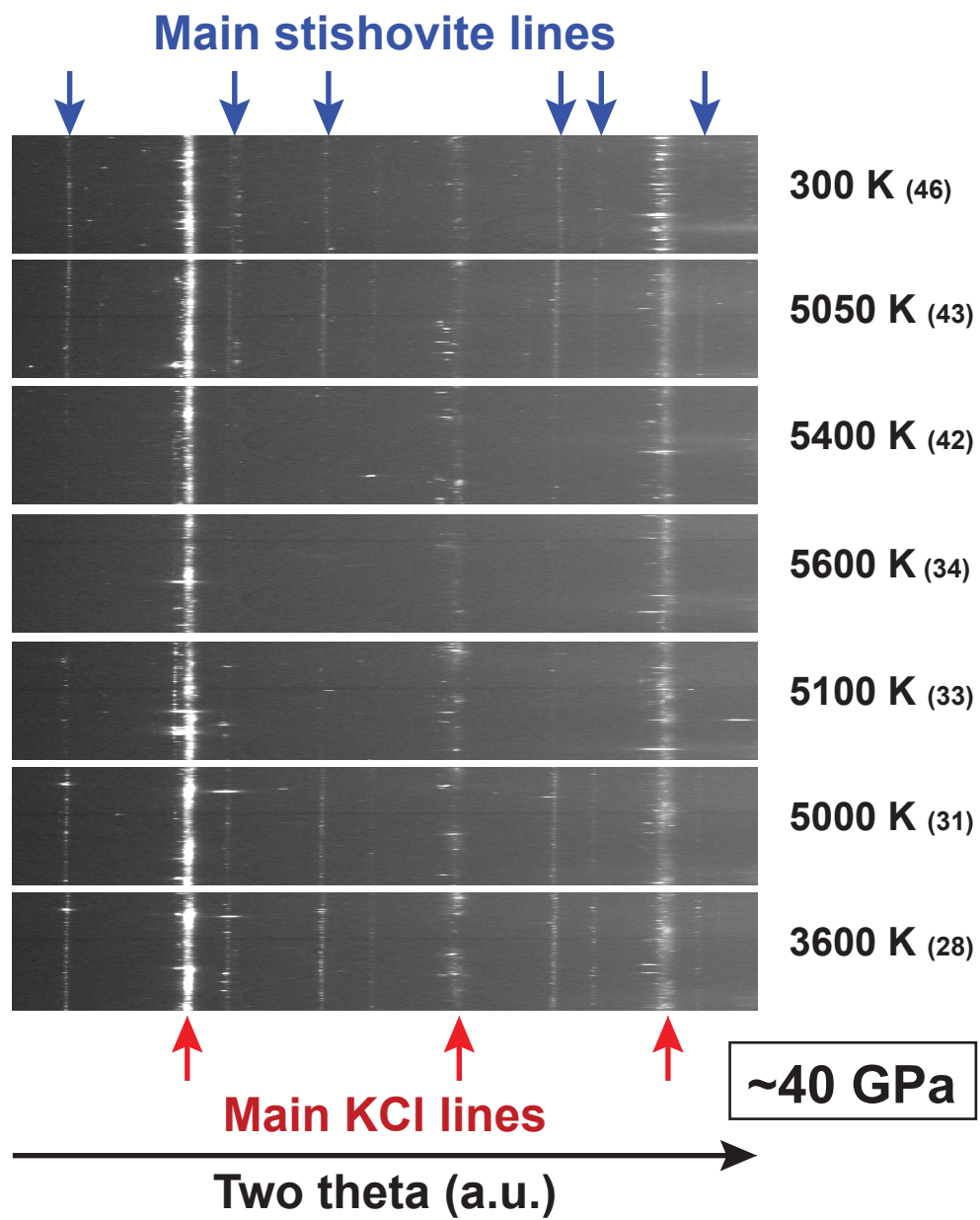


Fig. 2B

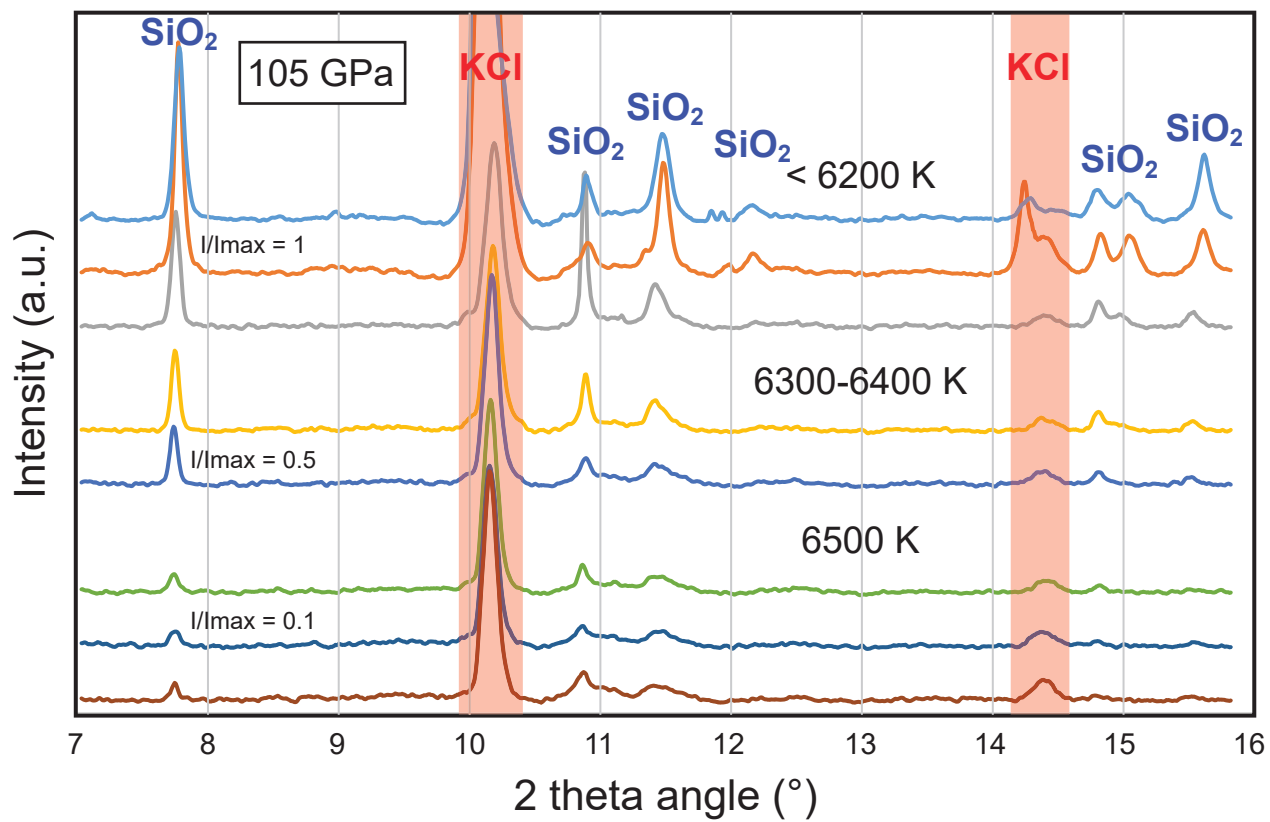


Fig. 3

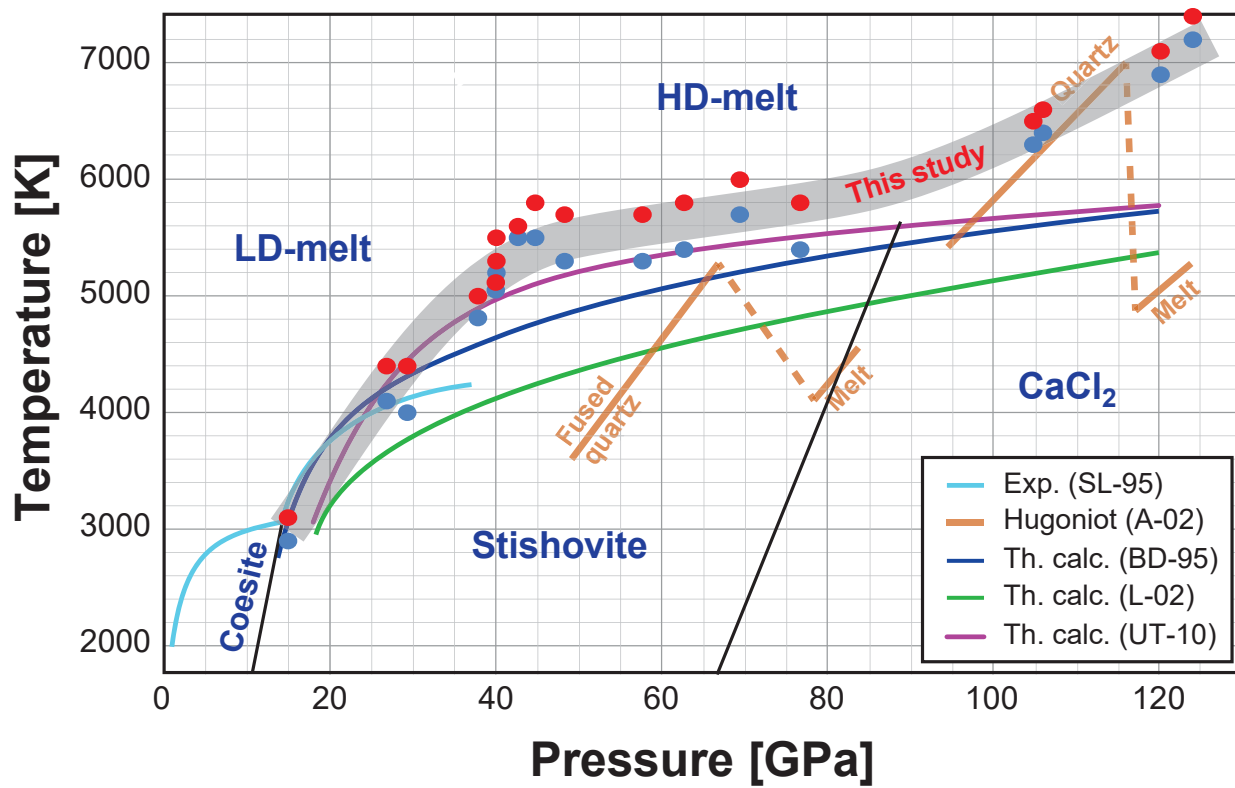


Fig. 4

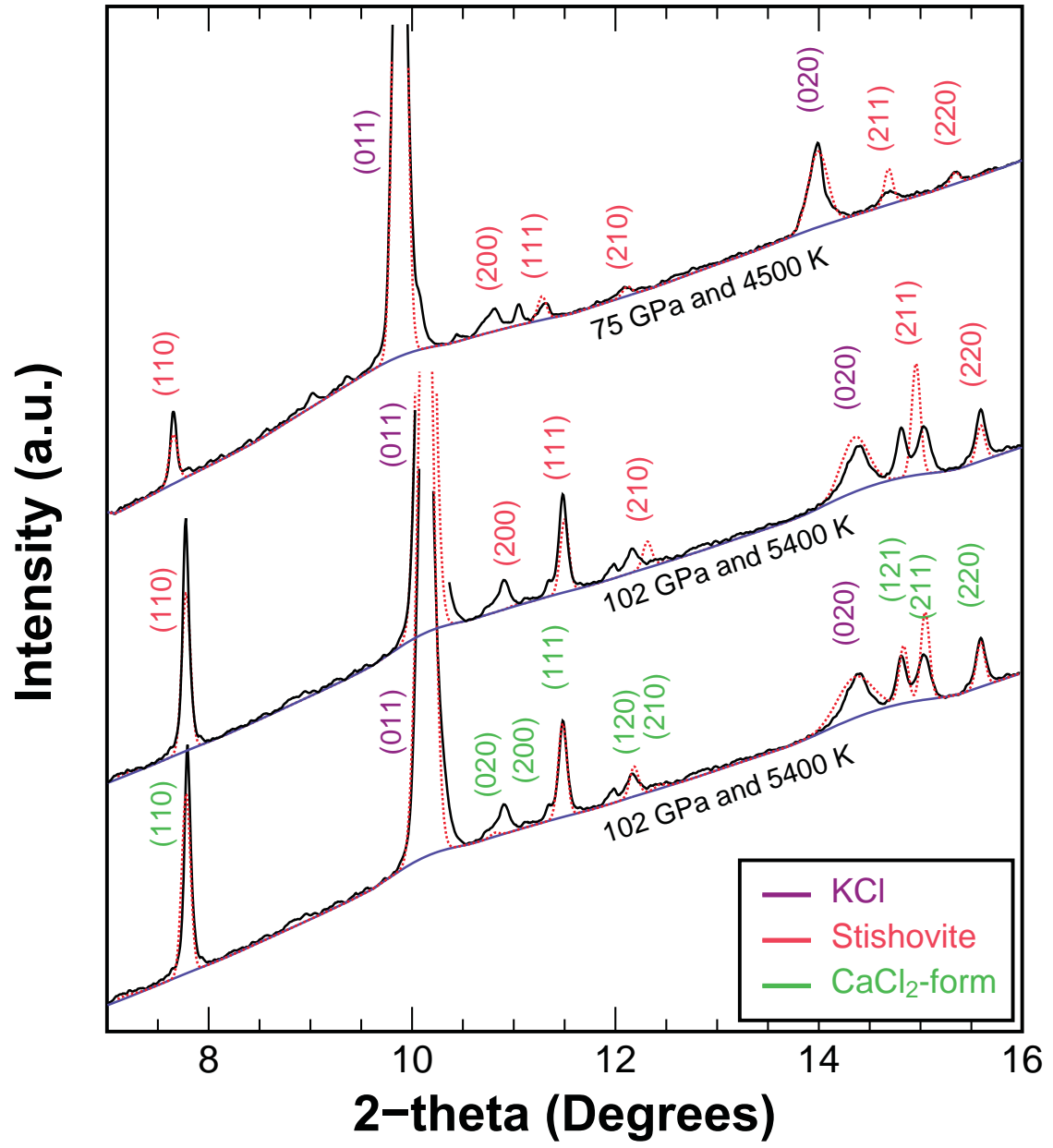


Fig. 5

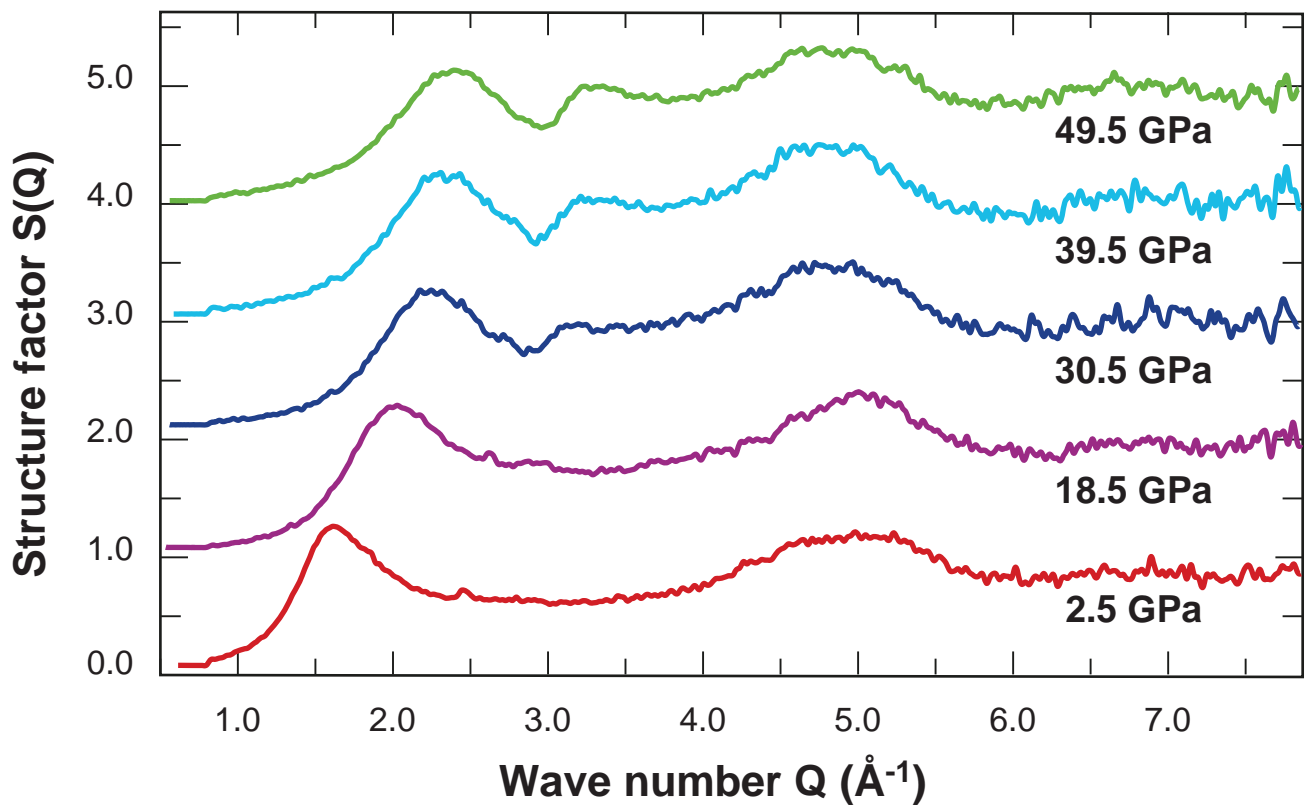


Fig. 6

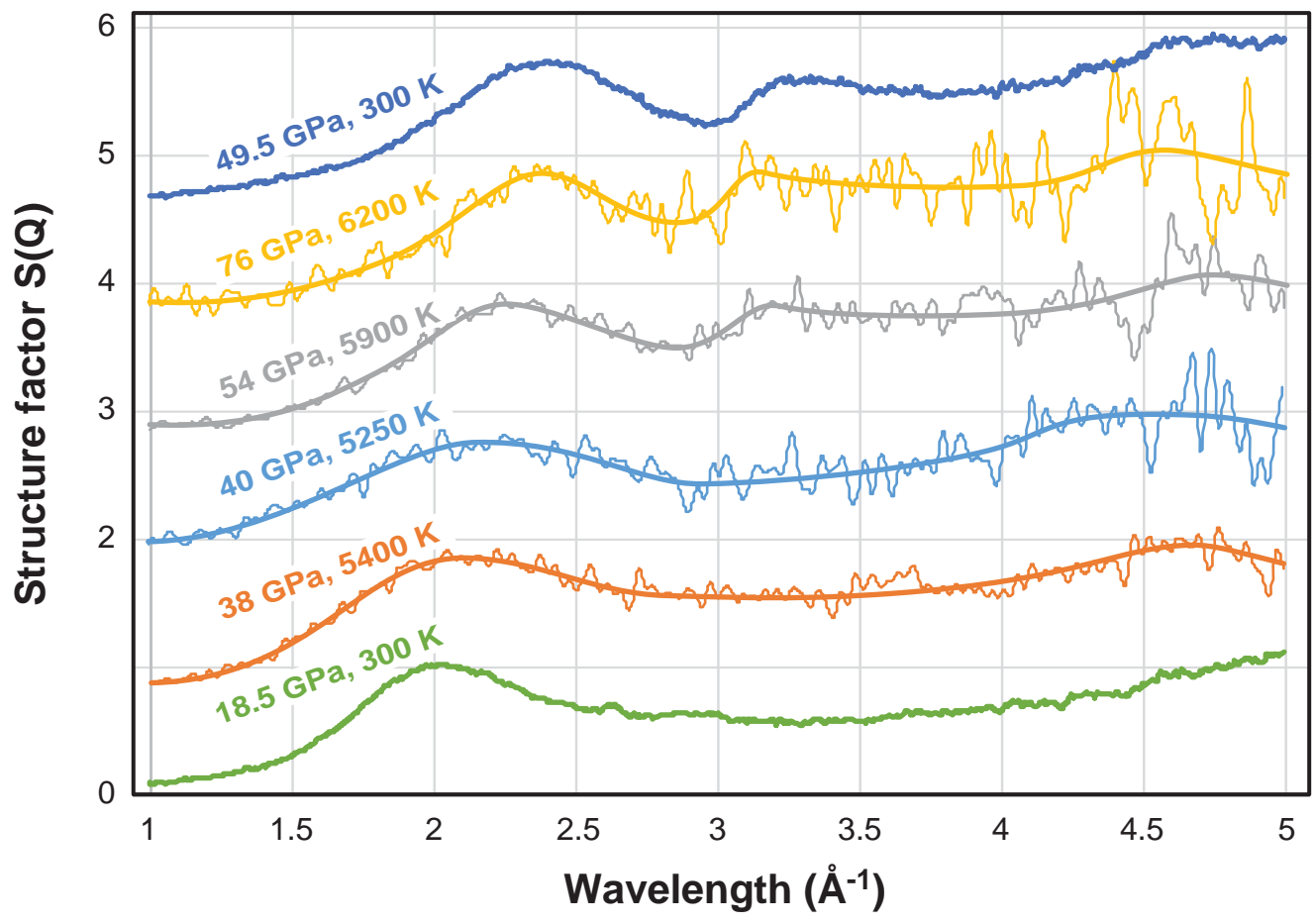


Fig. 7

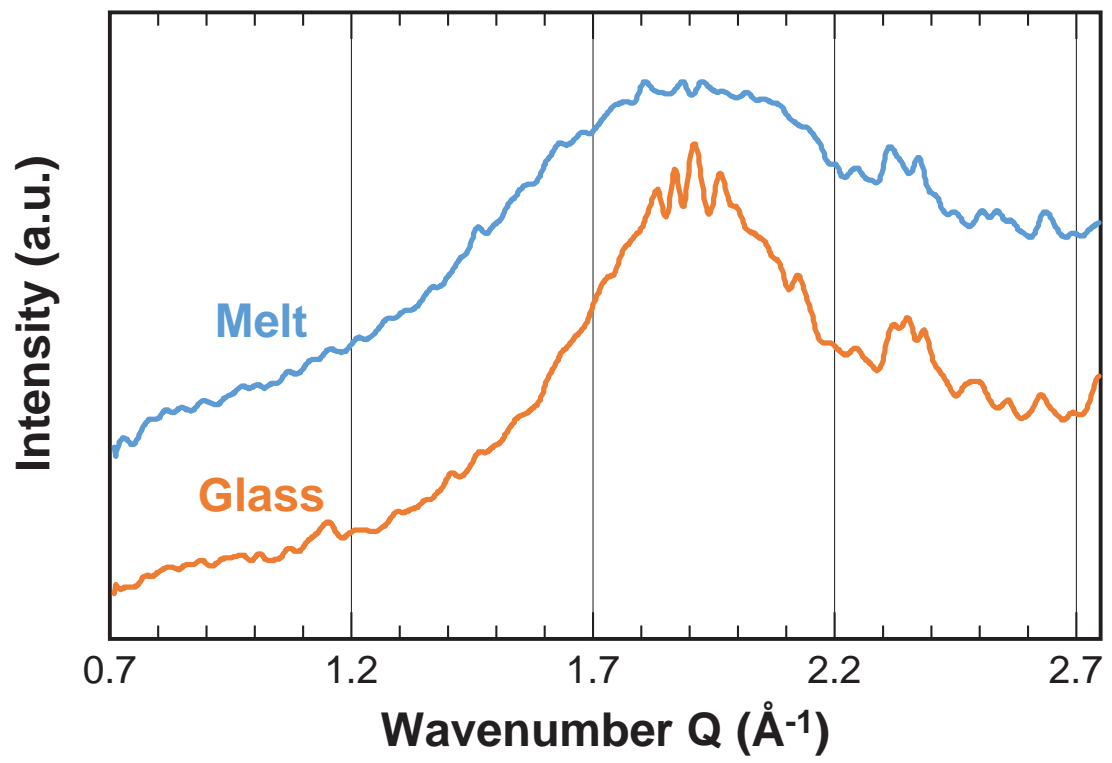


Fig. 8

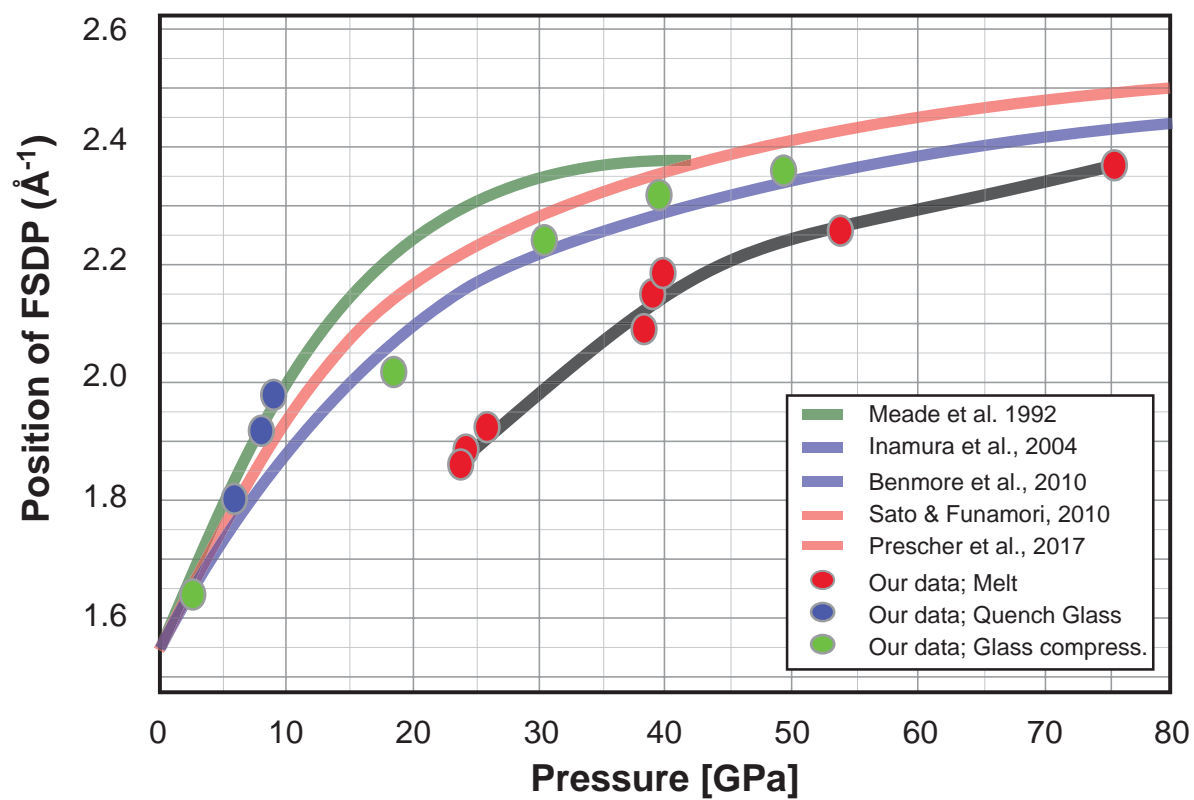


Table-2

Transition considered	Press. GPa	Temp. K	dT/dP K/GPa	DS mol/K	DV cm ³ /mol	Vstish cm ³ /mol	Vcoes cm ³ /mol	VLDM cm ³ /mol	VHDM cm ³ /mol	DV/V
C => S	15	3023	312 a	-15.28 a	-4.76736 b	14.6916 g	19.459 h			-0.279 k
C => LDM	15	3023		74.9 d	0 e		19.459 h			
S => LDM	15	3023	80 *	59.59 b	4.76736 g	14.6916 g		19.459 i		0.2792 k
S => HDM	45	5400	12.5 *	74.59 d	0.9324 b	13.6434 g			14.5758 j	0.0661 k
LDM=>HDM	45	5400		-15 c	-3.83496 f			18.4108 i	14.5758 j	-0.233 k
S => HDM	45	5400	12.5 *	59.59 d	0.7449 b	13.6434 g			14.3883 j	0.0531 k
LDM=>HDM	45	5400		0 c	-4.02246 f			18.4108 i	14.3883 j	-0.245 k
S => HDM	45	5400	12.5 *	44.59 d	0.5574 b	13.6434 g			14.2008 j	0.04 k
LDM=>HDM	45	5400		15 c	-4.20996 f			18.4108 i	14.2008 j	-0.258 k

C, S, LDM and HDM stand for Coesite, Stishovite, low-density and high-density SiO₂ melts

*, this study

a, from Akaogi et al. (2011)

b, calculated based on the Clapeyron relation $dT/dP=DV/DS$

c, value assumed to be -15, 0 or 15 J/molK (see text)

d, derived from Clapeyron relations around the (C, S, LDM) or (C, LDM, HDM) triple points

e, derived from the flat melting curve of coesite between 9 and 14 GPa (Zhang et al., 1993)

f, calculated using $DV=VHDM-VLDM$

g, calculated at the considered P-T conditions using the EoS of Wang et al. (2012)

h, calculated using $Vcoes=Vsti+DV(C-S)$

i, calculated using $VLDM=Vsti+DV(LDM-S)$

j, calculated using $VHDM=Vsti+DV(HDM-S)$

k, DV of the transition normalized to the mean value between the two phases considered

Table-1

P(300K) GPa	Temp. K	P(high-T) GPa	Temp solid	Temp Melt
12	3000	15	2900	3100
16	4250	27	4100	4400
19	4200	29	4000	4400
19	5350	40	5200	5500
19.5	5100	40	5050	5100
20	5500	43	5500	5600
21	5600	45	5500	5800
21.5	4900	38	4800	5000
21.5	5100	40	5000	5300
26	5500	48	5300	5700
36	5500	58	5300	5700
39	5700	63	5400	5800
45	5800	69	5700	6000
54	5700	77	5400	5800
76	6500	106	6400	6600
76	6400	105	6300	6500
85	7300	124	7200	7400
85	7000	120	6900	7100