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# Chapter 6 - X-ray diffraction structure measurements

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## Abstract

This chapter describes how X-ray structural measurements can be done on molten silicates under high pressures, using either large volume presses or diamond-anvil cells, the latter combined with resistive heating or laser heating techniques. A brief summary of the data obtained so far is given, followed by a description of both energy-dispersive and angle-dispersive techniques, including challenges and how they may be overcome. Three areas of research are then highlighted: 1) structural measurements at extreme pressure conditions up to 100 GPa, 2) tracking the structural environment of minor/trace elements in magmas, and 3) the different ways to obtain the density of melts from X-ray diffraction data. Finally, some future prospects are discussed.

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## 1. Introduction

At ambient pressure, silicate melts are characterized by their network structure also referred to as the intermediate range order, with bridging oxygen atoms bonded to network-former cations (e.g. Si, Al, Fe<sup>3+</sup>), and non-bridging oxygen atoms bonded to network-modifier cations (e.g. Ca, Na, K). The degree of polymerisation strongly depends therefore on the SiO<sub>2</sub> content. Pressure ( $P$ ) will affect the structure of magmas, and consequently their bulk properties (density, viscosity, etc) in mostly three ways: by modifying the network structure, by changing the local environment around given atoms (coordination number or change of neighbouring atoms), by compressing bonds. All three type of compression mechanisms may be monitored by X-ray diffraction. X-ray diffraction may also be used to directly extract density information, and as a matter of fact, it is the only possible way to measure the density of magmas using static compression on magmas at very high  $P$ . The first *in situ* structural study of silicate melts at high pressure only dates from 2004, on molten CaSiO<sub>3</sub> and MgSiO<sub>3</sub>

15 up to 6 GPa (Funamori et al., 2004). It demonstrated that the most important struc-  
16 tural change in this  $P$ -range affects the network structure. Just above ten papers have  
17 been published since, mostly using large volume presses and energy dispersive X-ray  
18 diffraction (EDX). Processing X-ray diffraction liquid data has indeed long been con-  
19 sidered arduous. However, the technique is now well-established and structural data  
20 may now be routinely collected on user-friendly synchrotron beamlines, often provid-  
21 ing data processing softwares that they developed. In contrast, diamond-anvil cells  
22 have barely been used yet for melt structural measurements. The structure of  $\text{SiO}_2$   
23 glass and the evolution of the Si-O coordination number were first tracked under  $P$   
24 in 1992 (Meade et al., 1992) using angle-dispersive X-ray diffraction (ADX), results  
25 corroborated later with EDX data collected up to 100 GPa over a larger  $q$ -range (Sato  
26 and Funamori, 2008). For DAC studies on liquids, we only cite here a few benchmark  
27 papers on with the first reports on water and Ar up to 2 GPa (Eggert et al., 2002),  
28 molten Fe up to 60 GPa ?, and silicate melts up to 60 GPa (Sanloup et al., 2013a).  
29 In terms of chemical composition, have been investigated mostly end-member compo-  
30 sitions, i.e.  $\text{MgSiO}_3$  and  $\text{CaSiO}_3$  (Funamori et al., 2004),  $\text{NaAlSi}_3\text{O}_8$  (Yamada et al.,  
31 2011),  $\text{NaAlSi}_2\text{O}_6$  (Sakamaki et al., 2012),  $\text{CaMgSi}_2\text{O}_6$  (Wang et al., 2014),  $\text{Fe}_2\text{SiO}_4$   
32 (Sanloup et al., 2013b),  $\text{MgSiO}_3$ – $\text{Mg}_2\text{SiO}_4$  both dry and hydrous (Yamada et al., 2007,  
33 2011), and only two more complex compositions, i.e. basalt (Sakamaki et al., 2013;  
34 Sanloup et al., 2013a; ?) and hydrous haplogranite (Anderson et al., 2014; ?). The  
35 choice of simple end-member compositions is guided by the fact that unlike with X-ray  
36 absorption techniques that are chemically selective, all ion-ion distribution functions  
37 contribute to the X-ray diffraction signal, hence simple end-member are necessary to  
38 identify individual contributions. That said, considerable improvements in the tech-  
39 nique now allow to study some minor but key geochemical elements (?), such as heavy  
40 rare Earth's, and relate changes in their structural environment in melts to changes  
41 in their partitioning behaviour (mineral/melt or metal/melt). One can note that pure  
42  $\text{SiO}_2$  melt still remains a challenge due to the highest  $T$  involved. This chapter will  
43 first describe the experimental techniques, with a brief account on large-volume press  
44 data (readers are referred to Chapter by Sakamaki for results obtained using this tech-  
45 nique), and more details on how to collect X-ray diffraction data on silicate melts using  
46 diamond-anvil cells combined with either resistive heating or laser heating. Secondly,  
47 some results will be presented such as the highest current  $P$ - $T$  data on melts, probing  
48 the local environment of minor elements, monitoring density evolution while tracking

49 changes in the intermediate-range order. Finally, some challenges and future directions  
 50 will be highlighted.

## 51 **2. Experimental techniques**

### 52 *2.1. From X-ray diffraction data to structural information*

53 The measured experimental intensity,  $I(q)$ , contains scattering by both the sample  
 54 and background contributions, where  $q = \frac{4\pi}{\lambda} \sin \theta$  and  $\lambda$  is the x-ray beam wavelength.  
 55 In order to isolate the intensity that contains only the structural information, corrections  
 56 for background intensity,  $I_B(q)$ , and attenuation,  $A(q)$ , from the sample must be made  
 57 to the measured intensity given by

$$I(q) = I_s(q) + A(q)I_B(q) + I_{inc}(q), \quad (1)$$

58 where  $I_s(q)$  represents the scattering from the sample containing only structural  
 59 information, and  $I_{inc}(q)$  represents the incoherent scattering from the atoms, arising  
 60 from the sum of the self  $\sum_{\alpha} c_{\alpha} f_{\alpha}(q)^2$  and Compton scattering  $\sum_{\alpha} c_{\alpha} C_{\alpha}(q)$ , where  $c_{\alpha}$   
 61 is the concentration of species  $\alpha$ . The values for the self and Compton scattering  
 62 amplitudes are documented by Hajdu (1972); Hubbell et al. (1975). The Faber-Ziman  
 63 total structure factor,  $S(q)$ , (Faber and Ziman (1965)) is then determined by;

$$S(q) - 1 = \frac{K[I_s(q) - A(q)I_B(q)] - I_{inc}(q)}{\langle f^2(q) \rangle}, \quad (2)$$

64 where  $K$  is required to normalise the data to the incoherent scattering profile and the  
 65 total structure factor is normalised to the average scattering  $\langle f^2(q) \rangle = (\sum_{\alpha} c_{\alpha} f_{\alpha}(q))^2$ .  
 66 The radial distribution functions,  $G(r)$ , are then obtained from a Fourier transform of  
 67 the  $S(q)$  as:

$$G(r) - 1 = \frac{1}{2\pi^2 r n_0} \int_0^{\infty} q[S(q) - 1] \sin(qr) dq, \quad (3)$$

68 where  $n_0$  is the atomic density in atoms per  $\text{\AA}^3$ .

69 The technical challenges here are three-fold: 1) to reach high  $T$  conditions under high  
 70  $P$ , silicates being refractory materials with high melting points, 2) to have sufficiently  
 71 large sample volume probed by the X-rays, silicate melts being amorphous by nature  
 72 and with relatively low mean atomic number (circa 20-21) are consequently very weak  
 73 scatterers, and 3) to collect diffraction data on the largest  $q$  range possible as the

74 structural information contained in the radial distribution function,  $g(r)$ , is obtained  
75 by Fourier transforming the normalised intensity, i.e. the structure factor,  $S(q)$  (cf.  
76 equation 3).

## 77 2.2. Large-volume presses

78 By far the most used method, the energy-dispersive diffraction remains unrivalled  
79 in terms of accessible  $q$ -range on compressed amorphous samples ( $15\text{\AA}^{-1}$  routinely,  
80 occasionally higher), and consequent spatial resolution in real space. The maximum  
81  $P$  range however is still modest, up to 8 GPa maximum, as sample volume must be  
82 optimised.

83 *Energy-dispersive diffraction (EDX) set-up.* EDX is used with multi-anvil presses due  
84 to the limited angular access to the sample (unless using transparent anvils made of  
85 diamond or cBN, but this has not been done yet to study melts). Not that many  
86 changes in the technique, except the use in conjunction with the Paris-Edinburgh cell  
87 that necessitated efforts to adapt the cell-assembly but with the advantage of a larger  
88 angular access to the sample and therefore much increased  $q$ -range (up to  $22\text{\AA}^{-1}$  *vs*  
89  $15\text{\AA}^{-1}$  with a multi-anvil press. Other advantage of PE-EDX: higher signal/noise  
90 ratio as transparent materials can be inserted along the X-ray paths in a stable way  
91 Yamada et al. (2011). Measurements are taken at fixed detector  $2\theta$  angle (typically  
92 ten angles ranging between  $2^\circ$  and  $35^\circ$ ). This covers up to  $20\text{\AA}^{-1}$  in reciprocal space  
93 where  $q = 4E\sin(\theta)/12.398$  where  $E$  is energy in keV of the X-rays up to 120 keV.  
94 Background signal from the sample cell environment is geometrically filtered by the  
95 intersection between incident beam and detector angle (collimator). Unknowns are  
96 the white beam profile and  $xx$ , and can be obtained from the highest angle pattern,  
97 assuming that the diffuse signal from the molten sample is negligible at such high  $q$   
98 values (refer to C. Park manual). Alternatively, these parameters can be obtained by  
99 fitting the baselines on a crystalline data set ?. Peaks in the diffraction pattern may  
100 arise from Bragg peaks of the sample container (usually graphite, more rarely diamond)  
101 and fluorescence from indium on the detector and elements within the sample; peaks  
102 must all be removed. The scaling of the individual structure factors is achieved by  
103 fixing the oscillations of the data at highest  $q$  to oscillate around 1 as they must by  
104 definition. Then the other structure factors are scaled accordingly in reverse order from  
105 highest  $q$ . After merging, an error weighted spline is fit to the data in order to obtain  
106 an evenly spaced  $S(q)$  distribution. This fitting uses only parts of the individual  $S(q)$

107 that overlap in order that they can be fit together. More details on how to process EDX  
108 data on melts may be found in K-i Funakoshi 1997 (book chapter?). Note that EDX  
109 may also be used in conjunction with diamond-anvil cells, as illustrated for example by  
110 the structure of SiO<sub>2</sub> glass obtained up to 100 GPa (Sato and Funamori, 2010), so in  
111 principle this technique could be used for the study of melts as well. The main problem  
112 being the acquisition time (not given in SatoFunamori papers) of typically a few hours,  
113 a duration over which it is very challenging to maintain stable high  $T$  conditions in a  
114 diamond-anvil cell.

115 *Angle-dispersive diffraction (ADX) set-up.* ADX necessitates a large angular access to  
116 the sample, which is possible if using a device using two opposed anvils such as the Paris-  
117 Edinburgh press. Background removal by either subtracting pattern collected outside  
118 of the sample, or by filtering the signal using multichannel collector that acts similarly  
119 to the collimating slits with EDX. The latter efficiently removes the background (except  
120 at low angles), but loses efficiency at high energies as it becomes more transparent to  
121 the X-rays. Currently, molten basalt data collected up to  $8 \text{ \AA}^{-1}$  using this technique  
122 (Crépeisson et al., 2014), although up to  $18 \text{ \AA}^{-1}$  was achieved on molten Fe (Sanloup  
123 et al., 2000) using high energy X-rays (101.7 keV) without using a collimation system,  
124 which might remain necessary for low  $Z$  silicate melts. Collection times: 10-30 minutes.

### 125 2.3. Diamond-anvil cells

126 As mentioned above, only ADX set-ups have been used so far with diamond-anvil  
127 cells for the structure of molten silicates. DAC are very versatile tools and the most  
128 straightforward way to cover all  $P - T$  conditions relevant for planetary interiors. As  
129 for any ADX-based high  $P$  set-up, it is crucial to optimize the angular access to the  
130 sample that is necessarily restricted by the high  $P$  environment. Efforts to increase the  
131 accessible  $q$ -range have used transparent seats (beryllium or BN in Shen et al for Fe,  
132 + modified gaskets with transparent materials around the sample, check Eggert). The  
133 availability of Boehler-Almax anvils (ref) and adapted large-opening WC seats ( $70$  or  
134  $80^\circ$ ) have largely helped to democratise the technique, and are now the simplest way  
135 now to optimize the accessible  $q$ -range while also reducing Compton inelastic scattering  
136 from the diamonds as BA anvils are thinner than conventional ones ( $1.5 \text{ mm}$  thickness *vs*  
137  $2.0\text{-}3.0 \text{ mm}$ ). The elastic contribution of diamond anvils to the signal, i.e. Bragg peaks,  
138 may be minimized by rotating the DAC perpendicularly to the X-ray beam to avoid  
139 the most saturating peaks (Fig.1). All diamond Bragg peaks must then be removed

140 using masks. In DAC experiments, a very thin sample (maximum few tens of microns,  
141 often only a few microns thick) is squeezed between two diamond anvils (1.5 to 2 mm  
142 each). As a result, the largest contribution to the signal is the inelastic scattering from  
143 the diamonds. It must be precisely measured and removed from the total intensity in  
144 order to extract the sample signal. For this purpose, one can measure the empty cell  
145 background, i.e. remove the sample after the experiment, put the empty gasket back  
146 in place and collect XRD data. Ideally, the background may also be obtained from the  
147 crystalline pattern, after quenching the experiment to room  $T$ , and after removing all  
148 Bragg peaks from the integrated intensity. Silicate melts are often complex chemical  
149 compositions and crystallise as forest of peaks that cannot be individually removed. It  
150 is nonetheless helpful to scale the empty cell background up to the baseline. For further  
151 description of background removal methods, readers may refer for ADX data to Eggert  
152 et al. (2002) and ? (Rev Sci Instr), and for EDX data to Sato and Funamori (2010).

153 *Resistive-heating diamond-anvil cells (RH-DACs)*. Due to their relatively low melting  
154 points, only hydrous continental crust magmas may be studied using resistive heating  
155 techniques (maximum achievable  $T$  of 1300 K with metallic wires, up to 1800 K using  
156 graphite furnace in conjunction with a vacuum chamber, see Liermann et al. for a  
157 review of resistive heating techniques); this is nonetheless a large and important field  
158 of study. The advantages of RH-DAC are two-fold: good control on  $T$  and relatively  
159 large sample volume as no thermal insulation is required, therefore the gasket hole  
160 can be completely filled with the sample. On the relatively small  $P$  range over which  
161 continental crust magmas are molten below 1300 K, a large beam size is not an issue  
162 as one can use 250-300 micronm sample chambers; therefore the sample volume probed  
163 by the X-rays may also be enlarged by using a relatively large beam. The haplogranite  
164 (HPG) data shown on Figures 2 were collected on relatively thick samples for DAC  
165 experiments, 120 micronm, and using X-ray beam energy ranging from 30 keV to 60  
166 keV. Increasing the energy is essential to increase the  $q$ -range, with the draw-back  
167 that the beam intensity is usually highest in the 20-30 keV range and rapidly drops  
168 at higher energies(?). Comparison of data collected on the same HPG sample using  
169 different energies (Fig.2) shows that a good compromise between photon flux and  $q$ -  
170 range is reached at 47 keV. A 60 keV or higher energy set-up is necessary for the study  
171 of some minor/trace elements which contribution on  $g(r)$  would otherwise overlap too  
172 much with other ion-ion contributions, but it necessitates much longer acquisition times.

173 High energy X-ray diffraction data may be collected on synchrotron beamlines not



Figure 1: 2-D diffraction data collected on molten hydrous haplogranite. Right panel: at 33 keV on a MAR555 (ID09, ESRF); middle panel: at 42 keV on a MAR3450 (I15, Diamond); left panel: same as middle panel with masks for diamond Bragg peaks. NB: the strong inner diffuse ring is the first sharp diffraction peak.

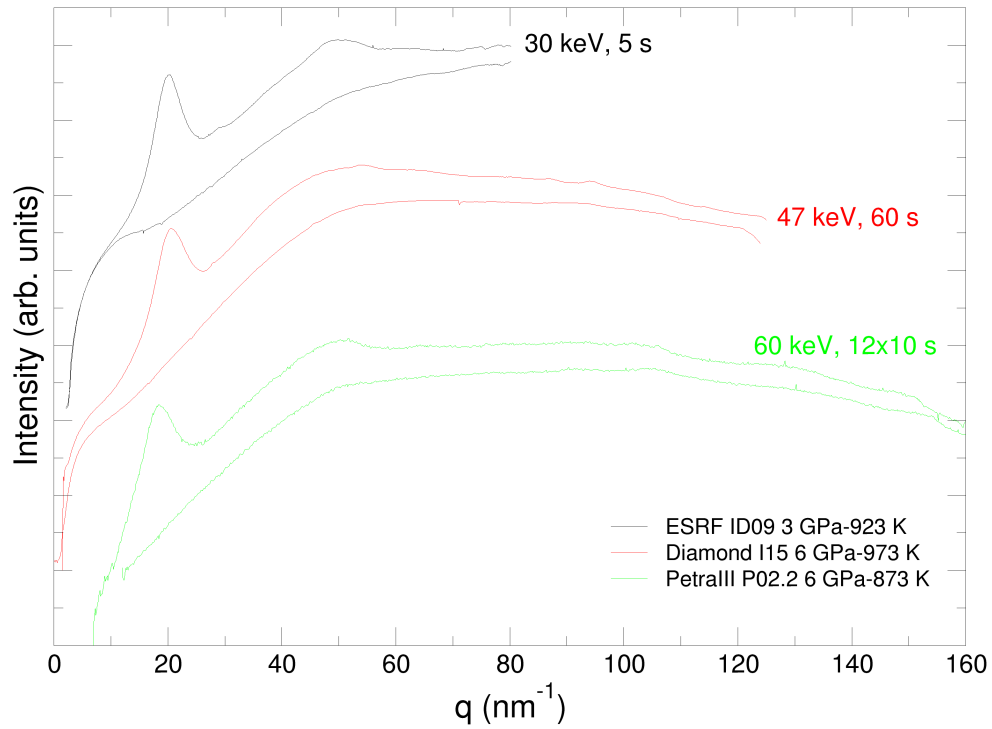


Figure 2: Integrated intensity on HPG melt ( $T > T_g$ ) and corresponding empty cell background using similar RH-DAC but different X-ray wavelength. Top (black curves): at 30 keV, data collected on ID09 at the ESRF for 5 seconds, 2xX micronm beam size; middle (red curves): at 47 keV, data collected on I15 in Diamond for 60 seconds, 20 micronm beam size; bottom (green curves): at 60 keV, data collected on P02.2 in PetraIII-DESY, 4micronm x6 micronm beam size.

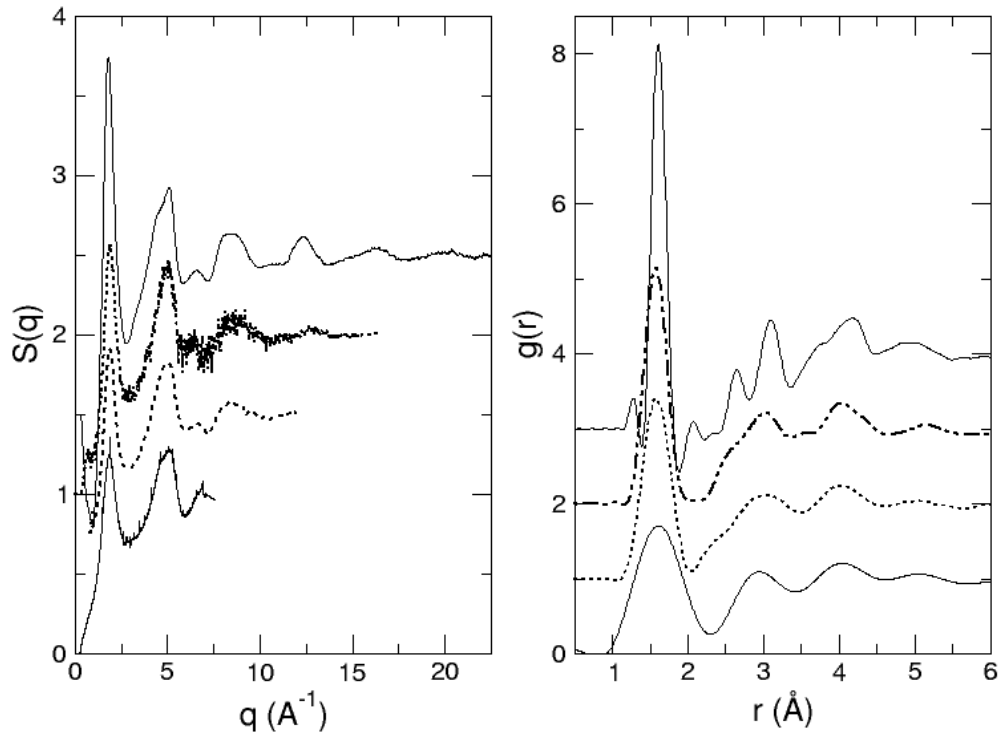


Figure 3: Structure factor,  $S(q)$ , and corresponding  $g(r)$ . From top to bottom: 1) free standing HPG glass, data collected on I15, ESRF at 72.9 keV for 10 msec, 2) molten hydrous HPG at X GPa and X K, data collected at 60 keV (PetraIII-DESY, P02.2), 3) molten hydrous HPG at X GPa and X K, data collected at same conditions as for Fig.2.

174 dedicated to high  $P$  experiments for amorphous samples. However, for combined high  
175  $P$  and high  $T$  experiments on melts, although it is possible for users to bring their own  
176 DAC heating set-up whether that be resistive furnaces or portable laser set-up, the  
177 use of dedicated high  $P$  beamlines is recommended due to the complexity of recording  
178 X-ray structural data on melts, including precise alignment procedures on systems that  
179 may not be stable over long durations.

180 *Laser-heating DACs.* This technique has been used to obtain the structure of molten  
181 Fe up to 58 GPa ? by directly heating the sample, or that of water up to 57 GPa  
182 Goncharov et al. (2009) using Ir foil that couples with the laser, to conductively heat  
183 the sample. Laser-heating requires that the sample be thermally insulated from the  
184 diamonds, as they are very good heat conductors. For silicate melts Sanloup et al.  
185 (2013a), pure silica platelets proved ideal as crystalline peaks are very thin and easy  
186 to remove from the 1-D integrated diffraction pattern, and no chemical contamination  
187 was observed on recovered samples at least on the short timescale of the experiment (10  
188 s heating). Laser heating in diamond anvil cells is currently most commonly achieved  
189 using a Nd-YAG laser that couples with 3d elements, typically Fe which is present in  
190 most natural magmatic compositions, and can be focussed to relatively small spot size  
191 (typically 20  $\mu\text{m}$ ). For these experiments, flash-heating is necessary as Fe tends to move  
192 away from the heated area due to the Soret effect. Flash-heating is achieved by ramping  
193 the laser to the target power with the shutter closed, and simultaneously opening laser  
194 and X-ray shutters for data acquisition (typically 10 s) before quenching. CO<sub>2</sub> IR  
195 laser can be used for Fe-free compositions, however focussing is arduous compared to  
196 YAG lasers, and only thin samples may be properly heated, thus further diminishing  
197 the signal intensity (Drewitt et al., 2015). It is preferable to use off-axis laser heating  
198 rather than on-axis laser heating as the latter is done using carbon mirrors that alter  
199 the signal significantly especially for low intensity scattering materials such as molten  
200 silicates (see kink in the signal at 20 degrees on Fig.4).

201 It is now possible to obtain accurate structural information on molten silicates up  
202 to the megabar range. But it remains very costly above 40-50 GPa as both diamonds  
203 get burned due to the large sample thickness (circa 30-40 micronm) necessary to obtain  
204 a sufficiently strong scattered intensity, and the consequent thinner thermal insulation  
205 layers (circa 10-15 micronm on both sides). Nd-doping might be useful in this respect.  
206 Preliminary experiments were conducted on synthetic Anorthite-Diopside composition  
207 doped with 3.8 wt.% Nd<sub>2</sub>O<sub>3</sub>. The Nd coupler proved to have many advantages over

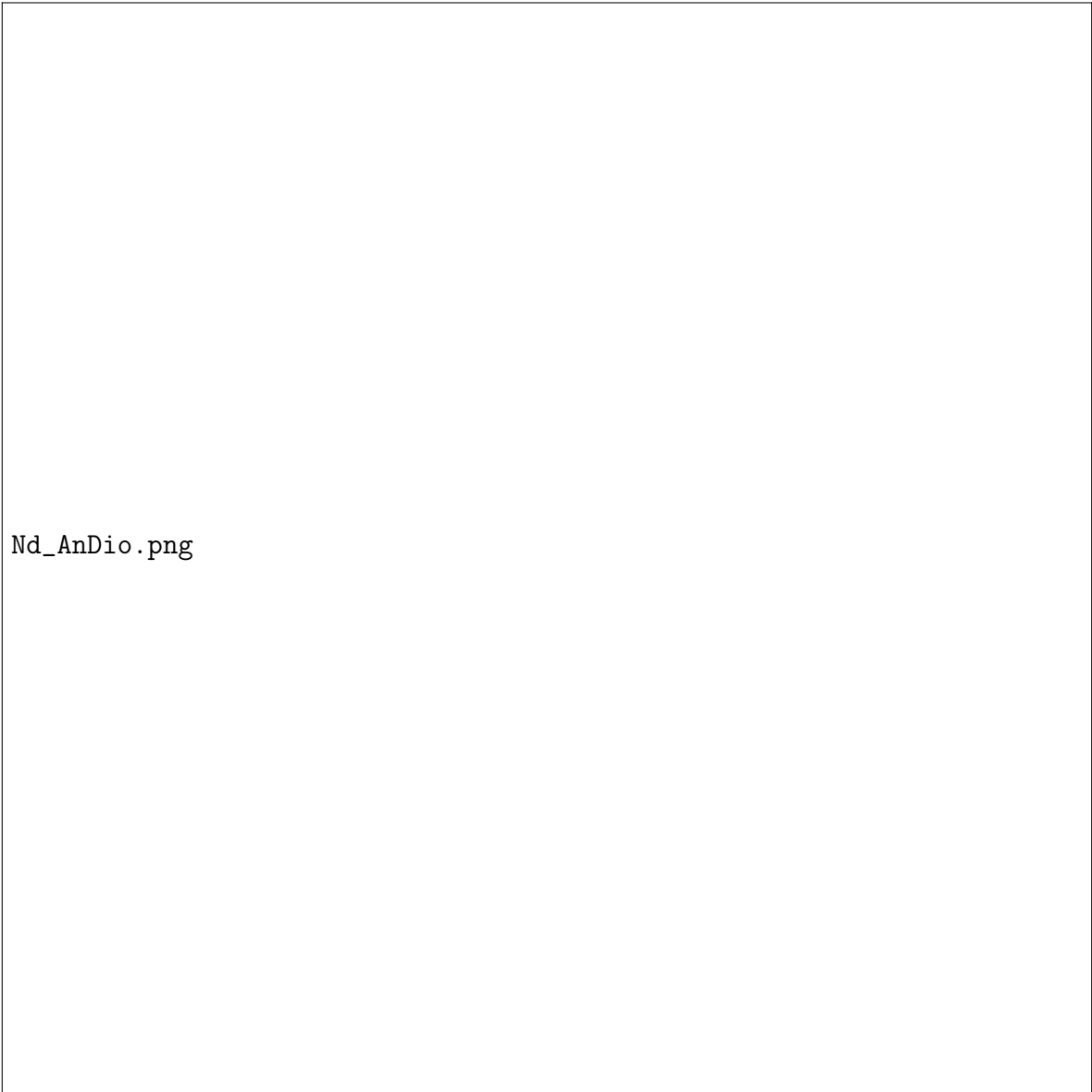
208 previous iron coupling measurements, including the ability to remelt the sample with  
209 identical quality, very localised heating, and preservation of the diamond anvils even  
210 at  $P > 50$  GPa and  $T > 2000$  K. When Fe has been used as a coupler (Sanloup et al.,  
211 2013a), if the same sample was melted more than once with the laser a considerable  
212 decrease in intensity was observed, indicating that Fe appeared to diffuse away from  
213 the sample spot. With Nd no such decrease in intensity was observed and the re-  
214 covered sample analysis suggests that Nd remained homogeneously distributed. The  
215 localisation of heating is improved with Nd compared to Fe as observed by the partial  
216 recrystallisation of the SiO<sub>2</sub> thermal insulation layer. In Fe-doped samples this layer  
217 always recrystallised resulting in considerably more Bragg peaks to remove and addi-  
218 tional uncertainty in the data processing. It is also this improvement in localisation of  
219 heating that appears to protect the diamond anvils from damage at high  $P$  and  $T$ .

### 220 **3. Examples of the results by the technique**

221 Three main areas: local environment around major cations, around minor cations,  
222 and medium-range order. And density.

#### 223 *3.1. Extreme P-T*

224 Only two studies have been published so far on the structure of silicate melts above  
225 the 10 GPa range, one on molten basalt up to 60 GPa (Sanloup et al., 2013a) and one on  
226 alumino-silicate melts up to 30 GPa Drewitt et al. (2015). First aim: X-O coordination  
227 number and bond length of major elements within 2-3 Å max, too many correlations  
228 afterwards and too much disorder. Coordination number vs P established now for Fe,  
229 Si, and Al at least on some P-range, all show increase of X-O over a given P-range (i.e.  
230 continuous transition). Remain to be measured in the melt: Mg (done in glass), Ca  
231 (difficult due to broad distribution). These data-sets provide a physical ground for the  
232 understanding of compression mechanisms in melts (Sanloup, 2016). Brief summary  
233 of Nature paper (Sanloup et al., 2013a). The  $P$ -range has now been pushed further,  
234 with acquisition of data up to 104 GPa (Fig.6) at which point both lasers were at  
235 their maximum power of 100 W each which prevented the acquisition of data at higher  
236  $P$ , i.e. with higher melting points. The level of intensity is similar to data collected  
237 up to 60 GPa, and should provide quantitative structural information once processed  
238 (results will be published elsewhere). We should then be able to test whether or not  
239 Si-O increases further than 6 as proposed for silicate glasses based on acoustic velocity



Nd\_AnDio.png

Figure 4: Molten anorthite-diopside at 3500 K (10 s) and quenched glass (60 s) at 9 GPa (data collected on GSECARS ID-13, APS at 40 keV using a Perkin Elmer detector); note the kink in the overall patterns at 20 degrees due to scattering from the carbon window used for laser heating at 90 degrees geometry. Left panel: intensity (melt, quenched glass, empty cell); middle panel: melt (red) and glass (black) structure factor,  $S(q)$ ; right panel: melt  $g(r)$  (continuous line) and fit of the first peak using CN Si-O=6, CN Al-O=5.2).



Figure 5: Microphotographs of a Nd-doped Fe-free anorthite-diopside sample after repeated laser-heating at 29.3 GPa (left), and of a basalt sample after three laser-heatings at 45 GPa (check for run 13) (right). Quenched molten zones appear as spheres on both samples.

240 measurements ?, and reported for glassy  $\text{GeO}_2$  structural measurements (?). Therefore  
241 in principle, X-ray data can be collected at least over the whole megabar range on  
242 molten silicates.

### 243 3.2. Minor elements

244 Context: element partitioning depends not only on crystal structure and how it  
245 changes with P, but also on melt composition, e.g. on melt structure. This well estab-  
246 lished fact at ambient pressure becomes more documented now under pressures. Our  
247 understanding of planetary differentiation, or any magmatism-related issue, therefore  
248 depends on our understanding of melt 'crystal-chemistry'. Complementary with X-ray  
249 absorption techniques. Limitations of XAS: only edges above 15 keV are accessible  
250 through a high pressure apparatus, and edges above 35 keV challenging due to low flux  
251 (check). This restrict the study to the following elements (?). Limitations of XRD: the  
252 X-O bond must not overlap too much with major elements bonds in order to be detected  
253 with the full chemical information given by radial distribution function. Only heavy el-  
254 ements accessible/detectable. Proved feasible for Lu ( $Z=71$ ). Ideal window: X-O bond  
255 ranging between Al-O and Ca-O bond length. Easier for HPG simple composition, but  
256 also feasible for more complex An-Dio composition (?). Conclusion: trace elements  
257 may change coordination number abruptly, or at least on much smaller P-range than  
258 reported for major elements. Clearly requires larger q-range than to solve major el-  
259 ements local environment. Data are now coming, need proper theoretical treatment  
260 now.



Figure 6: Intensity scattered by molten basalt at the highest  $P$  at 80 GPa and 104 GPa, the highest  $P$  investigated so far on molten silicates using static compression techniques (PetraIII-DESY, P02.2; 42 keV, 10×1 s acquisition).

261 *3.3. Tracking the medium-range order/compression mechanisms*

262 There are several ways to obtain the density of silicate melts using X-ray diffraction.  
 263 First, one can use the self-consistent method and obtain the density by minimising the  
 264 signal in  $g(r)$  at distances lower than the interatomic distances (see ? for the method  
 265 and Eggert et al. (2002) for its adaptation to diamond-anvil cell data). Second, for low  
 266  $P$  data, one may use the fact that  $S(q)$  limit at low  $q$  (?). From

$$\lim_{q \rightarrow 0} S(q) = \frac{nTk_B}{K_T} \quad (4)$$

267 and

$$K_T = \rho \left( \frac{\partial P}{\partial \rho} \right)_T \quad (5)$$

268 we get

$$\left( \frac{\partial P}{\partial \rho} \right)_T = \frac{\mathcal{N}_A k_B T}{MS(0)} \quad (6)$$

269 where  $k_B$  is the Boltzmann constant,  $\mathcal{N}_A$  is the Avogadro number, and  $K_T$  the isother-  
 270 mal bulk modulus. Equation 6 is valid for any isotropic liquid (Egelstaff, 1994), inde-  
 271 pendently on the nature of bonding within the melt. This second method may only be  
 272 used at low  $P$  as the noise on  $S(q)$  gets larger than  $S(0)$  for high density melts (i.e.  
 273 high bulk modulus), and it is not possible to determine

$$\lim_{q \rightarrow 0} S(q) = \frac{nTk_B}{K_T} \quad (7)$$

274 in such conditions.

275 Third, one can also constrain the density from the radial distribution function if the  
 276 coordination number of the main cations are known. For instance, the density,  $\rho$ , of the  
 277 HPG was estimated by fixing the Si-O coordination number to 4 which is reasonable  
 278 in this relatively low  $P$  range, and fitting the first peak on  $g(r)$  (give equation to see  
 279 where  $n$  and CN come into play). In order to compare with reported densities in the  
 280 literature, the calculated atomic number density,  $n$ , must be converted to g/cm<sup>3</sup>. This  
 281 is done using the formula

$$\rho = \frac{nM}{\mathcal{N}_A} \quad (8)$$

282 where  $M$  is the atomic mass of the sample. The densities for the hydrous glass and  
 283 melt samples are shown in Figure ?? and compared to hydrous granitic melt densities  
 284 reported by Malfait et al. (2014).

285 Fig.: HPG density from Charlotte.

286 Mention evolution of FSDP as the main compression mechanism at low  $P$  for silicate  
287 melts. Including effect of water by Yamada 2007 (?). But careful not to overlap too  
288 much on Sakamaki chapter. Cite Zeidler and Salmon work. Position of FSDP equal to  
289  $2\pi/\text{distance}$  (ring size?) cf ChemGeol 2016 and packing limit (Wang 2014).

290 Fig.: FSDP vs  $P$  HPG, dry and hydrous

## 291 4. Challenge and future perspectives

### 292 4.1. *How to further optimize the signal/diffracted intensity, and the accessible $q$ -range/spatial 293 resolution in direct space*

294 Using Soller slits on DACs (in fact not used to increase  $q$ -range that much but to get  
295 signal from low scattering materials)? May be mention and add that structure of molten  
296 water was obtained up to 57 GPa in DAC without Soller slits, eventually comparing  
297 the signal with recent data obtained with Soller slits (Datchi: donnees sur H2 a tres  
298 basse pression, et donnees sur CO2). Clearly increasing the energy is a better option.  
299 Katayama 2010: up to 17 GPa Datchi PRB 2016 on molten CO2 up to 10 GPa: data  
300 collected up to 10A-1 but cut at 7.4 A-1 due to noise/signal ratio Discuss dedicated  
301 HP high energy beamlines rather than bringing DACs on high-energy beamlines due  
302 to the challenging nature of the experiments. Or rather waiting for very high P-T in  
303 multi-anvil presses, might be the best option. What to expect from upgraded sources  
304 in terms of liquid diffraction.

### 305 4.2. *Switching from static to dynamic compression*

306 And most of all, shock wave data!! Shock wave data provide key constraints on the  
307 melting curve of planetary materials, including silicates (?). Liquid-liquid phase tran-  
308 sition has been reported (?), followed by metallisation of the melt at higher pressures.  
309 First quantitative structural data on molten materials obtain on bismuth in 2015 at 14  
310 GPa using free electron laser shock-wave experiments (?), and already getting decent  
311 signal on molten scandium at 82 GPa (?).with the exceptional advantage that there  
312 is no background to remove, and complementary good constraints on the pressure and  
313 bulk density of the shocked sample from VISAR diagnostic. The quality of the data is  
314 increasing rapidly, and this a very promising area for the structure of liquids at high  
315 pressure in general and silicate melts in particular, with implications ranging from un-  
316 derstanding the magma ocean area and its eventual remnants at the bottom of the  
317 lower mantle, to the formation, structure and dynamics of super Earths exoplanets.

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