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# **Rheology of partially molten plagioclase containing wetting silica-rich anhydrous melt abbreviated title: Rheology of partially molten plagioclase**

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8 **Rheology of partially molten plagioclase containing wetting silica-rich anhydrous melt**

9 abbreviated title: **Rheology of partially molten plagioclase**

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18

## 19 **Abstract**

20           The present work explores the effects of melt chemistry on diffusion controlled creep of partially  
21 molten labradorite plagioclase (An<sub>50</sub>) at anhydrous conditions. Using sol-gel and hot pressing techniques  
22 we produced: 1) nominally melt-free samples (Lab), with < 1 vol. % residual glass confined solely to  
23 multiple grain junctions; 2) SilLab1 and SilLab5 partially molten samples containing respectively 1 and  
24 5 vol. % excess amorphous silica, resulting in partial melts wetting numerous grain boundaries as thin (<  
25 10 nm) amorphous films. Energy dispersive X-ray analysis showed that the amorphous phases in Lab,  
26 SilLab1 and SilLab5 samples contained about ~ 70, ~ 85 and ~ 95 wt. % SiO<sub>2</sub>, respectively. Infrared  
27 spectroscopy showed that the initial traces of water (~ 0.05 wt. %) were dried out by annealing in air  
28 above 1100°C. Uniaxial creep tests performed at 1100 – 1250°C and 3 – 60 MPa flow stresses showed  
29 dominantly linear viscous flow, with a strong grain size dependence indicating grain boundary sliding and  
30 diffusion control. Counter-intuitively strength and activation energy increased with the content of melts,  
31 but in accord with the silica content of the latter, that is with their polymerization state. Our results show  
32 that the kinetics of grain boundary diffusion controlled creep strongly depends on melt chemistry. Instead  
33 of acting as short-cut for diffusion, thin films of highly viscous amorphous phases may in turn  
34 considerably reduce grain boundary transport properties.

35

36 **Key words:** rheology, plagioclase, partial melt, thin melt films, grain sliding, diffusion creep.

37

## 38 **1. Introduction**

39

40           The rheological properties of partially molten silicates may substantially deviate from those of  
41 their fully crystalline counterparts. The partially molten silicates are usually substantially weaker (Van  
42 der Molen and Paterson, 1979; Vigneresse et al., 1996), but the magnitude of weakening may differ

43 depending on the mineralogy and chemistry of the considered system, as well on the proportion of partial  
44 melt and its grain scale topology (Cooper and Kohlstedt, 1986; Hirth and Kohlstedt, 1995a; 1995b;  
45 Kohlstedt and Zimmerman, 1996; Dimanov et al., 1998; 2000). Understanding the rheological properties  
46 of partially molten silicates is therefore of fundamental importance for modelling the dynamics of various  
47 tectonic settings. For example, the stability of the high plateau in the collision context of the Himalayan-  
48 Tibetan orogen is proposed to be ensured by channel flow localized within the lower crust. The viscosity  
49 of the latter is supposedly exceptionally low, in relation with partial melting (see a review by Harris,  
50 2007). Another classical example is the accretion of the oceanic crust from the magma chambers beneath  
51 the mid-ocean ridges. In this case, plagioclases and clinopyroxene crystallizing from the basaltic liquid  
52 settle down from the crystalline mush at the bottom of the magmatic lens. The gabbroic material is further  
53 driven apart from the ridge by the convection of the upper mantle. This lateral flow occurs at partially  
54 molten state as demonstrated by the magmatic fabrics: bedding, shape preferred textures and lack of  
55 crystalline plasticity (Nicolas and Ildefonse, 1996; Ildefonse and Nicolas, 1997). However, magmatic flow  
56 is expected to occur for suspensions at relatively high liquid fractions ( $> 30$  vol. %), which disagrees with  
57 the estimations from seismic studies (Lamoureaux et al. 1999). Yet, based on microstructural observations  
58 Nicolas and Ildefonse (1996) and Lamoureaux et al. (1999), suggested that magmatic flow could still  
59 operate at low melt fractions ( $< 10$  vol. %) provided flow is accommodated by grain sliding and  
60 dissolution – precipitation processes. Such mechanisms have been experimentally observed by Dimanov  
61 et al. (1998, 2000) for partially molten plagioclase (labradorite) aggregates presenting melt fractions  
62 between 1 – 10 vol. %. The authors emphasized that the topology of the melt was critical with respect to  
63 the flow properties. They reported that Newtonian type of flow could be strongly enhanced even for very  
64 low melt fractions (1 – 3 vol. %) in the case where the partial melt was wetting most of grain boundaries.

65 Over more than two decades it was considered that the equilibrium melt distribution in a  
66 polycrystalline aggregate is essentially driven by surface tension forces and gradients of chemical

67 potentials in order to minimise the interfacial free energy (Beere, 1975; Waff and Bulau, 1979, 1982;  
68 Bulau et al., 1979; Cooper and Kohlstedt, 1984a; 1984b; 1986; Jurewitz and Watson, 1985; Von Bargen  
69 and Waff, 1986; Fujii et al., 1986; Bussod and Christie, 1991; Kohlstedt, 1992; Laporte and Watson, 1995;  
70 Laporte et al., 1997; Hirth and Kohlstedt, 1995a,b; Jung and Waff, 1998). From this perspective it can be  
71 shown that the equilibrium melt topology at hydrostatic conditions in a partially molten aggregate  
72 corresponds to a balance between interfacial tensions at triple points, where two neighbouring solid grains  
73 are in contact with the melt. Considering single phase solid matrix, single grain size value, isotropic solid  
74 – solid and solid – liquid interfacial energies ( $\gamma_{ss}$  and  $\gamma_{sl}$ , respectively), the latter equilibrium determines  
75 an unique dihedral angle  $\theta$  (the angle between the two solid – liquid interfaces of the two neighbouring  
76 grains), which satisfies  $2\cos(\theta/2) = \gamma_{ss}/\gamma_{sl}$ . In addition, because gradients of chemical potentials of the  
77 constituent species appear whenever the system presents solid – liquid interfaces with variable curvatures,  
78 the chemical and textural equilibrium requires a constant mean curvature of all the solid – liquid interfaces.  
79 In turns, this requirement ensures the minimization of solid – liquid interfacial area and implies concretely  
80 that the crystalline phase in contact with the liquid does not present sharp corners and flat surfaces. In  
81 summary of the previously cited works, we can consider that at low melt fractions for  $\theta > 60^\circ$  the molten  
82 phase resides in isolated pockets and interconnectivity occurs only above a critical melt fraction that  
83 increases with  $\theta$ . For  $0^\circ > \theta > 60^\circ$  a given fraction of the whole amount of melt, called the equilibrium  
84 melt fraction (that minimises the free interfacial energy of the system), forms an interconnected network  
85 along three – , four – and higher order grain junctions, whilst all exceeding amount of melt distributes in  
86 additional high aspect ratio pools. The smaller is  $\theta$  and the larger is the proportion of grain boundary area  
87 lost to the melt. Grain boundaries are expected to be completely wetted by melt only if  $\theta = 0^\circ$ . However,  
88 since most dihedral angles were found to fall between  $10 - 40^\circ$  in both mafic (olivine or peridotite and  
89 basalt, Kohlstedt, 1992) and felsic (granitic rocks and silicic melts, Laporte et al., 1997) systems, two  
90 grain boundaries were supposed to be melt-free. But despite the latter expectation, melt films spreading

91 at two grain boundaries were frequently found (Fujii et al., 1986; Bussod and Christie, 1991; Waff and  
92 Faul, 1992; Laporte and Watson, 1995; Hirth and Kohlstedt, 1995a,b; Laporte et al., 1997; Faul, 1997;  
93 Jung and Waff, 1998; Wark et al., 2003, Carapic et al., 2013). Moreover, instead of the expected smoothly  
94 curved solid – liquid interfaces straight flat interfaces (called F – faces) were often observed, suggesting  
95 that minimisation of interfacial free energy does not solely relate to minimisation of interfacial area. It  
96 was argued that the deviations from the ideal melt topology could relate a) to the polymineralic nature of  
97 some of the studied systems, b) to distributed grain sizes and ongoing grain growth, c) to the fact that  
98 interfacial free energies and dihedral angles depend on the relative crystal orientations, because silicates  
99 present anisotropic surface energies (Waff and Faul, 1992; Laporte and Watson, 1995; Jung and Waff,  
100 1998; Cmíral et al, 1998; Schäfer and Foley, 2002, Walte et al., 2003). Theoretical considerations on bi-  
101 crystals have shown that interfacial free energies i) are not necessarily much smaller than surface free  
102 energies, ii) strongly depend on interfacial misfits, or structural defects (van der Merwe, 2001), and hence  
103 on relative grain twist and tilt disorientation.

104         Conversely, non-hydrostatic conditions have also been considered to explain deviations from the  
105 ideal melt topology. Melt – wetted grain boundaries were often reported in experimentally deformed  
106 partial melts (Van der Molen and Paterson, 1979; Dell’Angelo et al., 1987; Dell’Angelo and Tullis, 1988;  
107 Bussod and Christie, 1991; Jin et al., 1994; Hirth and Kohlstedt, 1995a,b; Drury and FitzGerald, 1996;  
108 Daines and Kohlstedt, 1997; Zimmerman and Kohlstedt, 1999; De Kloe et al, 2000; Dimanov et al., 2000;  
109 Mecklenburgh and Rutter, 2003; Hier-Majumder et al., 2004). This behaviour was attributed to the non-  
110 equilibrium dynamic state and/or possibly to undrained conditions at high melt fractions. At high strains  
111 major microstructural changes may also occur: melt initially restricted to multiple grain junctions may  
112 segregate into high aspect ratio bands preferentially oriented at a small angle ( $\approx 20^\circ$ ) to the direction of  
113 maximum compressive stress (Zimmerman and Kohlstedt, 1999; Zimmerman et al., 1999; Holtzman et  
114 al., 2003; 2007; Katz et al., 2006; Spiess et al., 2012).

115 High resolution transmission electron microscopy (HRTEM) studies documented stable thin  
116 amorphous films (~ 1 – 10 nm) at grain boundaries in natural xenoliths (Wirth, 1996, Franz and Wirth,  
117 1997), in deformed synthetic olivine – orthopyroxene (Drury and FitzGerald, 1996; De Kloe et al, 2000)  
118 and plagioclase (Dimanov et al., 2000) aggregates. Many ceramic materials present the same scheme,  
119 with stable nm – sized thin amorphous silica-rich films at grain boundaries (see a review by Wilkinson,  
120 1998). It has been demonstrated that such films may be stable, because they tend to decrease the interfacial  
121 free energy (Clarke, 1987; Clarke et al. 1993). Conversely, based on HRTEM Hiraga et al. (2002) report  
122 that wetting of olivine grains by basaltic melt films is not a general feature. The authors indicate that stable  
123 basalt films (~ 10 nm) are only observed along grain boundaries where the grains present low index  
124 crystallographic planes.

125 In the specific case of diffusion-controlled creep of fine grained partially molten rocks with low  
126 melt fractions (< 15 vol. %) the strength depends strongly on melt content, but also on the grain – scale  
127 melt distribution. Theoretical (Raj, 1982; Pharr and Ashby, 1983; Cooper et al., 1989; Paterson, 2001)  
128 and experimental studies on olivine (Cooper and Kohlstedt 1984; 1986; Kohlstedt, 1992; Hirth and  
129 Kohlstedt, 1995a, b) and plagioclase (Dimanov et al., 1998; 2000) have shown that strain rates are  
130 substantially enhanced if melt films spread along grain boundaries, whilst partial melts that are confined  
131 to multiple grain junctions cause only moderate creep rate enhancement. Because diffusion in a molten  
132 phase is often orders of magnitude faster than along grain boundaries (see a review in Dimanov et al.,  
133 2000), the larger is the proportion of grain boundary lost to the melt, the larger is the proportion of  
134 interfaces providing high-diffusivity paths, and the lower is the strength of the partially molten aggregate  
135 (Cooper et al., 1989; Paterson, 2001). To date, the effect of melt chemistry on creep rates has essentially  
136 been considered from the view point of the dependence of dihedral angles on melt composition  
137 (Wanamaker and Kohlstedt, 1991; Kohlstedt, 1992; Wolfenstine and Kohlstedt, 1994). However, for a  
138 given melt topology, melt composition might also influence transport properties. In a previous work we

139 have shown that, at least at the experimental conditions, thin amorphous films were stable in plagioclase  
140 aggregates (Dimanov et al., 2000). Most grain boundaries being wetted, the flow strength of the  
141 plagioclase aggregates deforming by diffusion controlled grain boundary sliding was substantially  
142 depressed, event at very low melt fractions (~ 1 – 2 vol. %). Yet, the activation energy was found to be  
143 similar for melt – bearing and nominally melt – free aggregates. Based on extant diffusion data in melts  
144 and polycrystalline silicates Dimanov et al. (2000) suggested that in dry conditions the activation energy  
145 might be similar for diffusion of network formers along plagioclase grain boundaries and in silica – and  
146 aluminium – rich, plagioclase – like melts. In this study we further focus on the effect of the silica content  
147 of the wetting intergranular molten phase on grain boundary diffusion controlled creep of partially molten  
148 plagioclase aggregates.

149

## 150 **2. Experimental procedures**

151

### 152 **2.1. Specimen preparation**

153

154 We used fine grained (< 16  $\mu\text{m}$ ) labradorite glass powder (Corning Inc., kindly provided by R.C.  
155 Cooper). It has  $\text{An}_{50}\text{Ab}_{50}$  chemical composition and X – ray fluorescence (XRF, SRS 303AS) showed that  
156 the impurity content was less than 1 wt. % (Tab. 1). After being stored at 120°C in oven for 24 hours the  
157 powder was first uniaxially cold – pressed at 300 MPa in steel jackets of 20 mm in length, 10 mm in  
158 diameter and 0.5 mm thick. Secondly, the green bodies were hot – isostatically pressed (HIPped) for 3  
159 hours at 1150°C and 300 MPa in a gas-medium Paterson apparatus in order to obtain nearly glass – free  
160 polycrystalline material, with about 1 vol. % residual glass (Dimanov et al., 1998; 1999; 2000; 2003;  
161 Rybacki and Dresen, 2000). However, this procedure results sometimes in spherulites due to fast  
162 crystallization kinetics (Rybacki and Dresen, 2000). Hence, the HIPed samples were re-crushed and

163 milled in alcohol in an agate mortar in order to obtain homogeneously grained crystalline powders. Laser  
 164 – particle analysis (Fritsch analysette 22) showed that about 80% of the grains were < 10  $\mu\text{m}$ . The larger  
 165 particles were mostly due to clustering of smaller grains. The chemical composition of the powder was  
 166 checked by XRF (Table 1). To remove adsorbed water the crystalline powders were annealed at 800°C  
 167 for 24 hours in air and subsequently stored in an oven at 120°C prior to further processing.

168

169 Table 1. Composition of starting materials and partial melts

Element	An50 glass powder*	An50 crystal powder*	Sol-gel silica*	An50 residual glass**	SilLab5 melt**	SilLab1 melt**
Na <sub>2</sub> O(wt.%)	5.68	5.16	0.04	5.5	1.1	2.7
Al <sub>2</sub> O <sub>3</sub> (wt.%)	28.43	29.07	0.23	29.0	3.3	8.7
SiO <sub>2</sub> (wt.%)	55.27	54.82	99.53	53.0	94.8	85.4
CaO(wt.%)	10.52	10.81	0.12	12.0	0.7	2.2
MgO(wt.%)	0.25	0.31	0.06	0.3	0.0	0.0
FeO(wt.%)	0.03	0.04	0.0	0.2	0.2	0.5
Cr <sub>2</sub> O <sub>3</sub> (wt.ppm)	0.0	0.0	0.0	0.0	0.0	0.3
ZrO <sub>2</sub> (wt.ppm)	173	166	0.0	0.0	0.2	0.1
Total(wt.%)	100.2	100.22	98.98	100	100.3	99.9

170 \* XRF analysis of powders, \*\*EDX analysis in TEM

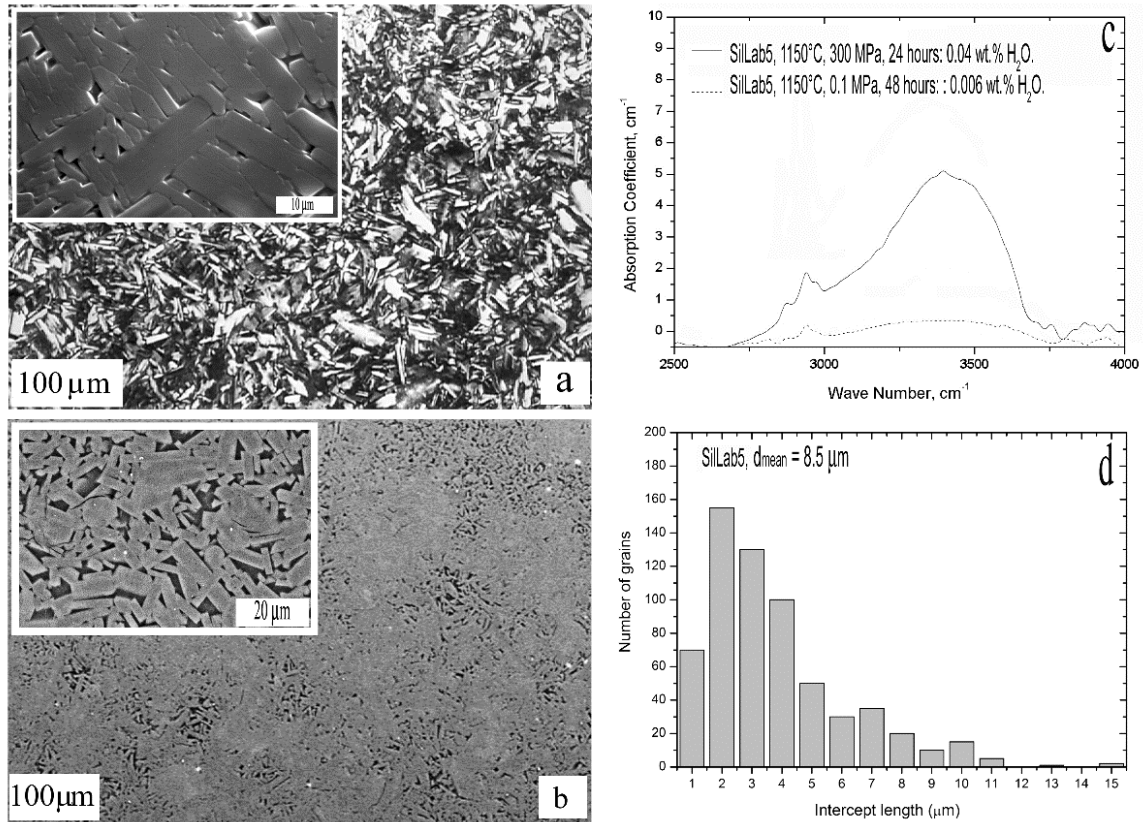
171

172 **2.1. a. Melt – “free” samples**

173

174 Crystalline powders were subjected to a second round of cold pressing, followed by HIPing for 24  
 175 hours at 1150°C and 300 MPa in order to obtain dense, melt – free polycrystalline materials, further  
 176 referred as Lab samples. Scanning electron microscopy (SEM, Zeiss DSM 962 and Jeol JSM 845) and the  
 177 line intercept method were applied on carefully polished and thermally etched specimens (Dimanov et al.,  
 178 1998, 1999, 2000; 2003). Figure 1a shows the obtained microstructures, with lath shaped grains  
 179 characterized by high aspect ratios and log – normal grain size distribution. We determined a mean  
 180 arithmetic grain size of  $9.8 \pm 3.2 \mu\text{m}$  from five different SEM micrographs. Transmission electron  
 181 microscopy (TEM, Philips CM 200 Twin) showed that grains present low average dislocation densities  
 182 and numerous growth twins (Fig. 2a).

183

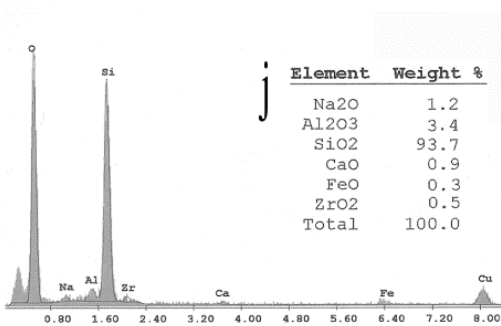
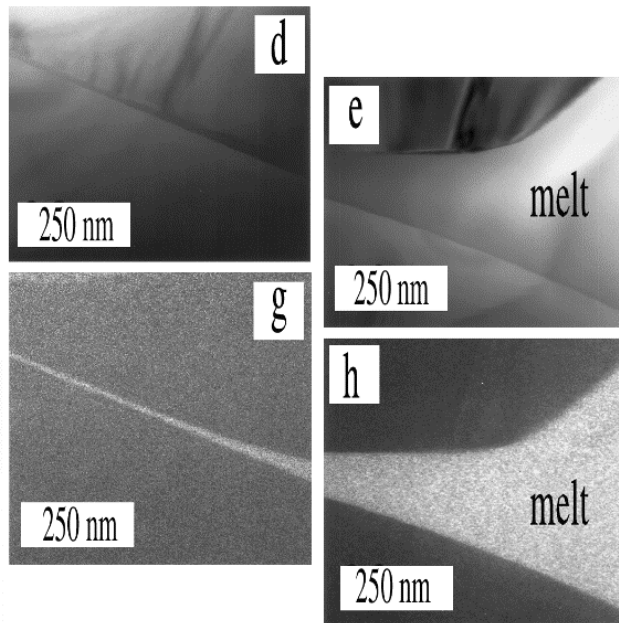
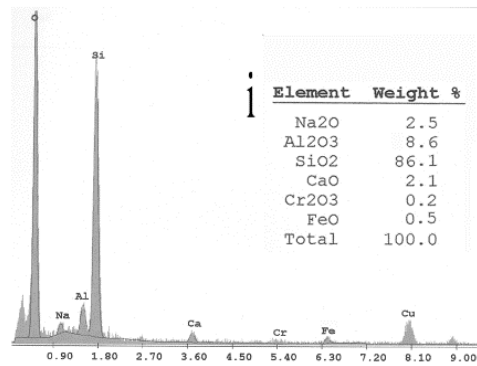
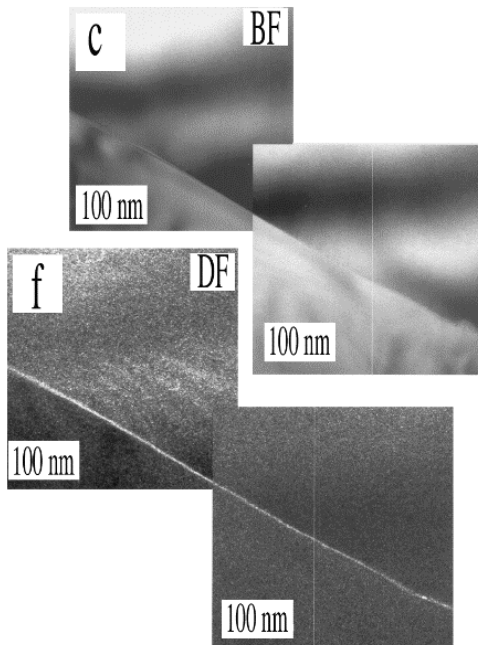
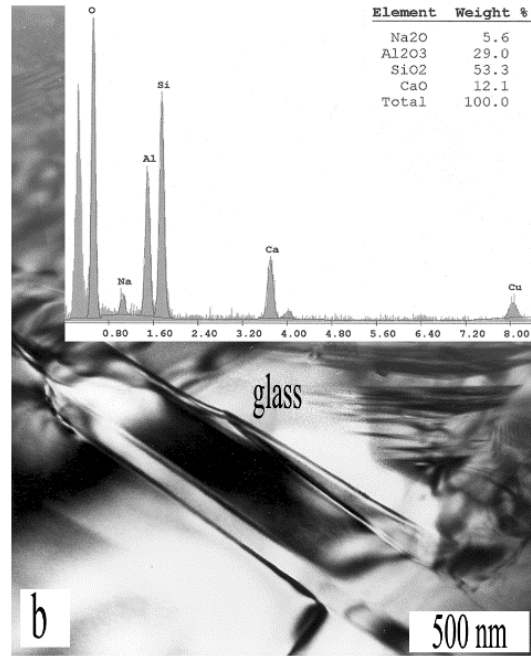
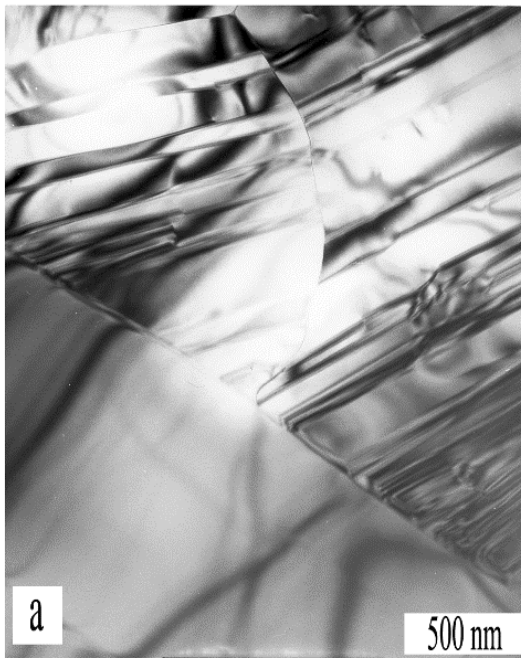


184

185 Fig. 1: Characterization of microstructures at optical and SEM scales. a) Optical micrograph of large representative area from  
 186 thin section and SEM micrograph (insert, SE mode) of polished and thermally etched melt - free specimen (Lab). b) SEM  
 187 micrographs (BSE mode) of polished melt - bearing specimen (SiLab5). At mm-scale melt distribution is somewhat  
 188 heterogeneous, with local melt fractions as high as 10 vol. % (insert). c) Water content after initial HIP and after drying anneal  
 189 from FTIR measurements on SiLab5 samples d) Grain size distribution for SiLab5 samples obtained by the intercept method  
 190 performed on SEM micrographs.

191

192 As previously observed by Dimanov et al., (1998), small amount (< 1 vol. %) of residual glass persisted,  
 193 but it was essentially restricted to multiple grain junctions (Fig. 2b). Fluid inclusions were also observed  
 194 within crystals, at grain boundaries and in the glassy-phase. Fourier transform infra-red spectroscopy  
 195 (FTIR, Brüker IFS 66v) was applied on 5x5 mm<sup>2</sup> doubly polished sections of 150 μm in thickness. We  
 196 operated in the range 2000 - 4000 cm<sup>-1</sup> and we applied a third - order polynomial fit for background  
 197 correction.



199 Fig. 2: Characterization of microstructures at TEM scale. a) Grains exhibit low dislocation densities, but growth twins are  
200 numerous. b) Residual glass pockets (< 1 vol.%) are commonly found at multiple grain junctions in Lab samples. EDX  
201 analyses (insert) show that their composition is comparable to plagioclase. c-h) SilLab1 and SilLab5 materials present  
202 amorphous pockets at multiple junctions, but most interfaces also show thin amorphous films (< 10 nm) extending from triple  
203 junction channels, as evidenced by bright versus dark field imaging. i-j) EDX analysis of amorphous phases performed at melt  
204 pockets located at multiple grain junctions in SilLab1 and SilLab5 samples.

205

206 As in previous studies (Dimanov et al., 1998; 1999; Rybacki and Dresen, 2000) we observed a  
207 broad absorption band centered at about  $3350\text{ cm}^{-1}$  (Fig. 1c), indicating free molecular water present in  
208 intra – and inter – crystalline fluid inclusions, and/or dissolved within the residual glass and at grain  
209 boundaries. But, a few sharper peaks indicated that hydrous species were also incorporated within the  
210 crystalline structure (Hofmeister and Rossman, 1985; Beran, 1986; 1987). We calculated the water content  
211 of the samples (in mol  $\text{H}_2\text{O}/\text{L}$  labradorite), based on Paterson (1982), and using the linear molar  
212 absorptivity coefficient for plagioclase ( $32\text{ L/mol/cm}$ , Beran, 1987). For that purposes, the integral of the  
213 spectrum is normalised by the half-width of the absorption band. Assuming a Gaussian approximation,  
214 this operation gives the height of the band, which is used together with the linear absorbtivity in the Beer-  
215 Lambert's law (see also Dimanov et al., 1998, 1999; Rybacki and Dresen, 2000). The samples contained  
216  $\approx 0.05 \pm 0.025\text{ wt. \% H}_2\text{O}$  ( $\approx 6000 \pm 3000\text{ ppm H/Si}$ ), which is mostly incorporated by adsorption onto  
217 the starting glass particles, and later onto the crystalline particles, during the temporary storage and  
218 handling at room condition for cold – pressing. Annealing of the samples for 24 – 48 hours in air at  
219 temperatures above  $1100^\circ\text{C}$  at  $0.1\text{ MPa}$  resulted in drying out most of the water traces down to  $< 0.002$   
220  $\text{wt. \% H}_2\text{O}$  (Fig.1, see also Dimanov et al., 1999).

221

## 222 **2.1.b Melt – bearing samples**

223 Dimanov et al. (2000) annealed plagioclase samples (similar to those used in this study) at  
224 hypersolidus conditions. The authors obtained partially molten specimens containing a few percent of  
225 silica – enriched melt, with up to 80 wt. % SiO<sub>2</sub>. In addition to multiple grain junctions the melt was  
226 present as thin films (< 5 nm) wetting many grain boundaries. The samples were about an order of  
227 magnitude weaker than melt-free specimens. In this study we aimed to investigate the effects of  
228 homogeneously distributed and wetting melts with higher silica contents. For this purpose we applied the  
229 sol – gel method (Hamilton and Henderson, 1968), which was previously used to precipitate synthetic  
230 basalt onto olivine crystalline powders (Cooper and Kohlstedt, 1984; Beeman and Kohlstedt, 1993; Hirth  
231 and Kohlstedt, 1995a). We used pure grade tetraethyl orthosilicate (Si(C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>, TEOS from Aldrich)  
232 diluted with ethanol in proportions of 10 to 1. Ammonium hydroxide solution (1 mol/l, Prolabo) was used  
233 as catalyst. In the solution, water hydrolyzes the TEOS and produces silanol groups (Si-OH), which  
234 interact through hydrogen bonding and form hydrolyzed silica. After drying out all volatiles, we  
235 performed XRF analysis on the precipitation product that consisted of nearly pure silica (Table 1). We  
236 prepared two aqueous solutions, where labradorite powders and diluted TEOS were mixed at the  
237 appropriate proportions in order to obtain 1 and 5 vol. % excess silica. The precipitation took place within  
238 a few minutes after the addition of the ammonium hydroxide, but the suspensions were continuously  
239 stirred for an hour. The precipitation products were dried at 100°C for 24 hours and ground in agate mortar.  
240 The resulting powders were fired into platinum crucibles at 700°C (in air) for 24 hours in order to release  
241 remaining volatiles. Finally, the silica – coated powders were stored in an oven at 120°C. The coated  
242 crystalline powders were cold pressed and HIPed for 24 hours at 1150°C and 300 MPa in order to obtain  
243 dense and equilibrated melt – bearing polycrystalline samples for deformation. Samples containing 1 and  
244 5 vol. % excess silica glass are called SilLab1 and SilLab5, respectively. SEM investigations were applied  
245 to carefully polished and thermally etched specimens (Fig. 1). The microstructure is comparable to those  
246 of melt – free samples, with prismatic and lath shaped grains, and with log – normal grain size distributions

247 (Fig. 1d). The intercept method determined mean arithmetic grain sizes of  $8.6 \pm 3.4$  and  $9.3 \pm 3.2$   $\mu\text{m}$  for  
248 SilLab5 and SilLab1 samples, respectively. The amorphous phases are more or less homogeneously  
249 distributed at multiple grain junctions, as evidenced by SEM in back scattering mode (Fig. 1b). TEM  
250 consistently showed that the amorphous phases are present at most multiple grain junctions, with variable  
251 apparent dihedral angles. Additionally, most two grain boundaries are wetted by thin amorphous layers <  
252 10 nm in thickness. These features are shown in Figures 2c to 2h. In spite of apparently large dihedral  
253 angles melt films extend from triple junctions within grain boundaries. In addition, the melt film  
254 thicknesses gradually increase in the vicinity of the triple junctions, hence suggesting that there are not  
255 finite wetting angles. These observations are in part similar to those of Dimanov et al. (2000) for partially  
256 molten plagioclase and of Hiraga et al. (2002) for olivine – basalt system, but we did observe some  
257 differences too. In the present study we observed that 1) the melt thickness stabilizes at around 10 nm at  
258 distances of less than a micrometer from the triple junction, 2) the melt films are a general feature and not  
259 exclusively related to low index crystallographic planes as in the latter study. Energy dispersive X ray  
260 analysis (EDX) was performed at triple junctions and evidenced that during HIPing the precipitated silica  
261 equilibrated chemically with the residual labradorite glass ( $\approx 1$  vol. %), resulting in liquid phases with  $\approx$   
262  $95 \pm 2$  wt. % and  $\approx 85 \pm 2$  wt. %  $\text{SiO}_2$ , respectively for SilLab5 and SilLab1 samples (Fig. 2i and 2j, Tab.  
263 1). TEM also evidences the presence of nm scale fluid inclusions in the amorphous phases. FTIR  
264 spectroscopy showed similar broad absorption bands and corresponding hydroxyl concentrations ( $\approx 0.05$   
265  $\pm 0.025$  wt. %  $\text{H}_2\text{O}$ ) for both melt – bearing and melt – free samples (Fig. 1c). The traces of water could  
266 be substantially dried out by annealing in air above  $1100^\circ\text{C}$  for 48 hours (Fig. 1c).

267

## 268 **2.2. Experimental deformation**

269

270 Specimens with dimensions of  $2.5 \times 2.5 \times 5 \text{ mm}^3$  were cut from hot pressed samples with low speed  
271 diamond saw. Compression and observation surfaces were polished to  $1 \text{ }\mu\text{m}$  and  $0.3 \text{ }\mu\text{m}$  finish,  
272 respectively. Uniaxial creep tests were performed stepwise at constant temperatures and constant loads in  
273 a dead-load apparatus (Dimanov et al., 1998; 1999; 2000, 2003). Finite strains for individual steps ranged  
274 from 3 to 0.5 %. We used alumina pistons and spacers, with thin platinum foils in order to avoid chemical  
275 and to limit frictions. The fixed part of the deformation column was isolated from the outer atmosphere  
276 by o – ring tightened alumina tubing, whilst the mobile part benefited from a frictionless oil bath sealing.  
277 Dry argon flowed continuously in the furnace tubing. Sample shortening was measured using two linear-  
278 variable displacement transducers (LVDT), which inner cores were mounted on two alumina rods ending  
279 respectively at the top and bottom spacers. Accordingly, the differential measurements were not affected  
280 by temperature fluctuations and allowed for strain rates lower than  $10^{-8} \text{ s}^{-1}$ . Stress and temperature steps  
281 were performed between 3 – 60 MPa and 1100 – 1225°C. Steady state creep rate was generally achieved  
282 within less than 0.5 % strain. Total sample strain was less than 15 %. Samples were cooled under load at  
283 a rate of  $50^\circ/\text{min}$  was in order to preserve at best the in-situ melt topology. However, due to the furnace  
284 inertial rapid cooling (within less than 10 mn) was only achieved down to about  $900 \text{ }^\circ\text{C}$ , whilst further  
285 cooling down to room temperature lasted for about two hours.

286

### 287 **3. Results**

288

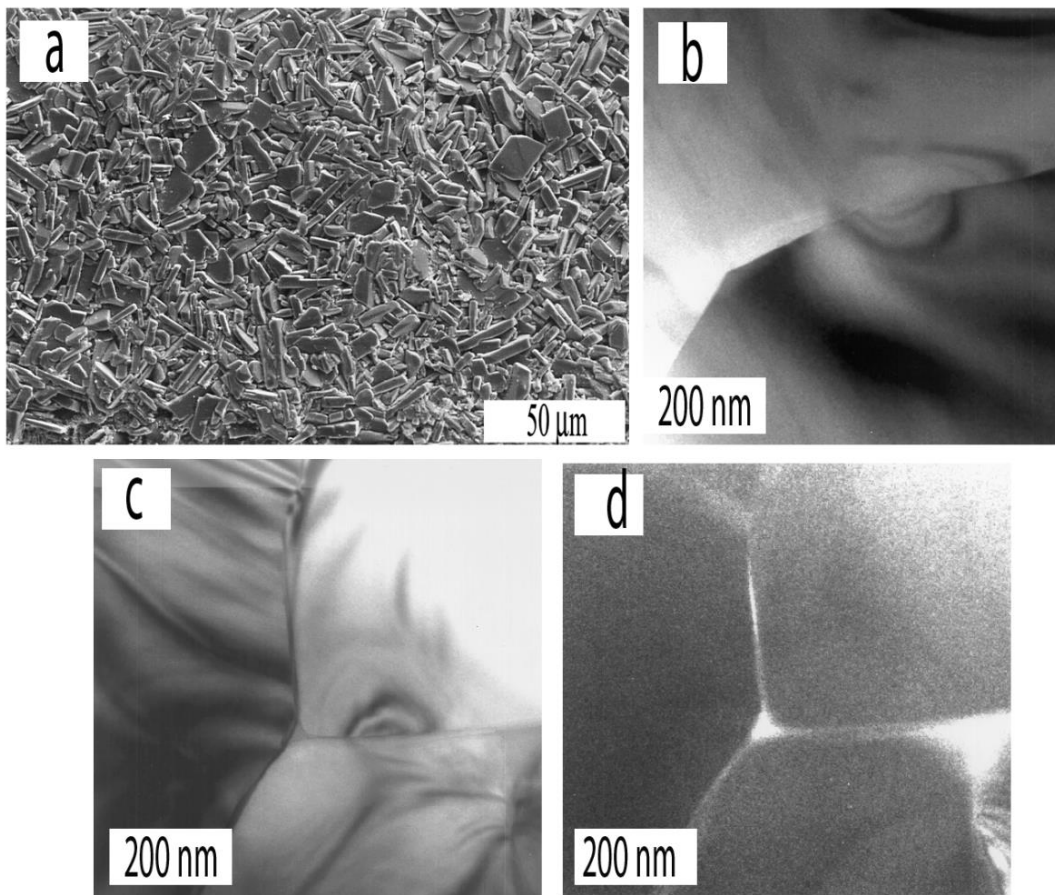
#### 289 **3.1. Microstructures**

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291 SEM observations did not show any shape preferred orientation of grains in deformed samples.  
292 SEM and TEM observations and EDX analysis did not show obvious evolution of melt proportion (within  
293 1 vol. %), topology, or chemistry (within 2 wt. %) during creep. For Lab samples the small amount of

294 residual glass was never found along grain boundaries. There was no indication for dynamic wetting of  
 295 grain boundaries during deformation as observed sometimes in olivine-basalt assemblages (Jin et al.,  
 296 1994; Hier-Majumder et al., 2004). For SilLab1 and SilLab5 samples the initial melt distribution did not  
 297 obviously change either: most of the melt still resided at multiple grain junctions and the thin melt films  
 298 were still present at most grain boundaries. Yet, we could evidence some local redistribution of melt along  
 299 wetted interfaces.

300



301

302 Fig.3: SEM and TEM micrographs of deformed SilLab1 material. a) SEM shows topography development on the sample  
 303 surface, indicating grain boundary sliding processes. b-c) Bright field images showing dislocation-free grains and whirl shaped  
 304 strain contrasts next to melt filled pockets (b) or along interfaces (c), which indicate local residual stress related to “dry”  
 305 contact area (see text). d) Dark field image corresponding to c) showing the presence of amorphous material at interfaces.

306

307 Figure 3 shows that along some wetted interfaces the grains present hemispherical strain contrast  
308 features. According to Burger et al. (1997), such “strain whirls” result from residual elastic strain,  
309 corresponding to local stress enhancement associated with the establishment of local dry contacts along  
310 wetted interfaces during creep of glass-ceramic systems. This local phenomenon may be compared with  
311 the theoretical island structure proposed by Raj (1982). However, we did not observe massive  
312 redistribution of the melt as observed by Jin et al. (1995) in crept glass-ceramic samples or complete melt  
313 expulsion out of normally stressed grain boundaries as described for olivine–basalt systems (Jin et al.,  
314 1994). Our observations rather support previous authors arguing about the stability of thin amorphous  
315 interfacial phases in both static (Clarke, 1987; Hess, 1994) and dynamic conditions (Drury and FitzGerald,  
316 1996).

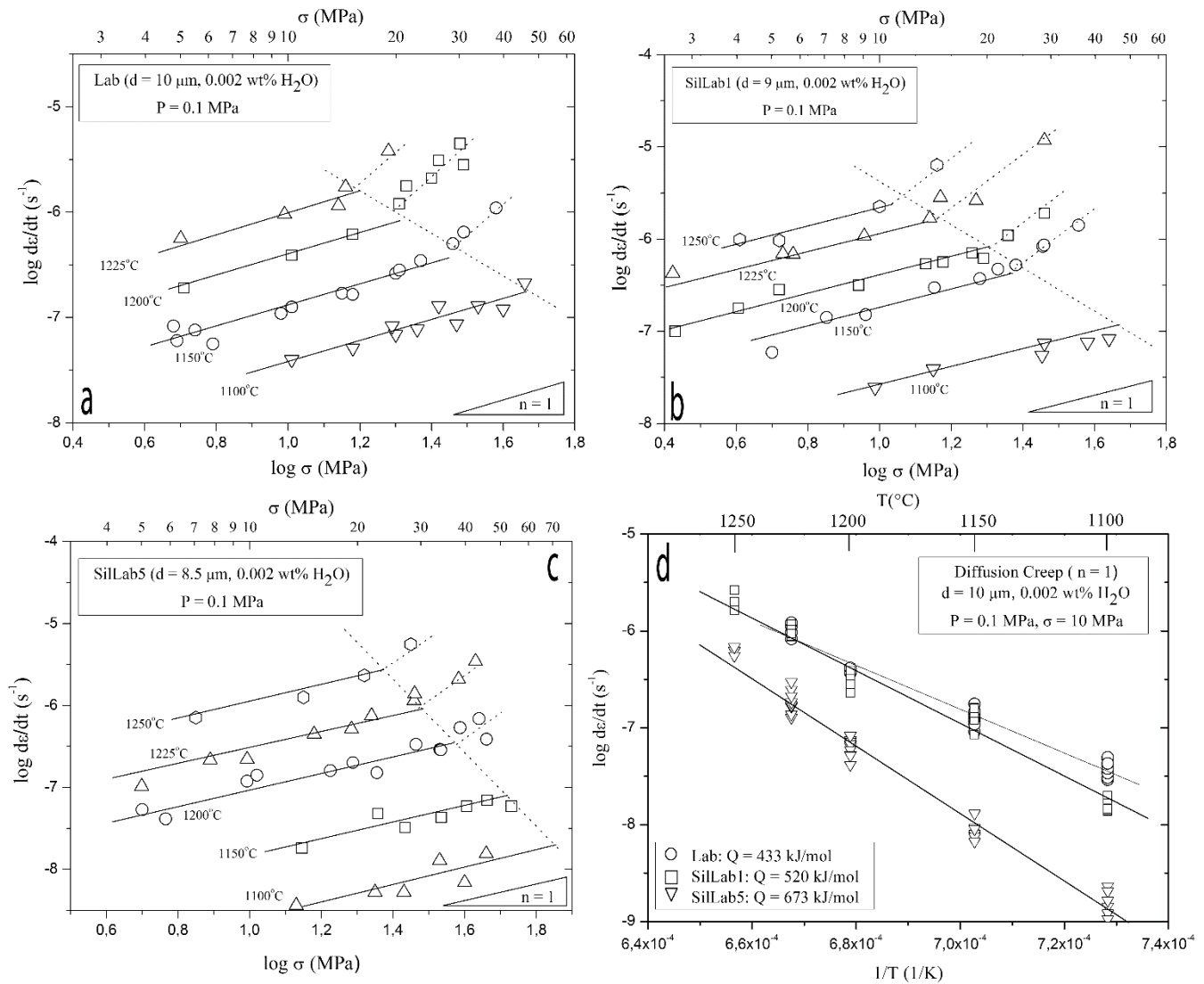
317 Curved free dislocations and dislocation arrays could be occasionally observed, but usually  
318 dislocation densities,  $\rho$ , remained low ( $\rho \approx 10^{10} - 10^{11} \text{ m}^{-2}$ ), which is consistent with Newtonian viscous  
319 flow operating by grain sliding accommodated by diffusional mass transfer mechanisms. Growth twins  
320 are very common in undeformed specimens, hence it is difficult to estimate if mechanical twinning could  
321 contribute to deformation. In opposition to polished samples which simply experienced static thermal  
322 etching (see Fig. 1), deformed samples present a strong development of surface topography (Fig. 3). Some  
323 previous studies on high temperature creep of fine grained zirconia based ceramic materials (Clarisse et  
324 al., 2000; Duclos et al., 2002) and superplastic alloys (Huang and Langdon, 2002) report the development  
325 of grain scale topography onto the sample free surfaces, which characteristic was interpreted as evidence  
326 for grain sliding.

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## 328 **3.2. Mechanical Data**

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### 330 **3.2.1. Stress sensitivity**



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Fig. 4: Thermo-mechanical data for all tested materials presented in log Stress - log Strain rate plots (a, b and c for Lab, SilLab1 and SilLab5 samples respectively) and in Arrhenius diagram (d). All materials show dominantly linear viscous (Newtonian) flow (stress exponent  $n = 1$ ) and a transition (indicated by dot-line) to non-linear behaviour (dislocation creep) at the highest temperatures and stresses, which is in agreement with previous works on similar materials (Dimanov et al., 1998; 1999; 2000). Data corrected for grain size (see text) and recalculated to 10 MPa differential stress are used to establish the Newtonian flow laws (d). Lab and SilLab materials present comparable strain rates, whilst SilLab5 material is considerably more resistant. Activation energy increases with melt content.

342 Table 2. Mechanical data.

Sample	T(°C)	T(h)	$\sigma_{diff}$ (MPa)	$d\varepsilon/dt$ (1/s)
lab-01	1150	31	5.48	$7.52 \times 10^{-8}$
	1150	13	10.34	$1.25 \times 10^{-7}$
	1150	8.4	15.25	$1.66 \times 10^{-7}$
	1150	2.4	20.49	$2.82 \times 10^{-7}$
	1150	1.5	30.54	$6.41 \times 10^{-7}$
	1200	0.8	21.34	$1.79 \times 10^{-6}$
	1200	0.5	26.20	$3.06 \times 10^{-6}$
	1200	0.5	31.06	$2.82 \times 10^{-6}$
	1150	25	4.76	$8.36 \times 10^{-8}$
	1150	3.5	20.01	$2.65 \times 10^{-7}$
lab-02	1100	17.2	26.19	$1.30 \times 10^{-7}$
	1100	23	19.43	$8.33 \times 10^{-8}$
	1100	19.4	22.79	$7.75 \times 10^{-8}$
	1100	15.2	34.13	$1.29 \times 10^{-7}$
	1100	8.4	45.36	$2.15 \times 10^{-7}$
lab-03	1100	66	10.14	$4.02 \times 10^{-8}$
	1100	21	14.98	$5.17 \times 10^{-8}$
	1100	24.7	19.82	$6.89 \times 10^{-8}$
	1100	24	29.73	$8.62 \times 10^{-8}$
	1100	8.5	39.64	$1.21 \times 10^{-7}$
	1200	4.8	5.16	$1.90 \times 10^{-7}$

	1200	1.6	14.98	$6.20 \times 10^{-7}$
	1200	2.22	10.29	$3.88 \times 10^{-7}$
	1200	0.97	20.28	$1.19 \times 10^{-7}$
	1200	0.48	25.12	$2.07 \times 10^{-7}$
	1200	0.23	29.96	$4.43 \times 10^{-7}$
lab-05	1150	20	4.92	$6.01 \times 10^{-8}$
	1150	24.4	9.48	$1.10 \times 10^{-7}$
	1150	6.4	14.08	$1.69 \times 10^{-7}$
	1150	2.0	28.61	$5.03 \times 10^{-6}$
	1150	18	6.17	$5.62 \times 10^{-8}$
	1150	3.12	23.70	$3.50 \times 10^{-7}$
	1150	1.13	38.09	$1.08 \times 10^{-6}$
	1225	2.5	5.01	$5.60 \times 10^{-7}$
	1225	1.5	9.84	$9.53 \times 10^{-7}$
	1225	0.72	14.31	$1.74 \times 10^{-6}$
	1225	0.41	19.18	$3.79 \times 10^{-6}$
	1225	0.48	13.79	$1.14 \times 10^{-6}$
SiLab1-01	1150	21	7.11	$1.41 \times 10^{-7}$
	1150	3.7	14.23	$2.98 \times 10^{-7}$
	1150	3.23	21.34	$4.73 \times 10^{-7}$
	1150	1.5	28.59	$8.63 \times 10^{-7}$
	1150	15	9.15	$1.51 \times 10^{-7}$
	1150	1.78	28.79	$8.33 \times 10^{-7}$

	1150	1.83	35.91	$1.44 \times 10^{-6}$
silab1-02	1200	4	4.04	$1.78 \times 10^{-7}$
	1200	16	2.69	$9.97 \times 10^{-8}$
	1200	2.77	8.74	$3.13 \times 10^{-7}$
	1200	1.14	13.45	$5.37 \times 10^{-7}$
	1200	1.15	15.02	$5.60 \times 10^{-7}$
	1200	1.45	18.16	$7.10 \times 10^{-7}$
	1200	1.01	22.87	$1.09 \times 10^{-6}$
silab1-03	1100	30	9.72	$2.45 \times 10^{-8}$
	1100	24.2	14.14	$3.93 \times 10^{-8}$
	1100	14	28.37	$5.47 \times 10^{-8}$
	1100	11.4	13.45	$7.59 \times 10^{-8}$
	1225	2.63	2.65	$4.27 \times 10^{-7}$
	1225	1.33	5.74	$6.85 \times 10^{-7}$
	1225	0.75	9.06	$1.08 \times 10^{-6}$
	1225	1.45	13.79	$1.68 \times 10^{-6}$
	1225	1.01	18.56	$2.62 \times 10^{-6}$
silab1-04	1200	3.1	5.25	$2.82 \times 10^{-7}$
	1200	1.9	19.5	$6.17 \times 10^{-7}$
	1200	1.1	28.84	$1.91 \times 10^{-6}$
	1100	12	28.84	$7.41 \times 10^{-8}$
	1100	10	43.65	$8.32 \times 10^{-8}$
	1150	14.1	5.01	$5.89 \times 10^{-8}$

	1150	2.8	19.06	$3.72 \times 10^{-7}$
	1150	1.4	23.99	$5.25 \times 10^{-7}$
	1225	1.2	5.37	$6.92 \times 10^{-7}$
	1225	0.8	14.79	$2.82 \times 10^{-6}$
	1225	0.14	28.84	$1.18 \times 10^{-5}$
	1225	2.4	4.07	$9.87 \times 10^{-7}$
	1225	2.2	5.25	$9.67 \times 10^{-7}$
	1225	1.2	10	$2.26 \times 10^{-6}$
	1225	0.2	14.45	$6.37 \times 10^{-6}$
silab5-01	1100	22.4	22.63	$5.25 \times 10^{-9}$
	1100	28.3	34.12	$1.28 \times 10^{-8}$
	1100	36	46.17	$1.54 \times 10^{-8}$
	1150	24.2	22.8	$4.81 \times 10^{-8}$
	1150	20.5	34.31	$4.26 \times 10^{-8}$
	1150	27	45.99	$6.95 \times 10^{-8}$
	1200	30.8	5.84	$4.16 \times 10^{-8}$
	1200	8.2	16.79	$1.61 \times 10^{-7}$
	1200	4.7	22.63	$1.52 \times 10^{-7}$
	1200	2.35	33.94	$2.91 \times 10^{-7}$
	1200	3.2	45.8	$3.90 \times 10^{-7}$
	1200	7.15	34.12	$2.87 \times 10^{-7}$
silab5-02	1200	23.2	5.00	$5.37 \times 10^{-8}$
	1200	17.0	9.84	$1.19 \times 10^{-7}$

	1200	4.1	19.39	$2.01 \times 10^{-7}$
	1200	2.55	29.08	$3.36 \times 10^{-7}$
	1200	2.65	38.62	$5.33 \times 10^{-7}$
	1200	2.5	43.62	$6.11 \times 10^{-7}$
	1225	10.2	5.0	$1.03 \times 10^{-7}$
	1225	3.00	9.84	$2.20 \times 10^{-7}$
	1225	3.2	19.23	$5.16 \times 10^{-7}$
	1225	1.0	28.77	$1.15 \times 10^{-6}$
	1225	0.65	38.32	$2.09 \times 10^{-6}$
silab5-03	1100	163	13.64	$3.63 \times 10^{-9}$
	1100	125	26.65	$5.26 \times 10^{-9}$
	1100	55.8	40.08	$6.88 \times 10^{-9}$
	1150	61.6	14.01	$1.83 \times 10^{-8}$
	1150	27	27.15	$3.27 \times 10^{-8}$
	1150	25	40.29	$5.89 \times 10^{-8}$
	1150	20.6	53.8	$5.83 \times 10^{-8}$
silab5-04	1225	19.2	7.83	$2.17 \times 10^{-7}$
	1225	4.3	14.99	$4.47 \times 10^{-7}$
	1225	2.5	21.8	$7.50 \times 10^{-7}$
	1225	1.1	28.84	$1.39 \times 10^{-6}$
	1225	0.27	42.92	$3.46 \times 10^{-6}$
silab5-05	1250	3.0	7.01	$7.10 \times 10^{-7}$
	1250	1.0	14.01	$1.60 \times 10^{-6}$

	1250	0.5	21.02	$2.33 \times 10^{-6}$
	1250	0.2	28.25	$5.60 \times 10^{-6}$

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Table 2 reports the experimental data set. Figures 4a, 4b and 4c report the diagrams of log strain rates versus log flow stresses obtained at different temperatures for the different types of materials. All materials showed dominantly a linear relation between strain rates and flow stresses (stress exponent  $n \approx 1$ ), evidencing Newtonian linear viscous flow. Thought, a transition to a power law creep ( $n \approx 3$ ) could be marginally observed at the highest stresses. Depending on temperature and material type the transition stress ( $\sigma_t$ ) ranges between  $\sigma_t \approx 20 - 60$  MPa. These results are phenomenologically similar to those previously reported for fine grained plagioclase, clinopyroxene and plagioclase-clinopyroxene aggregates (Dimanov et al., 1998; 1999; 2003; Rybacki and Dresen, 2000; Bystricky and Mackwell, 2000; Dimanov and Dresen, 2005; Hier-Majumder et al., 2005), and olivine aggregates (Hirth and Kohlstedt, 1995; Mei and Kohlstedt, 2000; Mei et al., 2002). They indicate two dominant creep mechanisms, which are usually considered as being independent and acting in parallel, with overall dominance of the most effective one. The linear viscous flow that dominates at low stresses is grain size sensitive (gss) and often advocated as being diffusion-controlled creep, whilst the highly non-linear viscous flow that dominates at higher stresses is usually found to be nearly grain size insensitive (gsi) and is attributed to dislocation creep. It has been evidenced that for heterogeneous and/or polyphase materials these mechanisms may be locally concomitant and co-operational (Dimanov et al., 2011), but for homogeneous single phase silicates they are consensually considered as mutually independent. The general flow law resulting from the parallel contribution of both mechanisms is therefore of the form:

$$\frac{d\varepsilon}{dt} = A_{gss} \sigma d^{-m} e^{-\frac{Q_{gss}}{RT}} + A_{gsi} \sigma^n e^{-\frac{Q_{gsi}}{RT}} \quad (1)$$

363 where  $\frac{d\varepsilon}{dt}$  ( $s^{-1}$ ) is the strain rate,  $\sigma$  (MPa) is the differential stress,  $n$  (usually between 3 and 5) is the stress  
 364 exponent for the dislocation creep component,  $d$  ( $\mu m$ ) is the grain size,  $m$  is the grain size exponent,  $Q_{gss}$   
 365 and  $Q_{gsi}$  (kJ/mol) are the activation energies for the diffusion and the dislocation creep components,  
 366 respectively.  $R$  is the molar gas constant and  $T$  is the absolute temperature (K).  $A_{gss}$  ( $s^{-1} MPa \mu m^m$ ) and  
 367  $A_{gsi}$  ( $s^{-1} MPa^{-n}$ ) are material related constants corresponding to the diffusion and the dislocation creep  
 368 components, respectively. In this study we are essentially interested in the grain size sensitive (Newtonian)  
 369 regime. Hence, we will further focus only on the data described by the constitutive equation:

$$370 \quad \frac{d\varepsilon}{dt} = A_0 \sigma e^{-\frac{Q}{RT}} = A \sigma d^{-m} e^{-\frac{Q}{RT}} \quad (2)$$

371  
 372 where  $A$  ( $s^{-1} MPa^{-n} \mu m^m$ ) is the material related constant, that may be written as  $A_0$  ( $s^{-1} MPa^{-n}$ ) if  
 373 incorporating the microstructural parameter  $d$  ( $\mu m$ ).

### 375 3.2.2. Grain size sensitivity

376 To estimate the strain rate dependence on grain size for nominally melt – free samples ( $< 1$  vol.  
 377 % non-wetting residual glass) we considered the present data for Lab samples with a mean grain size of  
 378  $9.8 \mu m$  and data from Dimanov et al. (1998) for similar nominally melt – free labradorite, but coarser  
 379 grained with a mean grain size of  $16 \mu m$ . We obtained a grain size exponent  $m = 2.6 \pm 0.3$ , which is in  
 380 agreement with previous results for anorthite plagioclase (Wang et al., 1996; Dimanov et al., 1999).  
 381 Previous studies on olivine and olivine – basalt systems (Hirth and Kohlstedt, 1995) documented similar  
 382 grain size sensitivities ( $m \approx 2.5 - 3$ ) indicating grain boundary diffusion controlled creep (Coble, 1963).  
 383 Dimanov et al. (2003, 2007) also reported similar grain size exponents for fine grained diopside samples,  
 384 and Dimanov et al., (2007) documented microstructural evidences for grain sliding mechanisms  
 385 accommodated by diffusional mass transfer in fine grained anorthite and diopside two – phase aggregates.

386 According to Coble (1963) and Ashby and Verall (1973), the present data indicate that grain sliding  
387 accommodated by grain boundary diffusion most likely operated in the linear – viscous regime.

388

### 389 **3.2.3. Activation energy**

390 In Figure 4d we reported the flow laws for the different materials in an Arrhenius type of diagram,  
391 where log strain rates (for a fixed grain size and flow stress) are plotted as a function of the inverse absolute  
392 temperature. The slopes of the linear regressions provide the activation energies  $Q = 433 \pm 14$  kJ/mol,  $Q$   
393  $= 520 \pm 21$  kJ/mol and  $Q = 673 \pm 18$  kJ/mol for diffusion controlled creep of dry Lab, SilLab1 and SilLab5  
394 samples, respectively (Tab. 3). The activation energy and the strain rates for our Lab samples are  
395 comparable with those for diffusion controlled creep of labradorite (An60) and anorthite plagioclase  
396 aggregates, deformed uniaxially at 0.1 MPa (Dimanov et al., 1998, 1999). Figure 4d also shows that i) the  
397 strain rates are nearly identical for Lab and SilLab1, ii) SilLab5 samples (which contain the highest  
398 proportion of melt) show substantially lower strain rates, iii) the activation energy increases with the  
399 addition of silica – rich melt.

400

### 401 **3.2.4 Melt effects**

402 Mechanical characterization (stress exponent, grain size exponent) and microstructures indicate  
403 that all kind of samples deformed dominantly by grain sliding mechanisms accommodated by grain  
404 boundary diffusion. These results agree with previous studies on high temperature creep of partially  
405 molten labradorite An60 containing either non – wetting residual An60 glass (Dimanov et al., 1998), or  
406 wetting partial melt obtained at sub solidus conditions (Dimanov et al., 2000). For instance, Dimanov et  
407 al. (2000) have shown that samples containing  $\approx 2 - 3$  vol. % of wetting partial melt (thin melt films  
408 present at numerous grain boundaries) were substantially weaker than melt – free samples, or than samples  
409 containing similar amounts of non – wetting residual glass (present only at multiple grain junctions).

410 Conversely, in the present study we clearly observed that the presence of thin amorphous films at grain  
 411 boundaries did not weaken the samples. SilLab1 samples exhibited comparable strain rates and activation  
 412 energy as for melt – free Lab samples, whilst counter intuitively SilLab5 showed to be substantially  
 413 stronger and to have much higher activation energy than any other tested samples. The present results  
 414 indicate that the mechanical behaviour of the partially molten samples does not only depend on the melt  
 415 proportion and distribution, but also on the melt chemistry and more specifically on the silica content of  
 416 the amorphous phase: the higher was the silica content and the lower was the creep rate, and hence the  
 417 diffusion kinetics controlling mass transfer.

418

### 419 **3.2.5 Flow laws**

420 The flow law parameters that we obtained by least square regression fits of equation (2) to the  
 421 mechanical data of the Newtonian regime for Lab, SilLab1 and SilLab5 materials are listed respectively  
 422 below for a grain size  $d = 10 \mu\text{m}$  (assuming  $m = 3$ ):

423

424 For Lab :  $\log A_0 (\text{s}^{-1}\text{MPa}^{-n}) = 9.026 \pm 0.524, n = 1, Q = 432.889 \pm 14.234 \text{ kJ/mol}$

425 For SilLab1 :  $\log A_0 (\text{s}^{-1}\text{MPa}^{-n}) = 12.079 \pm 0.757, n = 1, Q = 520.484 \pm 21.000 \text{ kJ/mol}$

426 For SilLab5 :  $\log A_0 (\text{s}^{-1}\text{MPa}^{-n}) = 16.732 \pm 0.642, n = 1, Q = 673.342 \pm 17.864 \text{ kJ/mol}$

427

## 428 **4. Discussion**

429

430 To our knowledge, the only previous work concerned with high temperature creep of silicate  
 431 polycrystalline material containing excess pure silica is from Wolfenstine and Kohlstedt (1994). In the  
 432 latter study synthetic Nickel – based olivine aggregates containing 3 % pure silica in excess have been  
 433 deformed in uniaxial compression. The presence of the amorphous silica did not affect the creep properties

434 of the samples. Marked weakening was observed only at temperatures promoting kinetic decomposition  
435 of the Ni – olivine. However, the material preparation procedure was different. Also, the authors observed  
436 that the excess silica was exclusively restricted to multiple grain junctions, whilst two grain boundaries  
437 remained melt-free. It is therefore impossible to directly compare the results of Wolfenstine and Kohlstedt  
438 (1994) and the present findings. Conversely, our present data may be compared with the results of  
439 previous works of Dimanov et al. (1998; 2000). These former studies have clearly documented that for  
440 partially molten plagioclases samples containing plagioclase – like partial melts (with silica content < 80  
441 wt. %), and deforming by diffusion controlled grain sliding, the creep strength depends mostly on the melt  
442 topology. Dimanov et al. (2000) concluded that the samples exhibiting amorphous films along most grain  
443 boundaries are substantially weaker than samples presenting an interconnected amorphous network along  
444 multiple grain junctions but crystalline grain boundaries. The present study further shows that for diffusion  
445 controlled grain sliding at dry conditions (< 0.002 wt.% water), when the physical structure of grain  
446 boundaries is amorphous (presence of thin melt films), the chemistry of the amorphous phase (and more  
447 specifically the silica content) is the key criterion for the creep strength. On the one hand, materials which  
448 are nominally fully crystalline and materials containing  $\approx 2$  vol. % of wetting partial melt with  $\approx 85$  wt.  
449 % silica have similar creep strengths. In opposition, samples with  $\approx 6$  vol. % wetting partial melt, but  
450 containing  $\approx 95$  wt. % silica present pronounced strengthening. Though astonishing, this situation is not  
451 unique. Numerous studies show that silicon nitride and silicon carbide ceramics almost always present  $\approx$   
452 1 – 2 nm amorphous silica films along most grain boundaries. Still, these materials present exceptional  
453 creep strengths at high temperatures (see a review of Meléndez-Martínez and Domínguez-Rodríguez,  
454 2004 and references therein). Kajihara et al. (1995) have shown that between 1200 – 1380°C tetragonal  
455 zirconia polycrystals with amorphous silica present at grain boundaries is characterized by superplasticity  
456 involving grain boundary sliding and diffusion controlled viscous flow of the silica phase, with an  
457 activation energy of 635 kJ/mol. Ojovan and Lee (2004) reported that enthalpies of formation and

458 migration of defects in pure silica are respectively of 197 and 515 kJ/mol, which summation is in  
459 astonishing agreement with both the latter activation energy and the value we report for creep in SilLab5  
460 samples (673 kJ/mol), where the controlling mechanisms is supposedly grain boundary diffusion through  
461 extremely silica-rich melt films. Considering that we observe diffusion controlled creep and clear effects  
462 of the melt chemistry it is useful to estimate the viscosities and the diffusion properties of the melts present  
463 in our samples in order to provide a physical – chemical explanation of the creep strength of our materials.

464

#### 465 **4.1. Viscosities of the silicate melts**

466

467 The estimation of the viscosities of natural silicate melts is a crucial issue in earth sciences.  
468 Therefore, their dependence on temperature and composition has been extensively studied experimentally  
469 and theoretically (see Giordano et al. 2006, 2008 and references therein). From a general view point the  
470 viscosity of a melt essentially depends on the degree of polymerisation of its structural units (Mysen,  
471 1983). The latter is often expressed in terms of the NBO/T number, which is the number of non-bridging  
472 oxygen per tetrahedron. Species in tetrahedral coordination (in particular  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ , but also  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$   
473 ...) tend to polymerize the melt by establishing a tri-dimensional network of tetrahedrons and are thus  
474 called network formers, whilst metal, alkaline and earth alkaline cations have the opposite tendency and  
475 are therefore called network destroyers. The NBO/T directly relates to the relative amounts of network  
476 formers and network destroyers. The lower is the NBO/T the more viscous is the considered melt. For  
477 example, basalts are characterized by NBO/T ranging between 1 – 2 and are many orders of magnitude  
478 less viscous than granitic and plagioclase like melts, not even mentioning fully polymerized amorphous  
479 silica, which is characterized by NBO/T = 0. Based on numerous experimental data sets Giordano and  
480 Dingwell (2003), and more recently Giordano et al. (2006, 2008), proposed semi empirical models for  
481 predicting viscosities of anhydrous and hydrous silicate melts over a wide compositional range (from

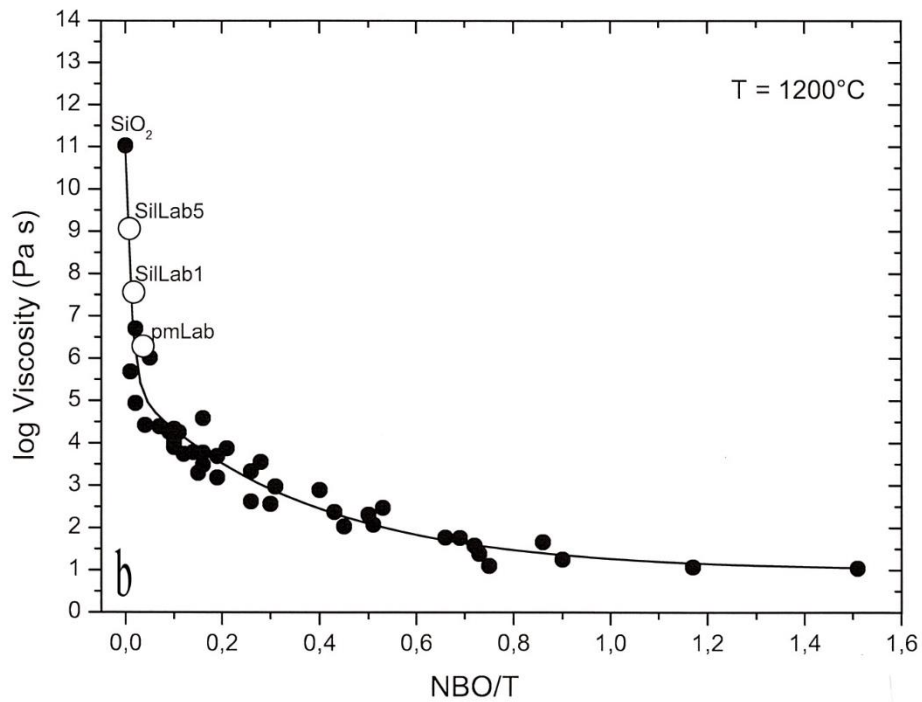
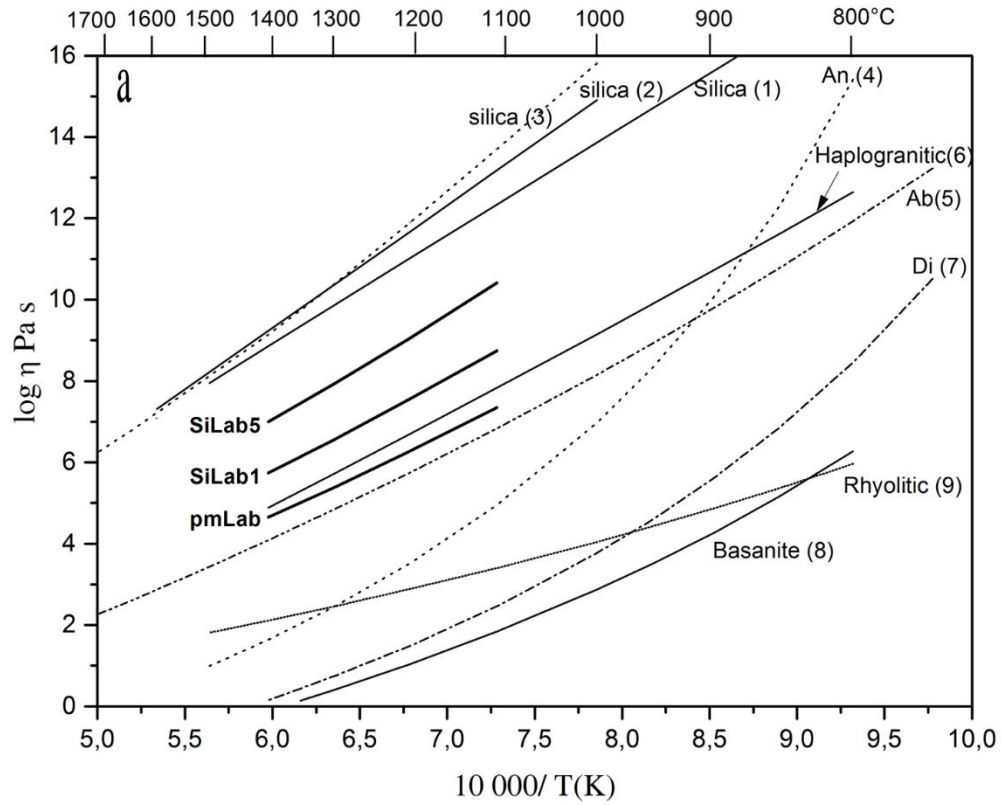
482 haplogranitic to basaltic compositions). Data sets were first described with the well-known Vogel-  
 483 Flucher-Tammann empirical relation:

$$484 \log \eta = A + \frac{B}{T - C} \quad (3)$$

486  
 487 where  $\eta$  is the viscosity (in Pa s),  $T$  is the absolute temperature (in K),  $A$ ,  $B$  and  $C$  are the fitting  
 488 parameters. The analysis is further constrained by the hypothetical assumption that the viscosities of all  
 489 silicate melts converge to a common value at extremely high temperatures. This analysis implies that: i)  
 490  $A$  is composition independent, ii)  $B$  and  $C$  are correlated and accommodate all compositional effects. In  
 491 particular,  $B$  and  $C$  correlate with the polymerization degree and the composition. The authors express the  
 492 latter by the  $SM$  (structure modifier) parameter, which is (for anhydrous melt) the sum of the molar  
 493 proportions of alkalis and earth alkaline network modifiers ( $SM = \Sigma \text{ mol. \%} = \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO}$   
 494  $+ \text{MnO} + \text{FeO}_{\text{Tot}}/2$ ). Based on (3) Giordano et al. (2006) computed the isothermal viscosities for 44  
 495 different melt compositions (44 different  $SM$ ) corresponding to different peraluminous, metaluminous  
 496 and peralkaline silicate melts. The obtained isothermal viscosity values were further fitted to empirical  
 497 equations of the form:

$$498 \log \eta = a_1 + \frac{a_2 a_3}{a_3 + SM} \quad (4)$$

500  
 501 where  $a_i$ , ( $i = 1, 2, 3$ ) are empirical (temperature dependent) fitting parameters. According to the  
 502 adjustments of the model to the experimental data for 44 different melts the authors derived  $a_1$ ,  $a_2$ ,  $a_3$  as  
 503 functions of temperature between 700°C and 2000°C (Tab. 4, Giordano et al., 2006).



505 Fig. 5: Comparison between calculated or measured viscosities of typical silicate melts and viscosities calculated for the melt  
 506 compositions of those present in our materials. a) Arrhenius plot of viscosities of typical silicate melts (not exhaustive, but  
 507 covering the whole range of viscosities from basaltic composition to vitreous silica) and those of the melts present in our  
 508 samples (SilLab1 and SilLab5) and in the partially molten samples (pmLab) of Dimanov et al. (2000), computed with the  
 509 model of Giordano et al. (2008). Data for silica are: (1) from Giordano et al., (2005), (2): from Nascimento and Zanotto,  
 510 (2006), Silica (3): from Ojovan and Lee (2004) and from experimental data of Urbain et al., 1982 and Hetherington et al  
 511 (1964). Anorthite (An(4)) and Diopside (Di(7)): from Russel and Giordano (2005), Haplogranitic(6), Albite (Ab(5)) and  
 512 Rhyolitic(9): from Giordano et al. (2005), Basanite(8): from Giordano et al. (2006). b) Comparison of the experimental  
 513 viscosities used by Giordano et al. (2008) to set the parameters of their model and the viscosities computed with the latter for  
 514 compositions of melts as those present in our materials as a function of the NBO/T number. The model predicts very well the  
 515 viscosities of the melts present in our samples.

516

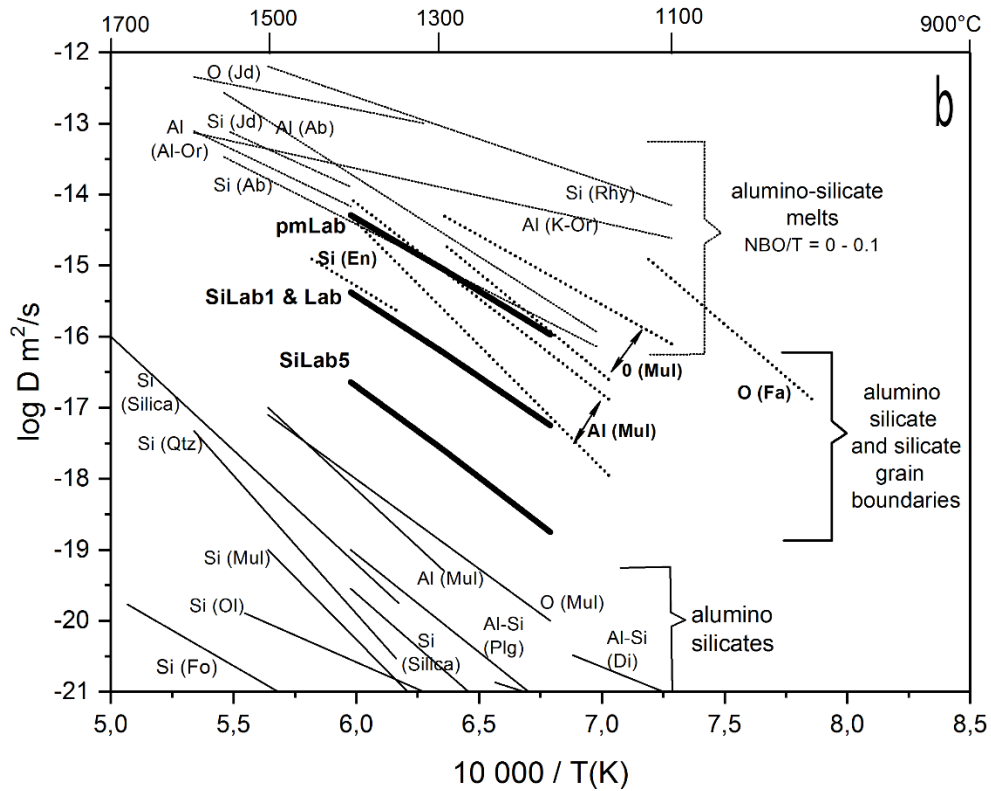
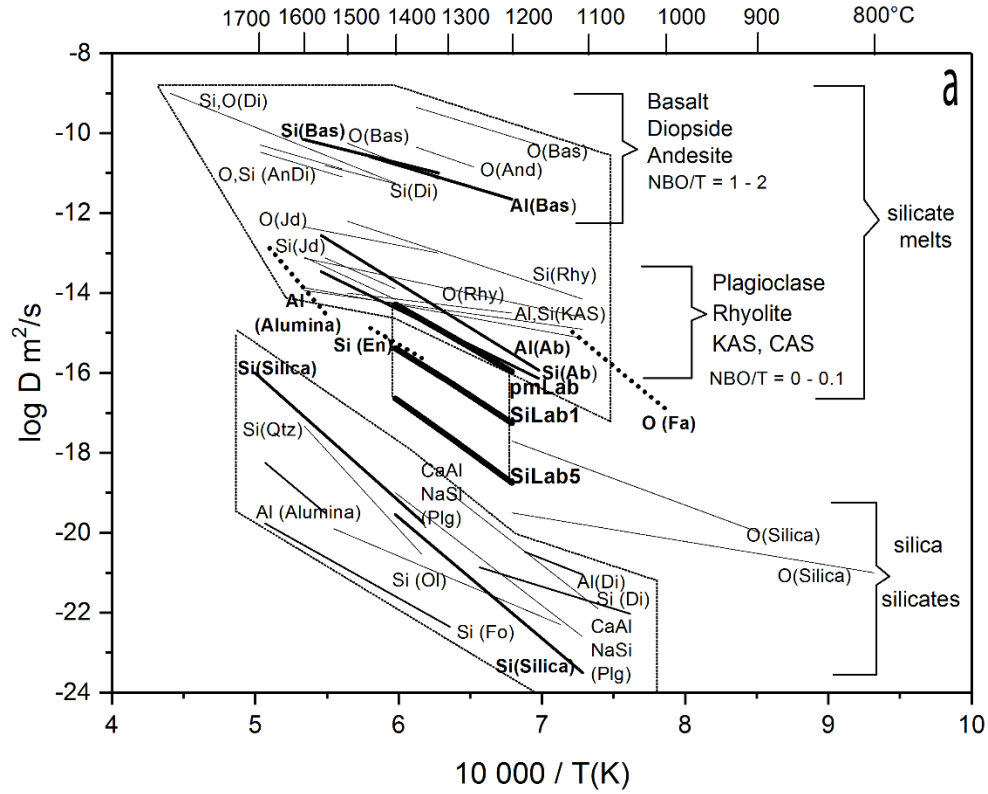
517 The phenomenological model of Giordano et al. (2006) was initially derived on the basis of  
 518 experimental results from silicate melts which silica content did not exceed 80 wt. % (rhyolitic melt), but  
 519 according to Giordano et al. (2008) the model may be applicable for melts containing up to 90 wt. %  
 520 silica, which is the case for the melt present in our SilLab1 materials ( $\approx 85$  wt. %  $\text{SiO}_2$ ,  $\text{SM} = 5.15$ ). Due  
 521 to the lack of any alternative model, and as a first order approximation, we also used the equation (4) and  
 522 the  $a_i$  parameters given by Giordano et al. (2006) in order to calculate the viscosity for the melt present in  
 523 our SilLab5 ( $\approx 95$  wt. %  $\text{SiO}_2$ ,  $\text{SM} = 2.56$ ) samples. The viscosity results are plotted as functions of the  
 524 inverse absolute temperature in Figure 5a. One can see that the melt present in SilLab5 samples (our silica  
 525 – richest melt) is about one to two orders of magnitude more viscous than the melt present in SilLab1  
 526 samples. We have also reported for comparison (i) the computed viscosities for diverse anhydrous silicate  
 527 melts (haplogranitic, plagioclases, rhyolitic, diopside and basanite) calculated by Russel and Giordano  
 528 (2005) and Giordano et al. (2006) on the basis of equation (4), (ii) some experimentally derived viscosities  
 529 for silica, albite and basalt melt (see references in figure caption). The data in Figure 5a show that silica  
 530 is the most possibly viscous melt, whilst mafic and rhyolitic melts are the less viscous ones. Plagioclase

531 and haplogranitic melts present intermediate viscosities. The viscosities we obtain for the melts present  
532 in our samples are in between those for pure silica and haplogranitic/albitic melts, which is fully consistent  
533 with the fact that their silica contents are extremely high. We also considered for comparison the  
534 composition data for the silica – rich ( $\approx 80$  wt. %  $\text{SiO}_2$ ,  $\text{SM} = 8.39$ ) partial melt present in the partially  
535 molten labradorite (called pmLab) from Dimanov et al. (2000). The corresponding viscosity is  
536 substantially lower (one to three orders of magnitude) than those of the melts investigated in the present  
537 study, and compares well with the viscosities for haplogranitic or albitic melts.

538 We also calculated the NBO/T for the melts in the present study and the study of Dimanov et al.  
539 (2000) following the approach of Mysen (1983, 1988; 2003). As a first order approximation we considered  
540 only the major cations present (Si, Al, Na, Ca). In particular, all Al present was assigned to tetrahedral  
541 coordination (network former), as its content does not exceed the sum of the charge weighted contents of  
542 Na and Ca ( $\text{Al} < \text{Na} + 2\text{Ca}$ ). We obtained NBO/T values  $\approx 0.01$ ,  $0.02$  and  $0.06$  for SilLab5, SilLab1 and  
543 pmLab respectively, which clearly indicate polymerization states in agreement with the calculated  
544 viscosities. In addition, we realized a comparison of the viscosities of the melts present in our samples  
545 and the material from Dimanov et al. (2000) and the viscosities of all the different melts reported by  
546 Giordano et al. (2006) against their NBO/T numbers, at  $1200^\circ\text{C}$  (Fig. 5b). The data set is fully consistent,  
547 including for the silica-richest melt from our SilLab5 material. The calculated viscosities of the melts  
548 from SilLab5, SilLab1 and pmLab materials correlate very well with the viscosity suite for all the melts  
549 considered by Giordano et al. (2006), which suggests that the extrapolation we made in using their model  
550 for the silica-richest melt from SilLab5 sample is reasonable.

551

## 552 **4.2. Melt diffusivities versus grain boundary diffusivities**



554 Fig. 6: Arrhenius diagram of volume and grain boundary diffusion of network formers (Si, Al and O) in silicates and oxides  
 555 and in silicate melts (in dry or unsaturated conditions). **a:** The dot line delimited upper and lower fields represent the data for  
 556 Si, Al and O diffusion in silicate melts and silicate single crystals, respectively. The data are recalculated for a pressure of 0.1  
 557 MPa (when activation volumes were available). Bas is basalt, Rhy is rhyolitic melt, Di and Jd refer to diopside and jadeite  
 558 melts, Ab and KAS are albite and potassium-aluminosilicate melts. Diffusivity of Si in silica falls within the lower field for  
 559 volume diffusion. Diffusivities of O in silica fall in-between the two fields. Grain boundary diffusivities (recalculated for a  
 560 grain boundary width of ~ 3 nm) are represented by heavy dot lines. The larger vertical brackets indicate the type of diffusivity.  
 561 For diffusion in melt the smaller brackets indicate the compositional ranges and the corresponding NBO/T numbers. The  
 562 diffusivities calculated for our melt compositions (see text and Fig. 5) are reported as heavy lines  
 563 **b:** Close up from (a) comparing the existing grain boundary diffusivities (light dotted lines) in aluminosilicates and silicates  
 564 (Mullite: Mul, Enstatite: En, Fayalite: Fa) and calculated diffusivities for the present highly polymerized aluminosilicate melts  
 565 (pmLab, SilLab1 and SilLab5). It appears that grain boundary diffusivities are in general comparable to the lowest diffusivities  
 566 in alumino-silicate melts, as do the diffusivities for pmLab and SilLab1 melts. The diffusivity for SilLab5 melt shows however  
 567 substantially lower, in-between the lowest diffusivities in alumina-silicate melts and the highest diffusivities in alumina-  
 568 silicate single crystals.

569 Diffusion data for melts are from Baker (1990, 1992, 1995), Shimizu and Kushiro (1984, 1991), Canil and Muehlenbach  
 570 (1990), Wendlandt (1991), Chakraborty et al. (1995), Kress and Ghiorso (1995), Leshner et al. (1996), Harmer and Brook  
 571 (1980), Brebec et al. (1980), Reid et al. (2001).

572 Data for grain boundary diffusion in silicates, aluminosilicates and alumina are from Rubie (1986), Fislner and Mackwell  
 573 (1994), Fislner et al. (1997), Fielitz et al. (2004, 2007, 2016). Data for volume diffusion in silicates, aluminosilicates and  
 574 alumina are from Bejina and Jaoul (1996), Houlier et al. (1990), Jaoul et al. (1981, 1991), Grove et al. (1984), Yund (1986),  
 575 Le Gall et al. (1994), Fielitz et al. (2007).

577 Ion diffusion properties in aluminosilicate melts inversely correlate with their viscosities, that is  
 578 to say with their NBO/T (Hofmann, 1980; Shimizu and Kushiro, 1991; Mysen, 1988). The latter explicitly  
 579 depends on the relative proportion of network formers and network destroyers, and hence the silica content  
 580 is straightforwardly a first order parameter in determining NBO/T, viscosity and diffusivity. The lower is  
 581 the NBO/T and the higher is the viscosity (Fig. 5). For example, the NBO/T is between 1 and 2 for

582 andesitic to mafic compositions (basalts), whilst it is  $< 0.1$  for felsic compositions (rhyolites) and strictly  
583 zero for dry silica. Consequently, the lower is the NBO/T and the lower is the diffusivity. An illustration  
584 is given by Liang et al. (1996), who measured self-diffusivities in calcium aluminosilicate (CAS) melts  
585 with low water contents between 0.04 – 0.07 wt.%. They show that  $D_{Si}$ ,  $D_{Al}$ ,  $D_O$  and  $D_{Ca}$  are respectively  
586 about 20, 10, 13 and 4 times lower in the melt with 20, 15 and 65 wt.% CaO,  $Al_2O_3$  and  $SiO_2$  (NBO/T =  
587 0.305) than with 40, 20, 40 wt. % CaO,  $Al_2O_3$  and  $SiO_2$  (NBO/T = 0.978).

588 In Figure 6 we present a compilation for diffusivities in silicates, considering: i) volume diffusion  
589 in single crystals, ii) grain boundary diffusion in polycrystals, and iii) diffusion in melts. The considered  
590 data were intentionally restricted to the slowest diffusing network formers (Al, Si and O), which are the  
591 species susceptible to control the kinetics of diffusion controlled creep. To be in accord with the present  
592 work, we further restricted our consideration to data obtained for dry systems. In the experimental  
593 temperature range of interest the diffusion rates of Si and Al in silicate melts decrease over many orders  
594 of magnitude with decreasing NBO/T, that is to say with increasing silica content and correspondingly  
595 decreasing contents of network destroyers. In general, the diffusion rates are the fastest in basalts,  
596 intermediate in rhyolitic melts and substantially lower in plagioclase melts. The extreme lowest diffusion  
597 rate of Si in pure amorphous silica is nearly comparable with Si diffusion in single crystal pure quartz.  
598 These observations are qualitatively consistent with our findings from creep data, which indicate: i) the  
599 highest diffusivity for the partially molten samples of Dimanov et al. (2000), which contain amorphous  
600 grain boundaries with  $\approx 80$  wt.% silica, ii) intermediate diffusivity for our SilLab1 samples, which present  
601 amorphous grain boundaries with  $\approx 85$  wt.% silica, iii) the lowest diffusivity for our SilLab1 samples,  
602 which present amorphous grain boundaries with  $\approx 95$  wt.% silica.

603 Yet, it is most important to address the question whether any silicate melt present along labradorite  
604 grain boundaries may enhance the diffusion rates with respect to the crystalline grain boundaries. On the  
605 one hand, the data of Dimanov et al. (2000) indicate that thin melt films with  $\approx 80$  wt. % silica provide

606 substantially faster pathways for grain boundary diffusion as compared with labradorite grain boundaries.  
 607 On the other hand, the present data for SilLab1 samples indicate that thin melt films with  $\approx 85$  wt.% silica  
 608 have no noticeable effect, whereas our data for SilLab5 samples indicate that grain boundary diffusion is  
 609 substantially slowed down within thin melt films with  $\approx 95$  wt.% silica. In order to be more quantitative  
 610 we need to estimate the effective diffusivities in our different samples and to compare the latter with  
 611 diffusivities in silicate melts and grain boundaries. For this purpose we considered the Eyring equation,  
 612 relating diffusivity and viscosity of liquids:

$$D_{eff} = \frac{k_B T}{\lambda \eta} \quad (5)$$

613  
 614  
 615  
 616 where  $D_{eff}$  and  $\eta$  are respectively the effective diffusivity and the viscosity, and where the molecular radius  
 617  $\lambda$  is taken as an approximation for the jump distance of the mobile species. For instance, the Eyring  
 618 equation is especially considered as applicable to the network formers in viscous silicate melts and glasses  
 619 (Mungal, 2002; Nascimento and Zanotto, 2006). Based on equation (5) and taking  $\lambda = 10^{-10}$  m as a first  
 620 order approximation, we calculated the diffusivities of the melts present in SilLab1, SilLab5 and in the  
 621 partially molten labradorite (pmLab) of Dimanov et al. (2000). We show in Figure 6a that the latter are  
 622 intermediate between volume diffusion and grain boundary diffusion in silicates. Unfortunately, direct  
 623 measurements of grain boundary diffusivities for plagioclase materials are not available. Indirect  
 624 estimations of grain boundary diffusivities in plagioclase, pyroxene and forsterite from the kinetics of  
 625 reaction rim growth do exist (Liu et al., 1997; Yund, 1997; Yund and Farver, 1999; Milke et al., 2001;  
 626 Abart et al., 2004), but only for water present conditions, which precludes any direct comparison in the  
 627 present study. However, Figure 6b shows that the existing grain boundary diffusion data for dry silicates,  
 628 oxides and aluminosilicates (dotted lines) correspond to the slowest diffusivities in the most polymerized  
 629 aluminosilicate melts (rhyolite, albite). This observation is in agreement with recent findings based on

630 molecular dynamics, which indicate strong similarities between the cooperative molecular motion at grain  
631 boundaries and in glass forming liquids (Zhang et al., 2009). According to the data, the calculated  $D_{eff}$  in  
632 labradorite partial melt (pmLab) corresponds very well to the measured Si and Al diffusivities in albite  
633 melt. On the other hand, we can highlight the fact that within the experimental range (1100 – 1300°C)  $D_{eff}$   
634 in labradorite partial melt (pmLab) exceeds by about an order of magnitude the existing grain boundary  
635 diffusivities in enstatite, alumina and mulite. This observation is consistent with the findings of Dimanov  
636 et al. (2000), who reported that the partially molten labradorite samples (pmLab) were about an order of  
637 magnitude weaker than the fully crystalline samples. Conversely, the effective diffusion through melt  
638 films with 85 wt.% silica (SilLab1) seems slow enough to mimic grain boundary diffusion rates. This  
639 observation provides an explanation why the SilLab1 and the fully crystalline Lab samples have  
640 comparable strengths. Most interestingly, diffusion through melts with 95 wt. % silica (SilLab5) appears  
641 to be much slower than in any other melt, or at grain boundaries. The corresponding effective diffusivity  
642 is only one to two orders of magnitude faster than volume diffusion processes in aluminosilicate single  
643 crystals involving network formers (diffusion of Al and O in mullite and CaAl – NaSi interdiffusion in  
644 plagioclase). This observation clearly suggests very slow grain boundary diffusion rates for SilLab5  
645 samples, which is fully consistent with the fact that the latter are considerably stronger than the SilLab1  
646 and Lab samples.

647

#### 648 **4.3. Grain boundary diffusivity versus melt – grain interfacial diffusivity**

649

650 We estimated on the basis of equations (4) and (5) the effective diffusivities for the different  
651 amorphous silicate materials present along grain boundaries in our partially molten plagioclase samples.  
652 The results are in good agreement with the extant diffusion data in dry conditions for Si, Al and O (network  
653 formers and rate limiting species) in both aluminosilicate melts and along grain boundaries (Fig. 6). From

654 this comparison it appears that i) diffusivity in plagioclase – like partial melt (80 wt. % silica) is  
655 substantially faster than diffusivities along grain boundaries; ii) diffusivities along grain boundaries  
656 correspond to the diffusivity in silica – rich melt (85 wt. % SiO<sub>2</sub>); iii) diffusivity in extremely silica – rich  
657 melt (95 wt. % silica) is substantially slower than along grain boundaries. The first point indicates that  
658 partially molten plagioclase containing plagioclase – like melt forming films along grain boundaries  
659 should be weaker than nominally crystalline plagioclase, which is precisely what Dimanov et al. (2000)  
660 observed. The second and the third points imply that partially molten plagioclase with silica – rich (85 wt.  
661 % SiO<sub>2</sub>) and extremely silica – rich (95 wt. % SiO<sub>2</sub>) melt films along grain boundaries should be,  
662 respectively, as strong- and stronger than nominally crystalline plagioclase, which is what we did observe.  
663 Our evaluation of diffusivities from melt viscosities, which were previously evaluated from melt  
664 chemistry, is only a first order approximation. Nevertheless, in spite of the roughness of this approach,  
665 the order of magnitude and the consistency of the estimated results are convincingly reasonable when  
666 compared with i) the experimental data for melts (Figures 5 and 6); ii) our creep data interpreted in terms  
667 of efficiency of interfacial diffusion. However, these observations open some additional questions about  
668 the structure and the diffusivities at the interfaces between the grains and the intergranular amorphous  
669 films, which are developed below.

670         Solid state diffusional mass transfer operates owing to crystallographic structural defects. Volume  
671 diffusion relies on point defects, such as vacancies, interstitials, substitution impurities and their  
672 associations. Alternatives for faster volume diffusion are provided by extended linear and planar defects,  
673 such as dislocation cores and twin boundaries or sub – grain boundaries. The latter are special low – angle  
674 tilt – boundaries, which result from the rearrangement of free dislocations (dislocation pile-up) driven by  
675 the associated decrease in free energy of the system. Twin boundaries and low – angle tilt – boundaries  
676 may be called are coherent semi – coherent, respectively, because they present the most numerous  
677 coincident crystallographic sites. Conversely, the common high angle, tilt and twist grain boundaries

678 present the lowest densities of coincident lattice sites. The lower is the density of the coincident lattice  
679 sites and inversely higher is the density of the structural defects (local lattice distortion, dangling bonds,  
680 impurity segregation...) of the considered interface. Interfacial diffusion is conditioned by the density of  
681 interfacial structural defects, and hence, diffusion along common grain boundaries is orders of magnitude  
682 faster than diffusion along coherent interfaces and volume diffusion. The classical hypothesis that  
683 diffusion creep is controlled by the slowest species diffusing through the fastest path ways implies in the  
684 case of nominally crystalline plagioclase creep control by the diffusion of network formers along grain  
685 boundaries. Conversely, the fastest path ways would be the interfacial melt films, if providing fastest  
686 diffusion kinetics than the crystalline interfaces. It may be, however, more difficult to identify the fastest  
687 path ways if the interfaces contain amorphous material where diffusion is supposedly slower than at  
688 crystalline high angle grain boundaries. If diffusion occurs through the melt films, the material would  
689 strengthen with respect to the nominally crystalline one, which is what we did observe. Still, a question  
690 remains whether faster diffusion could not proceed along the grain – melt interfaces, in which case the  
691 macroscopic behaviour would differ. In order to clarify this point it is necessary to compare the nature  
692 and the density of structural defects at a melt – grain interface with respect to a common grain boundary,  
693 which we attempt in the following.

694         Low – angle tilt – boundaries are low – energy (favoured) grain boundaries that present the highest  
695 densities of coincident lattice sites. From a geometrical viewpoint their cores have been recognized to  
696 form regular arrays of “structural units”, i.e. small atomic groups organized in a characteristic  
697 configuration (Sutton and Vitek, 1983). Conceptually, the “structural unit model” is equivalent to describe  
698 the interface as closely spaced lattice dislocations (sometimes called primary dislocations) whose elastic  
699 stress field concentrates closely to the core interface (Baluffi and Bristowe, 1984). As a consequence, such  
700 grain boundaries present little lattice distortion at long-range. More random interfaces (tilt and twist  
701 boundaries) were tentatively described by mixing different types of structural units corresponding to

702 different types of favoured boundaries (Sutton and Vitek, 1983), which was shown i) to be equivalent to  
703 the classical grain boundary dislocation (or secondary dislocation) structure (Baluffi and Bristowe, 1984),  
704 ii) to be of limited success (Sutton, 1989). Furthermore, considering such general interfaces Sutton and  
705 Baluffi (1987) concluded that a simple geometric framework cannot provide general rules for optimized  
706 (low energy) configurations, because the atomistic and bonding structures must be considered as well.  
707 Therefore, random interfaces necessarily exhibit the highest densities of structural misfits and  
708 correspondingly the high interfacial energies. The latter are actually partly compensated by local  
709 relaxation (rearrangement) of atomic positions at and near the core interface (Merkle, 1997). Relaxation  
710 results in various crystallographic distortions of the core boundary. The net result is a strong short range  
711 interfacial disordering, which makes the dynamic properties (mobility, co-operational transport and  
712 viscosity) of grain boundaries to mimic those of amorphous phases (Zhang et al., 2009). Therefore, the  
713 common (high – angle, twist and tilt) grain boundaries are characterized by the highest density of  
714 ionic/molecular crystal structural defects (impurities, vacancies, interstitials and their associations), but  
715 also extended crystal structural defects (dislocations, sub-grain boundaries, vacancy clusters...), which all  
716 contribute to the structural misfits, the so called “packing frustration” and the presence of unsatisfied  
717 dangling bonds. As the interfacial free energy relates to the density of the interfacial structural defects  
718 (van der Merwe, 2001), it increases gradually from twin – and low angle – to high angle boundaries, which  
719 exhibit the highest interfacial energies.

720 For ceramic materials (alumina, zirconia, SiC, Si<sub>3</sub>N<sub>4</sub>, SrTiO<sub>2</sub>...) it has been demonstrated that thin  
721 (nm – sized) amorphous films may be thermodynamically stable at grain boundaries, because they may  
722 contribute to lower the interfacial free energy of the system (Clarke, 1987; Clarke et al., 1993; Wilkinson,  
723 1993; Bobeth et al., 1999). In other words, an amorphous interphase may contribute to partly compensate  
724 for the inherent interfacial structural defects. For instance, in order to minimise the excess free energy  
725 associated with interfacial misfits the surrounding crystalline lattices can only modestly relax by limited

726 distortion. Conversely, a viscous amorphous phase could more efficiently accommodate to any interfacial  
727 structural misfit, providing molecular units to satisfy dangling bonds. The net result would be the  
728 reduction of interfacial lattice distortions and interfacial free energy, and thus, of the density of structural  
729 defects. If so, the diffusivities at the crystal – melt interface should be lowered with respect to the common  
730 grain boundary diffusivities as well. So finally, whether the presence of an interfacial amorphous phase  
731 would slow down or enhance the grain boundary diffusion rates would essentially depend on the diffusion  
732 properties through the amorphous material itself. In the present case, the extremely silica – rich amorphous  
733 phase present along grain boundaries of SilLab5 material tends to slows down the diffusion properties  
734 and the samples appear stronger.

735

## 736 **5. Conclusions**

737

738 We investigated high temperature ( $>1000^{\circ}\text{C}$ ) diffusion controlled creep of plagioclase aggregates  
739 containing limited amounts of partial melt (2 – 6 vol. %), with respect to the physical structure (crystalline  
740 / amorphous) of the grain boundaries. We specifically focused on the effect of melt chemistry in the  
741 situation of thin amorphous films ( $< 10\text{ nm}$ ) wetting grain boundaries. For this purpose we applied sol –  
742 gel techniques and isostatic hot – pressing (300 MPa,  $T = 1150^{\circ}\text{C}$ ) in order to synthesize i) nominally  
743 crystalline plagioclase material (SilLab), ii) two types of partially molten plagioclase materials (SilLab1  
744 and SilLab5), containing limited amounts of silica – rich partial melt, with contrasting chemistries. The  
745 SilLab nominally melt – free samples contained  $< 1\text{ vol. \%}$  residual glass. The SilLab1 and SilLab5  
746 partially molten plagioclase samples contained 2 and 6 vol. % of aluminosilicate melts with c.a. 85 wt. %  
747 and 95 wt. %  $\text{SiO}_2$ , respectively. The hot-pressed materials were fine grained ( $< 15\text{ }\mu\text{m}$ ) and contained  
748 about 0.05 wt. % water species that could be dried out by annealing at  $1100^{\circ}\text{C}$  and at atmospheric pressure.  
749 Uniaxial compression creep tests were performed at temperatures and flow stresses between 1100 –

750 1250°C and 3 – 60 MPa, respectively. All samples showed dominantly linear viscous flow with a stress  
751 exponent  $n \sim 1$  and nominally melt – free samples showed a grain size exponent  $m \sim -3$ , indicating grain  
752 boundary diffusion control. Activation energies were  $433 \pm 14$  kJ/mol,  $520 \pm 21$  kJ/mol and  $672 \pm 18$   
753 kJ/mol for nominally melt – free samples, and for samples containing  $\sim 2$  vol. % and 6 vol. % silica – rich  
754 melts, respectively. The samples containing  $\sim 6$  vol. % melt presented the highest activation energy and  
755 were substantially stronger than all other samples. We explained the fact by the presence of the highly  
756 polymerized and viscous melt, with the highest silica content ( $\sim 95$  wt. %  $\text{SiO}_2$ ), and thus, with the lowest  
757 diffusion rates.

758         Based on viscosity models for aluminosilicate melts (Giordano et al., 2006) we estimated the  
759 viscosities and the effective diffusivities of the melts present in our samples and in previously studied  
760 partially molten plagioclase samples ( $\approx 80$  wt. %  $\text{SiO}_2$ , Dimanov et al., 2000). The data we obtain are in  
761 agreement while considering the extant diffusion data of network formers in silicate melts, with respect  
762 to their silica contents and polymerization states in dry conditions. Furthermore, we considered volume  
763 diffusion data in single crystals and grain boundary diffusivities in silicates and oxides polycrystals.  
764 Amorphous silica apart, volume diffusion data in single crystals are the lowest, whilst melt diffusivities  
765 are the highest. For the latter, the diffusivities inversely correlate with the polymerization degree. Grain  
766 boundary diffusion data are much higher than volume diffusion data, but they overlap with the diffusivities  
767 in highly polymerized aluminosilicate melts. Our findings indicate that grain boundary diffusivity in  
768 polycrystalline melt-free labradorite is i) comparable to those in highly polymerized silica-rich melts ( $\sim$   
769 85 wt. %  $\text{SiO}_2$ ), ii) considerably lower than those in labradorite partial melt ( $\sim 80$  wt. %  $\text{SiO}_2$ ), iii)  
770 substantially higher than in extremely silica-rich melt ( $\sim 95$  wt. %  $\text{SiO}_2$ ).

771         We demonstrated strong physical – chemical couplings between plagioclase rheology based on  
772 grain boundary diffusion controlled creep and the presence of aluminosilicate melts. In the particular case  
773 where grain boundaries present amorphous structure the rheological properties are strongly related to the

774 melt chemistry, and more specifically to the silica content. The latter determines the polymerization  
775 degree and hence the diffusion properties, depending on which samples may either weaken or strengthen.  
776 Counter intuitively, our data show that the presence of thin amorphous films at grain boundaries may not  
777 always ensure faster diffusion path ways. In turn, in dry conditions grain boundary transport properties  
778 may be strongly hindered in the presence of melt films with extreme silica contents ( $> 90 - 95$  wt. %  $\text{SiO}_2$ ).

779

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781

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786 investigation data are available.

787

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