Zircon survival in shallow asthenosphere and deep lithosphere 1

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ABSTRACT

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Zircon (ZrSiO₄) is the most frequently used geochronometer of terrestrial and extraterrestrial 44 processes. To shed light on question of zircon survival in the Earth's shallow asthenosphere, 45 high-temperature experiments of zircon dissolution in natural mid-ocean ridge basaltic 46 (MORB) and synthetic haplobasaltic melts have been performed at temperatures of 1250 -47 1300°C and pressure from 0.1 MPa to 0.7 GPa. Zirconium measurements were made in situ 48 by electron probe microanalyses (EPMA) at high current. Taking into account secondary 49 fluorescence effects in zircon-glass pairs during EPMA, a zirconium diffusion coefficient of 50 2.87E-08 cm²/sec has been determined at 1300°C and 0.5 GPa. When applied to the question 51 52 of zircon survival in asthenospheric melts of tholeiitic basalt composition, the data are used to infer that typical 100 µm zircon crystals dissolve rapidly (~10 h) and congruently upon 53 reaction with basaltic melt at mantle pressures of 0.2 - 0.7 GPa. We observed incongruent (to 54 crystal ZrO₂ and SiO₂ in melt) dissolution of zircon in natural mid-ocean ridge basaltic melt at 55 low pressures < 0.2 GPa and in haplobasaltic melt at elevated 0.7 GPa pressure. Our 56 57 experimental data raise questions about the origin of zircon crystals in mafic and ultramafic rocks, in particular, in shallow oceanic asthenosphere and deep lithosphere, as well as the 58 meaning of the zircon-based ages estimated from the composition of these minerals. The 59 origin of zircon in shallow (ultra-) mafic chambers is likely related to crystallization of 60 intercumulus liquid. Large size zircon megacrysts in kimberlites, peridotites, alkali basalts 61 and carbonatite magmas suggest fast transport and short interaction between zircon and melt. 62 63 The origin of zircon megacrysts is likely related to metasomatic addition of Zr into the mantle as an episode of mantle melting should eliminate them on geologically short timescales. 64

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INTRODUCTION

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Zircon is the most frequently used mineral for dating terrestrial and extraterrestrial rocks (e.g., 68 Valley et al. 2014a) using a variety of isotopes in the U-Th-Pb system (Schmitt et al., 2014). 69 Furthermore, zircon has high closure temperatures for a wide range of elements (and their 70 71 isotopes), making this mineral well suited for reconstructing sources and formation conditions. For example, Ti content is used for temperature estimates (Watson et al., 2006) 72 while O and Hf isotopic compositions and trace element contents are commonly employed to 73 provide insight into the source of zircon crystals and their magmatic or/and hydrothermal 74 protoliths (e.g., Iizukaa et al., 2015, Valley et al., 2014a). 75

The use of zircon as a petrogenetic tool requires knowledge of the stability field of this 76 mineral, in addition to quantification of solubility limits and crystallization/dissolution rates at 77 relevant P-T conditions and fields of melt composition. Experimental work to determine 78 79 zircon solubility, dissolution rates and diffusion coefficients of Zr in silicate liquids began in the early 1980's, but has concentrated on felsic and intermediate compositions of variable 80 H₂O contents at high temperatures and pressures (Watson, 1982; Harrison & Watson, 1983; 81 Ellison & Hess, 1986; Baker & Watson, 1988; Baker et al., 2002; LaTourrette et al., 1996; 82 Nakamura & Kushiro, 1988; Mungall et al., 1999; Koepke & Behrens, 2001; Lungstrom 83 84 2003; Watson et al., 2006; Rubatto & Hermann, 2007; Behrens & Hahn, 2009; Burnham & Berry. 2012: Boehnke et al., 2013: Zhang & Xu, 2016: Holvcross & Watson, 2016: 2018: 85 Shao et al., 2018; Borisov & Aranovich, 2019). In contrast, there are few experimental studies 86 on basaltic systems, an exception being the study of Dickinson & Hess (1982) on lunar 87 systems, before more recent studies of synthetic terrestrial basaltic melts (Boehnke et al., 88

2013; Holycross & Watson, 2016; Shao et al., 2018; Borisov & Aranovich, 2019) and dunites
(Anfilogov et al., 2015).

Interest in more mafic systems has been spurred by growing evidence for the presence 91 92 of zircon grains in a wide range of terrestrial mafic and ultramafic rocks such as diorites, gabbros and gabbroids, peridotites, kimberlites, dunites, chromitites, garnet-pyroxenites, 93 dolerites, including spectacularly large grains of zircon in carbonatites (e.g., Bea et al., 2001; 94 Belousova et al., 2002; 2015, Kaczmarek et al., 2008; Kostitsyn et al., 2009; 2012; 2015; 95 González-Jiménez et al., 2017; Bychkova et al., 2019a,b; Bea et al., 2020 and references 96 therein) as well as in basaltic meteorites (Ireland & Wlozka, 1992; Humayun et al., 2013, 97 Valley et al., 2014b, Iizukaa et al., 2015; Bellucci et al., 2019). However, there is current 98 debate concerning the formation mechanisms of zircon in terrestrial mafic and ultramafic 99 rocks that can reach 3.2 Ga in age. Hf and O isotope composition coupled with U-Th-Pb 100 geochronology has led to various ideas, including delamination/recycling of continental 101 lithosphere, direct involvement of fragments of continental lithosphere or an ancient event of 102 103 fluid-rock interaction followed by long-lasting storage at mantle conditions (Kostitsyn et al., 2009; 2015; Ashwal et al., 2017; Bea et al., 2020 and references therein). 104

However, current experimental data in mafic systems are sparse and sometimes 105 contradictory, and generally insufficient to distinguish between these different formation 106 scenarios. For example, reaction with fluids, silicate melts and and/or other minerals (e.g., 107 olivine, chromite), may lead to modifications of the primary zircon elemental and isotope 108 signatures through diffusion or dissolution-precipitation (Geisler et al., 2007; Bea et al., 109 2018), but there are no experimental data on the survival of zircon and preservation of Pb-U-110 Th-O-Ti-REE signatures at high temperature-pressure-volatile content conditions in mafic and 111 ultramafic systems. These gaps in knowledge prevent robust interpretation of the ages derived 112 from zircon in terrestrial and extraterrestrial rocks. 113

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In light of the fact that interaction of zircon with natural terrestrial basaltic liquid has 114 never been studied experimentally, and with the overall aim of providing constraints for a 115 general model of zircon stability in natural shallow asthenospheric melts of basaltic 116 composition, an experimental program has been initiated to constrain the solubility limit and 117 dissolution kinetics of zircon at high pressure and temperature in mafic systems. In this first 118 contribution we present the results of interaction between natural Mud Tank zircon and 119 natural and synthetic basaltic and haplobasaltic melts at 1250 - 1300°C at pressures from 0.1 120 MPa to 0.7 GPa. 121

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METHODS

124 Starting materials

The zircon crystals used in this study are from the \sim 730 Ma Mud Tank carbonatites (Crohn 125 and Moore, 1984; Gain et al., 2019) provided as crystals ~1cm in size by Sebastien Meffre 126 (UTAS, Hobart, Australia). These crystals were first prepared as doubly polished ~1000 µm-127 thick sections, then made into smaller double-polished chips by slight pressing of the section. 128 129 The mid-ocean ridge basalt glass used in our experiments is a typical moderately differentiated (8.2 wt.% of MgO, M = 3.3; G = 2.5, Supplementary Material) glassy 130 tholeiitic basalt (number 3786/3) from Knipovich ridge of the Mid Atlantic Ridge sampled by 131 during 38th Research Vessel Adademic Mstislav 132 dredging Keldysh expedition (Sushchevskaya et al., 2000). The MORB glass (that contains no traces of olivine and/or 133 chromite phenocrysts) has been crushed to powder (<100 µm glass size). 134

The haplobasatic glass, corresponding the anorthite-diopside eutectic in the system (CaO-MgO-Al₂O₃-SiO₂) was synthetized using mixtures of reagent grade oxides and carbonates (SiO₂, Al₂O₃, MgO, CaCO₃) following the method of Toplis et al. (1994).

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140 Experimental techniques

The reaction of natural Mud Tank zircon with basaltic liquids has been investigated at pressures from 0.1 MPa to 0.7 GPa corresponding to the depths of crustal basaltic chamber (up to 20 km), typical of mafic magma transport conditions in oceanic settings. Seven experimental runs have been completed in this pressure range, at temperatures in the range 1250 - 1300°C and low ratios of zircon to basalt (0.04 to 0.16), (**Table 1, Fig. 1**).

Experiments were performed in Au₈₀Pd₂₀ capsules into which a double-polished zircon 146 chip was placed at the bottom, the upper part of the capsule being filled with basaltic glass 147 powder. Starting materials were weighed carefully to control zircon/melt ratio. Distilled 148 water^{MQ} has been added in one experiment (Z7) to study the effect of hydrous basalt (Table 149 1). This water was introduced with a micro-syringe to the basaltic powder when the sample 150 151 was already loaded into the capsule. Because of fast kinetics of zircon dissolution at high 152 temperatures and to avoid the complete dissolution of zircon chip, run durations had to be shorter than the time necessary to reach oxygen fugacity equilibrium with piston-cylinder 153 double-capsule techniques using mineral buffers (48 hours: Matjuschkin et al., 2015). The 154 redox conditions in our kinetic experiments are thus considered to be controlled by the initial 155 Fe²⁺/Fe³⁺ ratios of the natural samples used as starting materials (MORB glass), possibly 156 affected by partial exchange of Al₂O₃ with pressure media (in piston cylinder experiments). 157 The redox conditions established were estimated to range from FMQ(+1.5) to FMQ(+3.6)158 (where values indicate logarithmic units compared to the FMQ, fayalite-magnetite-quartz 159 buffer) (Borisova et al., 2020). These redox conditions were estimated from the olivine-160 chromite assemblages using equations of Ballhaus et al. (1991) and from mole fraction of 161 ferric iron Fe^{III} obtained by XANES (X-ray absorption near edge structure). 162

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Two piston-cylinder systems have been used in our experiments. The experiment (Z1) 163 164 used the Max Voggenreiter[®] end-loaded Boyd-England piston-cylinder apparatus at the Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI), Bayreuth, 165 Germany. Talc cells 3/4 inch in diameter with Pyrex sleeves were used. A tapered graphite 166 furnace was inserted in each cell (Fig. 2a). Alumina (Al₂O₃) spacers were used as pressure-167 transmitting medium. An Au₈₀Pd₂₀ capsule loaded with starting materials was set in the 168 central part of the assembly. A 20% pressure correction was applied for the friction between 169 the talc cell and pressure vessel. A molybdenum disulfide (MoS₂) lubricant was introduced to 170 minimize the friction. The temperature in the upper part of the capsules was controlled by a 171 172 EUROTHERM (2404) controller via either W₃Re₉₇/W₂₅Re₇₅ (type D) or Pt₆Rh₉₄/Pt₃₀Rh₇₀ (type B) thermocouple accurate to $\pm 0.5^{\circ}$ C. The uncertainty on pressure was estimated to be \pm 173 0.04 GPa. The sample was compressed to 0.5 GPa during a period of 20 minutes and then 174 175 heated up to the run temperature (1300 °C) at a rate of 100 °C/min. The samples were maintained at run conditions for the desired duration, then guenched by switching off the 176 power supply. Decompression then lasted 20 minutes to 2 hours. The quench rate to room 177 temperature was up to 80°C/min. 178

Experiments (Z4, Z6, Z7) used the end-loaded Boyd-England piston-cylinder 179 apparatus at the Korzhinskii Institute of Experimental Mineralogy, Chernogolovka, Russia. 180 Standard talc-Pyrex cells 3/4 inch in diameter, equipped with tube graphite heaters and inserts 181 made of MgO ceramics were used as pressure-transmitting medium (Fig. 2b). The pressure at 182 elevated temperatures was calibrated against two reactions of brucite = periclase + H_2O and 183 albite = jadeite + quartz equilibria. A pressure correction (12%) was introduced for the 184 185 friction between the cell and hard-alloy vessel. To minimize friction, a Pb foil and molybdenum disulfide (MoS₂) lubricant were used. Au₈₀Pd₂₀ capsules with starting mixtures 186 were mounted in the central parts of the cells. The temperature in the upper part of the 187

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capsules was controlled to $\pm 1^{\circ}$ C using a MINITHERM controller via a W₉₅Re₅/W₈₀Re₂₀ 188 189 thermocouple insulated by mullite and Al₂O₃ without pressure correction. For the Pyrexbearing assemblies, the sample was heated to 550 - 600°C at low confining pressure (0.15 -190 191 0.2 GPa) for a few minutes in order to soften the Pyrex glass, then both temperature and pressure were increased simultaneously up to the desired run conditions. The uncertainty on 192 pressure was estimated to be ± 0.04 GPa. Samples were maintained at run conditions for 193 194 desired durations then quenched by switching off the power supply. The quench rate was 100-200°C/min. 195

Experiments Z2 – Z3 used a vertical gas-mixing furnace at one atmosphere pressure, 196 197 1300°C and controlled oxygen fugacity at IRAP, Toulouse, France. Redox conditions in the furnace were controlled by mixtures of CO and CO₂ corresponding to the favalite-magnetite-198 quartz (FMQ) buffer. The closed, but unsealed, Au₈₀Pd₂₀ capsules loaded with starting 199 materials were held on a Pt wire (0.3 mm in diameter) and introduced into the hot spot of the 200 gas-mixing furnace. Samples were rapidly quenched (~1000°C/s) by dropping the sample into 201 202 the cold zone of the furnace, in the CO-CO₂ atmosphere, by melting a thin Pt suspension wire with an electric shortcut. After evacuation of the CO, the samples were recovered and 203 mounted in epoxy and polished with SiC sandpapers. 204

For the experiment Z10, we have used an internally heated gas pressure vessel at the 205 Korzhinskii Institute of Experimental Mineralogy, Chernogolovka, Russia. The pressure in 206 the system was created by pure Ar gas. The system was heated by a furnace with two 207 windings (to minimize the thermal gradient). The temperature was set and measured by a 208 TRM-101 OVEN controller through two S-type (Pt₉₀Rh₁₀ vs Pt₁₀₀) thermocouples. The 209 210 thermocouples were mounted at the top and close to the bottom of the run hot spot to monitor the temperature gradient. The duration of experiment was 5 h and the experiment was 211 quenched by switching off the furnace. The pressure during the quench was maintained 212

constant down to 550 °C, and then slowly released. The cooling rate from 1250 to 1000 °C
was 167 °C/min, and then 90 °C/min down to 550 °C. Runs Z5, Z8, and Z9 were unsuccessful
because of technical issues. After the runs, all successful run capsules were cut in two parts
using a diamond saw, mounted in epoxy, and then polished using SiC sand papers and
diamond pastes.

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219 Microanalytical methods

To study the trace element profile of Zr in the reaction zones we have used electron probe 220 microanalysis (CAMECA SX-Five). Major element analyses of minerals and glasses (Fig. 3, 221 Supplementary Material) and the sample imaging were made at the Géosciences 222 Environnement Toulouse (GET, Toulouse, France) laboratory and at the Centre de 223 Microcaractérisation Raimond Castaing (Toulouse, France). The main experimental phases 224 (baddeleyite, zircon and glasses) in the samples have been identified by EDS microprobe 225 226 technique using a scanning electron microscope (SEM) JEOL JSM-6360 LV with energy-227 dispersive X-ray spectroscopy (EDS) in GET, Toulouse, France. Major and minor (Zr) elements in the crystals and glasses were analyzed using a CAMECA SX-Five microprobe in 228 Centre Castaing, Toulouse, France. For the electron microprobe CAMECA SX Five, 229 operating conditions were: an accelerating voltage 15 kV, currents of 20nA for the major 230 elements depending on the resistance of the material under the electron beam, and 100 nA for 231 the minor Zr. Focused ($\sim 2 \mu m$) beam conditions were used for the major and trace (Cr, Zr) 232 element analyses of the glass phases. The following synthetic and natural standards were used 233 for calibration: natural albite (for Na), natural corundum (Al), natural wollastonite (Si, Ca), 234 natural sanidine (K), synthetic pyrophanite (Mn, Ti), natural hematite (Fe), natural periclase 235 (Mg), synthetic Cr₂O₃ (Cr), and reference natural zircon (Zr) provided by the Micro-Analysis 236 Consultants© Ltd.. Element and background counting times were 5 s for Na and K and 10 s 237

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for other major elements, whereas, peak counting times were 120 s for Cr, and 240 s for Zr. 238 239 The detection limit was 70 ppm for Cr and Zr, this value being derived from the Cameca SX Five software based on the MPI-DING standard glasses. Synthetic reference MPI-DING 240 glasses of mafic and ultramafic composition (KL2-G, ML3B-G, GOR132-G, GOR128-G, 241 Jochum et al., 2006) obtained from natural rock powders were analyzed as unknown samples 242 to monitor the accuracy of the major and trace element analyses. The accuracy estimated on 243 the reference glasses ranges from 0.5 to 5 % (1σ RSD = relative standard deviation), 244 depending on the element contents in the reference glasses. The starting MORB glass 245 containing 0.56 wt% H₂O was analyzed according to the method of Bindeman et al. (2012). 246

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248 Secondary fluorescence effect and kinetic modeling

Given that our overall aim is to model the behavior of zircon in ad-hoc natural systems, we 249 250 need to extract relevant parameters from our experimental data that can be used in generalized numerical models of dissolution. In this respect, there are two fundamental parameters that 251 control mineral dissolution: 1) the composition of liquid that is saturated in the phase of 252 interest (that can be simplified to the concentration of a limiting element, in our case Zr, at the 253 crystal-liquid interface), and 2) the diffusion coefficient of that limiting element in the liquid. 254 255 For both of these issues, a potential complication is secondary fluorescence during microprobe analyses that can introduce a spatially variable signature of the element of interest 256 around host crystals (Borisova et al., 2018). Particular attention must thus be paid to eliminate 257 258 this analytical artifact.

When possible, the interface melt content (C₀) has been obtained from all experiments. The linear interface between the zircon grain and glass allows to subtract the secondary fluorescence effect and to get the real Zr concentrations in the interface glasses (**Table 1; Fig. 1, Supplementary Materials**). An estimate of the Zr diffusion coefficient has been extracted

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from one diffusion profile of the sample Z1 following the method of Harrison and Watson 263 (1983). For that, Zr (ppm) profiles perpendicular to the zircon-glass interface in the Z1 sample 264 have been measured, correcting for secondary fluorescence effects measured between zircon 265 and the same (MORB) basaltic glass (Borisova et al., 2018). The corrected profile taking into 266 consideration the effect has been obtained by linear interpolation of the secondary 267 fluorescence effect with the function 'numpy.interp' of Python language (version 1.17). (e.g., 268 Oliphant, 2006) and by simple subtraction from the measured Zr concentration. The 269 mathematic transformation of the corrected Zr contents in the profiles to the error function 270 (erf^{-1}) correlates linearly with the distance from the interface with a slope of 0.022 (Fig. 3, 271 272 Supplementary Material), suggesting diffusional control of the Zr distribution due to zircon dissolution in the basaltic melt according to the criterion given by Harrison & Watson (1983). 273 Unfortunately, there is no way to extract the diffusion coefficient values from experiments 274 where zircon dissolves incongruently, compared to congruent dissolution in natural basaltic 275 system at ≥ 0.2 GPa. 276

Kinetic modeling of the bulk dissolution of a spherical zircon was completed using the MATLAB software of Bindeman and Melnik (2016) using spherical coordinates with the extracted diffusion coefficient $D_{Zr}=2.87E-08$ cm²/sec at 1300°C and 0.5 GPa (**Supplementary Materials**). The parameters used in the calculations were the interface concentration of Zr in the basaltic melt of 20,840 ± 104 ppm and the initial Zr concentration of 94.3 ppm in the starting basaltic melt (Borisova et al., 2020).

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284 **RESULTS**

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Z1 and Z10 samples are composed of partially dissolved zircon and basaltic glass with a linear interface between the zircon crystal and the final glass (Fig. 1). At the interface between these phases, profiles of Zr concentrations have been obtained for the Z1 sample as described above and illustrated in Figure 3.

290 Z2 and Z3 samples obtained at 0.1 MPa are made of partially and incongruently 291 dissolved zircon overgrown by baddeleyite micro-crystals associated with the zone of SiO₂-292 rich glass (**Fig 1**). Z4 sample contains optically homogeneous basaltic glass, whereas 293 chemical heterogeneity likely due to "vortex"-type convective mixing is of note on the BSE 294 image in the lower part of the capsule, suggesting congruent dissolution of zircon followed by 295 convective mixing of Zr-rich and Zr-poor melts.

In experiments Z6 and Z7, zircon in contact with haplobasaltic melt at 0.7 GPa transformed to a system characterized by partial overgrowths of baddeleyite micro-crystals associated with SiO₂-rich glass (**Fig. 1**).

A summary of the phase relations associated with zircon dissolution at 1250°C to 299 1300°C in (haplo-) basaltic melts (Fig. 4) shows that at 0.1 MPa, zircon dissolves 300 incongruently to form baddeleyite (ZrO₂) and a SiO₂-rich melt. Baddeleyite is also formed at 301 0.7 GPa in the synthetic haplobasaltic (low a_{SiO2}) melt, but no baddeleyite precipitation is 302 observed in the pressure range 0.2 to 0.7 GPa in natural terrestrial tholeiitic basalt melt. 303 The favorable experiment Z1 has been used to extract the diffusion coefficient of Zr, 304 as described above, providing a value of $D_{Zr} = 2.87E-08 \text{ cm}^2/\text{sec}$ at 1300°C and 0.5 GPa 305 (Supplementary Materials). For the question of the interface concentration of Zr, zircon 306 solubility is higher at 0.2 GPa pressure (Z10 run, Table 1) compared to that at 0.5 GPa (Z1 307 run), suggesting possible stabilization of zircon at high pressures. For modeling purposes, a 308 value of $20,840 \pm 104$ ppm Zr was used (corresponding to the value at 0.5 GPa and 1300°C), 309

310	and combined with the initial Zr concentration of 94.3 ppm measured in the starting basaltic
311	melt (Borisova et al., 2020).
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315	DISCUSSION
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317	Zircon versus baddeleyite stability during dissolution
318	In general terms the relative stability of zircon and baddeleyite in terrestrial and
319	extraterrestrial systems can be rationalized in terms of the silica activity of the silicate melt

320 associated with the reaction:

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$$\operatorname{Zr}(\operatorname{SiO}_4)^{\operatorname{Zrn}} = \operatorname{ZrO}_2^{\operatorname{Bdy}} + \operatorname{SiO}_2^{\operatorname{L}}$$
 (eq. 1)

where Zrn is zircon, Bdy - baddeleyite and L is silicate melt. Equation (1) implies that melts 322 of higher silica activity will favor zircon stability, consistent with the fact that zircon prefers 323 to crystallize in felsic, intermediate and silica-saturated (high a_{SiO2}), rather than mafic and 324 ultramafic systems (low a_{SiO2}). Indeed, equation (1) predicts baddeleyite stability in low a_{SiO2} -325 systems, such as ultramafic (e.g., carbonatite, kimberlite), and mafic (haplobasaltic) systems. 326 For example, Gervasoni et al. (2017) has investigated the system of zircon in low- a_{SiO2} 327 carbonanite melt at 0.7 GPa and these authors have described stability of baddeleyite and 328 incongruent dissolution of zircon crystals with formation of corona of baddeleyite. In contrast, 329 no baddeleyite crystallization has been observed by Shao et al., (2018) in a synthetic basalt 330 system at pressures 0.5 - 1.5 GPa, implying baddeleyite stability only at lower pressures (< 331 0.5 GPa) in their basaltic systems. The observed effect of pressure on the relative stability of 332

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zircon and baddelevite is consistent with the fact that increasing pressure tends to increase 333 silica activity of mafic silicate melts, as illustrated by the displacement of the olivine-334 orthopyroxene cotectic. In any case, decompression will favor incongruent rather than 335 congruent dissolution. We also note that comparison of Z2 and Z3 samples from the same 336 time series experiments implies an approximately constant rate of baddeleyite rim formation 337 of $0.9 \pm 0.2 \,\mu$ m/min at constant temperature, pressure and water contents. This rate may be 338 used as a kinetic indicator to calculate approximate timescales of the zircon megacryst 339 transport to the surface. 340

Comparison of runs Z6 and Z7 suggests that hydrous conditions (**Table 1**) favor congruent dissolution. Taken at face value, this would suggest that degassing leads to a tendency for incongruent dissolution, but we note that addition of water is generally accepted to decrease silica activity, a discrepancy that requires more study.

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346 Zr diffusivity and zircon solubility in silicate melts

Most existing models considering zircon solubility and dissolution are based on felsic and 347 intermediate and synthetic systems (zircon - felsic and intermediate silicate liquids, e.g., 348 349 Harrison and Watson, 1983; Boehnke et al., 2013; Zhang & Xu, 2016; and references therein). In those cases, zircon is apparently less soluble and more stable compared to the natural mafic 350 and ultramafic systems. The main factors controlling solubility of zircon in silicate melts are 351 temperature, the melt composition expressed in terms of ratio of nonbridging oxygens per 352 tetrahedrally coordinated cations (NBO/T) which is a simple measure of silicate melt structure 353 based on the ratio between network formers and network modifiers. For example, the factors 354 such as M (((Na + K + 2 \cdot Ca)/(Al \cdot Si)) (all in cation ratio)), G (where numerator (3 \cdot Al₂O₃ + 355 SiO₂) represents the network formers, whilst the denominator $(Na_2O + K_2O + CaO + MgO + K_2O + K_2O + CaO + K_2O + K_2$ 356

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FeO) represent the network modifiers of the melt) or B expressed in oxide mole fractions in 357 358 the melts $(0.14(X_{TiO2}/X_{SiO2}) + 1.3(X_{CaO}/X_{SiO2}) + 1.5(X_{Na2O}/X_{SiO2}) - 4.5(X_{K2O}/X_{SiO2}) - 4.5(X_{K2O}/X_$ $2.7(X_{A12O3}/X_{SiO2})^2 + (X_{MgO}/X_{SiO2})^2 - 3.7(X_{CaO}/X_{SiO2})^2 + 75(X_{K2O}/X_{SiO2})^2)$ as well as the melt 359 water contents have been proposed as factors controlling solubility of zircon in silicate melts 360 (e.g., Harrison & Watson, 1983; Gervasoni et al., 2016; 2017; Borisov & Aranovich, 2019 and 361 references therein). It is expected that the synthetic (Fe- and Ti-poor) and natural Fe- and Ti-362 containing basaltic melts would not be similar in respect to zircon solubility. Our natural 363 basaltic liquid (8.2 wt.% of MgO, M = 3.3; G = 2.5, B = 0.15) provides a theoretical zircon 364 solubility of 23,078 ppm (or 2.3 wt% of Zr) according to model of Borisov & Aranovich 365 (2019) which is in a very good accordance with the experimentally measured solubility of 366 $20,840 \pm 104$ ppm. The theoretical solubility of zircon in MORB melts is thus comparable to 367 experimental ones (2.2 - 3.6 wt% of Zr) obtained by Boehnke et al. (2013) for basaltic liquids 368 at 1225 °C and 1 GPa. The factors such as M, G and B are indicators of zircon solubility in 369 silicate melts but may be also used for prediction of Zr diffusivity, although the most efficient 370 factor controlling the elemental diffusivity in silicate melts besides temperature remains the 371 melt viscosity controlled primarily by the melt SiO₂ content (e.g., Mungall, 2002). 372

To predict zircon survival in natural basaltic systems, the diffusion coefficient of zirconium has been estimated based on the Z1 experiment, as described above (**Fig. 3**). Using the zirconium diffusion coefficient derived in this way (2.87E-08 cm²/sec) and the kinetic model of Bindeman and Melnik (2016), it is predicted that a sphere of zircon 100 microns in diameter will survive for ~10 hours, a sphere of 50 microns diameter for ~3 hours and a grain 10 microns in diameter for only ~10 minutes. At the other extreme, the dissolution of a 1 cm crystal such as Mud Tank zircon, would require ~96000 h (~11 years).

However, before reaching firm conclusions concerning the times scales of zircon
dissolution, we note that literature data on Zr diffusion in synthetic melts (Fig. 5) vary over

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more than 5 orders of magnitude. Despite this diversity, Zhang and Xu (2016) have proposed 382 383 a predictive model of Zr diffusivity as a function of the melt composition and water contents (but not taking into account halogen and CO₂ contents). Our experimentally measured Zr 384 diffusivity has been compared to equation 9 of Zhang and Xu (2016) for our studied melt 385 composition and experimental conditions (Supplementary Material) as well as to the 386 measured and calculated values from the other experimental works (Fig. 6). We note that our 387 measured Zr diffusivity in natural tholeiitic basalt is comparable to those of synthetic 388 haplobasalt (LaTourrette et al., 1996) and synthetic basalt (Holycross & Watson, 2016), close 389 to the line 1:1 on Figure 6, suggesting a good fit between the experiments for dry basaltic 390 391 systems and the theoretical model for the basaltic systems. Additionally, other experimental data (except for those of Koepke & Behrens, 2001) broadly spread along the line 1:1. We thus 392 conclude that the model of Zhang and Xu (2016) may be used to predict Zr diffusivity in 393 394 volatile-poor natural basaltic melts such as those studied here.

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IMPLICATIONS

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Our experimental data on zircon dissolution and solubility in a natural basaltic system shed light on the presence of zircon in terrestrial and extraterrestrial mafic to ultramafic magmas and rocks. First of all, we note that predicted survival times for zircon in mafic/ultramafic systems are very short compared to typical timescales for magma transfer from the mantle (e.g. 10^{-4} to 10^2 years, as compiled by Turner & Costa, 2007: **Fig. 7**). This suggests that most zircon megacrysts will be dissolved, even for the extreme case of 1 cm zircon crystals (such as Mud Tank) that only require 11 years to disappear.

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To explain the presence of zircon in tholeiitic basaltic melts at upper mantle 405 temperatures of 1300°C, Zr concentrations in melts have to reach 20,000 - 30,000 ppm 406 (Table 1). Thus, zircon crystallization directly from basaltic melt with common Zr 407 concentration of 10s to 100s ppm is virtually impossible. The presence of zircon in mafic and 408 ultramafic rocks may thus be related to some other processes that led to Zr enrichment. Such 409 processes include partial melting of hydrated peridotite (Borisova et al., 2017; Borisova et al., 410 411 2020), felsic lithosphere (e.g., continental crust and oceanic plagiogranite) and/or the felsic crustal involvement/recycling or zircon sealing (Belousova et al., 2015; Bea et al., 2018; 412 2020). 413

414 Alternatively, formation mechanisms of zircon may be related to lower temperature processes that include high degree of fractional crystallization in closed systems (e.g., Borisov 415 & Aranovich. 2019). total zircon dissolution and reprecipitation (Bea et al., 2001) and/or a 416 contribution of metasomatic Si-F-rich fluid (e.g., Louvel et al., 2013). It is also possible that 417 the final differentiates of metasomatised mafic/ultramafic magmas in the mantle, with 418 "special" peralkaline chemistry, and involving fluorine can lead to "pegmatitic" zircon 419 megacryst growth. Zircon solubility strongly depends on temperature, thus relatively cold 420 lithospheric roots with temperatures <1000°C are possible environments for these processes. 421

The presence of zircon in intercumulus residual melt from layered (ultra-) mafic intrusions and/or shallow magma chambers provides evidence in favor of these scenarios (**Fig. 8**). For example, according to the study of Bychkova et al. (2019a,b) closed-system fractional crystallization with convective mixing of magma in the chamber is capable of explaining zircon grains within the (ultra-)mafic layered series and the leucocratic granophyre rocks of the 1.8 Ga layered Kivakka intrusion (Karelia, Russia). We also note that zircon is present in granophyric Sandwich horizon of 56 Ma Skaergaard intrusion of Eastern

Greenland, as well as ultramafic pegmatitic segregations of its cumulus pile (Bindeman et al.
2008; Wotzlaw et al. 2012).

These examples of mafic/ultramafic layered intrusions indicate that similar interstitial 431 432 processes may take place in the mantle, perhaps helped by metasomatizing fluids (mantle metasomatism) and/or creation of localized felsic systems by partial melting or induced by 433 fluid-rock interaction. For example, isotopically homogeneous megacrysts such as Mud Tank 434 zircon (Valley, 1998; 2003; Gain et al., 2019) might be associated with such metasomatism 435 involving fluids rather than incompatible element-rich silicate melts. These zircon crystals 436 may have been formed at mantle conditions from some type of ultramafic melts/fluids. 437 438 However, the presence of these zircon megacrysts in carbonatite rocks is in contradiction to the recent experimental data by Gervasoni et al. (2016; 2017), suggesting that zircon is not 439 stable in a low-silica carbonatite melt and that zircon may not be a primary mineral in low-440 silica (carbonatite) melts. Kinetic constraints (i.e. slow reaction rates and incongruent 441 dissolution) may help to preserve metastable zircon, but this idea cannot be tested in the 442 absence of experimental data concerning zircon dissolution/precipitation rates and 443 mechanisms at relevant conditions. 444

Reconstructing the detailed formation history of Mud Tank zircon is beyond the scope 445 of this contribution, but it was clearly not in equilibrium with mafic-ultramafic melts at 446 magmatic temperatures. On the other hand, Mud Tank zircon has a strong mantle signature of 447 Hf isotope composition (the average ε_{Hf} at 731 Ma is +7.0 based on recent data of Gain et al., 448 2019 and CHUR 176 Hf/ 177 Hf_o = 0.282785 and 176 Lu/ 177 Hf_o = 0.0336 of Vervoort, 2014), 449 despite elemental and isotopic diffusion that are extremely sluggish (Cherniak, 2010) and 450 451 unable to lead to internal homogenization in the presence of melts or fluid (e.g., Bea et al., 2018; Bindeman et al., 2018). Thus, it appears likely that these zircon megacrysts are related 452 to mantle metasomatism with little or no crustal contribution, in agreement with conclusions 453

of Currie et al. (1992) concerning the origin of the Mud Tank Carbonatite complex as a whole
and detailed geochemical study of Mud Tank zircon crystals and the zircon-hosted inclusions
(Gain et al., 2019).

457 It should be noted also that the primitive mantle-normalized pattern of the primary carbonatite melts has no Zr and Hf anomalies (Walter et al., 2008) compared to the well-458 known strong Zr and Hf depletions in composition of the carbonatite rock and glasses from 459 the oceanic settings (e.g., Hauri et al., 1993). This fact implies that a deep magmatic process 460 (e.g., liquid immiscibility or/and fractional crystallization of a mineral phase) might have been 461 responsible for the formation of the strong negative Zr and Hf anomalies at high pressures 462 (perhaps, at ~9 GPa), due to differentiation of the primary carbonatite melts. Perhaps, zircon, 463 reidite or other high-pressure Zr-rich mineral phase (e.g., Timms et al., 2017) might be such 464 phase responsible for the Zr and Hf depletions and might be formed from the carbonatite 465 melts at deep asthenospheric conditions (> 1.0 GPa). However, zircon stability and solubility 466 have never been investigated experimentally yet at these high- to ultrahigh-pressure 467 conditions. 468

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CONCLUSIONS

471 1) Our data confirm high solubility of zircon in basalt of 20,000 – 30,000 ppm Zr, and
472 establish very fast congruent dissolution of zircon in natural basaltic melt at pressures of 0.2
473 to 0.7 GPa and a temperature of 1300°C.

474 2) We have calculated timescales of zircon survival in natural mafic liquids of tholeiitic basalt 475 composition (M = 3.3; G = 2.5; B = 0.15). For example, spherical zircon of 1 cm in diameter 476 will be completely dissolved at 1300°C and 0.5 GPa in tholeiitic basaltic liquid in ~11 years,

477 100 microns zircon in ~10 hours, a zircon sphere of 50 microns in ~3 hours and a 10 micron
478 sphere in ~10 minutes.

3) Zircon in natural ultramafic (carbonatite) and mafic (haplobasaltic) melts dissolves incongruently resulting in formation of a rim of baddeleyite microcrystals in association with SiO₂-rich melt. Incongruent dissolution of zircon at low pressures (< 0.2 GPa for natural basaltic melts) hampers the bulk zircon dissolution because of the formation of a baddeleyite halo associated with viscous SiO₂-rich melt. The estimated rate of rim formation (~0.9 μ m/min) may be used as a kinetic indicator to calculate approximate timescales of the zircon megacryst transport to the surface.

486 4) The new experimental data suggest fast zircon transfer to the surface during magma 487 generation and transport lasting hours to days. Formation and survival of zircon in the 488 lithosphere and asthenosphere, requires special conditions involving fluids and intercumulus 489 melts or/and fluids tracking geodynamic and geochemical conditions of the terrestrial mantle-490 crust system.

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726 Figure 1. (A) Back-scattered electron image of Z1 sample, demonstrating congruent dissolution of zircon (Zrn) in natural basaltic melt at 0.5 GPa. (B,C) Back-scattered electron 727 image of Z2 sample illustrating incongruent zircon dissolution in natural basaltic melt. A 728 reaction with basaltic melt at 0.1 MPa causes zircon replacement by baddeleyite and SiO₂-rich 729 melt. (D,E) Back-scattered electron image of Z3 sample demonstrating incongruent zircon 730 dissolution in natural basaltic melt. A reaction with basaltic melt at 0.1 MPa causes zircon 731 replacement by baddelevite (Bdy) and liberation of SiO₂-rich melt (L_{SiO2}). (F) Z4 sample: the 732 bulk zircon dissolution in natural basaltic melt at 0.7 GPa according to the congruent 733 mechanism. (G) Back-scattered electron image of Z6 sample illustrating incongruent zircon 734 735 dissolution in haplobasaltic melt. A reaction with the melt at 0.7 GPa causes zircon replacement by baddelevite and liberation of SiO₂-rich melt. (H) Back-scattered electron 736

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image of Z7 sample illustrating incongruent zircon dissolution in haplobasaltic melt. A reaction with the melt at 0.7 GPa results in zircon replacement by baddeleyite and SiO₂-rich melt (L_{SiO2}). (I) Back-scattered electron image of Z10 sample, demonstrating congruent dissolution of zircon (Zrn) in natural basaltic melt at 0.2 GPa.



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Figure 2(a) Principal schema of assemblage of piston cylinder applied at BGI (Germany).



745 Figure 2(b) Principal schema of assemblage of piston cylinder applied at KIEM (Russia).

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Figure 3. (A) The measured Zr contents versus distance (in μ m) from the zircon crystal in the Z1 sample (0.5 GPa, 1300°C, 5h, Table 1). **(B)** The corrected Zr profile in the Z1 sample as the function of erf⁻¹ (1-C_x/C_o) versus distance (in μ m) from the zircon crystal, suggesting zircon dissolution to be controlled by Zr diffusion in the basaltic melt. The uncertainty of the Zr concentrations (in ppm) are in the limit of 5 % RSD (relative standard deviation).

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Figure 4. Pressure versus run duration diagram of the composition of volatile-poor experimental samples after the runs on Mud Tank zircon-natural MORB-type basaltic melt pairs vs. the run duration. The experiments at 1250°C to 1300°C used different pressureloading techniques. BAS – homogeneous basaltic glass; Zrn + BAS – zircon with the reacted basaltic glass; Zrn + Bdy + BAS – zircon, baddeleyite with associated SiO₂-rich glass and the reactional basaltic glass as the result of the reaction.



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Figure 5. All available and new (this work) experimental data on Zr diffusivity (D) in dry and 763 hydrous silicate melts (in log(D), D in cm^2/s) vs. temperature (10000/T in K⁻¹). The (haplo-) 764 basaltic systems are represented by data of (1996 LaT) – (LaTourette et al., 1996), (2016HW) 765 - (Holycross & Watson, 2016) and this work. The other systems, such as (1983HW) 766 representing data of (Harrison & Watson, 1983), (1998NK) – (Nakamura & Kushiro, 1998), 767 (1999M) - (Mungall et al., 1999), (2001KB) - (Koepke & Behrens, 2001), (2002B) - (Baker 768 et al., 2002), (2016ZX) – (Zhang & Xu, 2016), (2018HW) – (Holycross & Watson, 2018) are 769 770 dry to hydrous intermediate to felsic systems.



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Figure 6. All available and new data on the measured Zr diffusivity $(log(D), D in cm^2/s)$ in 774 775 dry and hydrous silicate melts versus calculated Zr diffusivity (log(D), D in cm²/s) after Zhang & Xu (2016) (calculated on hydrous basis). The (haplo-) basaltic systems are 776 represented by data of (1996 LaT) - (LaTourette et al., 1996), (2016HW) - (Holycross & 777 Watson, 2016) and this work. The other systems, such as (1983HW) representing data of 778 779 (Harrison & Watson, 1983), (1998NK) - (Nakamura & Kushiro, 1998), (1999M) - (Mungall et al., 1999), (2001KB) - (Koepke & Behrens, 2001), (2002B) - (Baker et al., 2002), 780 (2016ZX) - (Zhang & Xu, 2016), (2018HW) - (Holycross & Watson, 2018) are dry to 781 hydrous intermediate to felsic systems. 782





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Figure 7. The calculated time of zircon dissolution in tholeiitic basaltic melt at 1300°C 786 according to the kinetic model of Bindeman & Melnik (2016) versus zircon size (in µm). The 787 shaded light grey field corresponds to the dissolution timescales from hours to years 788 789 according to the typical sizes of zircon crystals and megacrysts in carbonatites and kimberlites. The dark grey bar is a range of typical timescales for the magma transfer from 790 mantle (from 10^{-4} to 10^{2} years) according to Turner and Costa (2007), suggesting high 791 792 percentage of the zircon crystals and megacrysts to be dissolved upon their transport to the 793 surface.

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zircon size in µm

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Figure 8. H, m - height in meters versus Zr in ppm contents in rocks of the Kivakka maficultramafic layered intrusion, Northern Karelia, Russia. 'Zrn' indicates zircon-bearing horizons
of (ultra-) mafic rocks. The data are after Bychkova et al. (2019a,b). The main mechanism of
zircon crystallization in (ultra-) mafic systems is residual intercumulus melt crystallization.

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805	Table 1. Pressure-temperature-redox conditions of experiments on zircon dissolution in
806	natural basaltic and synthetic haplobasaltic melt

Sample	Techniques*	Conditions	Duration	Type of	Observed	Interface
number		(pressure,	(hours)	basalt & initial	final phases	melt C _o content
		temperature, redox conditions)		mass of Zrn to basalt to water ^{**}	(Bdy zone thickness in μm)	Zr (ppm) ^{***}
Z1	BGI, PC	1300°C, 0.5 GPa	5h	Zrn to	Partially	20,840 ±
				BAS 0.075	dissolved zircon (PDZ) Zrn, L _{bas}	348
Z2	IRAP, G	1300°C, 0.1	1h	Zrn to	PDZ,	N.A.
		MPa, FMQ	15min	BAS	Bdy, L _{bas}	
				0.086	(80 ± 20 μm)	
Z3	IRAP, G	1300°C, 0.1	15 min	Zrn to	PDZ,	N.A.
		MPa, FMQ		BAS 0.142	Bdy, L _{bas} (10 μm)	
Z4	KIEM, PC	1300°C, 0.7 GPa	5h	Zrn to BAS	L _{bas}	-
				0.037		
Z6	KIEM, PC	1300°C, 0.7 GPa	5h	Zrn to AnDi	PDZ, Bdy, L _{bas}	N.A.
				0.157	(100 ± 30 μm)	
Z7	KIEM, PC	1300°C, 0.7 GPa	5h	Zrn to	PDZ,	N.A.
				AnDi	Bdy, L_{bas}	
				0.097;	(10 µm)	
				$H_2O = 7.0 \text{ wt\%}$		
Z10	KIEM,	1250°C, 0.2 GPa	5h	Zrn to	PDZ,	23,438 ±
	IHPV			BAS	L _{bas}	554
				0.115		

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* BGI - Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI),
Bayreuth, Germany; IRAP - Institut de Recherche en Astrophysique et Planétologie (IRAP),
Toulouse, France; KIEM - Korzhinskii Institute of Experimental Mineralogy, Chernogolovka,
Russia. PS – piston cylinder; G - gas-mixing furnace at one atmosphere pressure; IHPV –
internally heated pressure vessel.

** - BAS – natural basaltic glass; AnDi – haplobasaltic glass; FMQ- fayalite-magnetite-quartz
 redox buffer; PDZ – partially dissolved zircon; Bdy – baddeleyite associated with SiO₂-rich
 glass; L_{bas} – basaltic glass.

^{***} - Interface melt concentration in ppm (C_o) (corresponding to zircon solubility) calculated taking into account the secondary fluorescence effect only for experiments with partially dissolved zircon (PDZ) and linear interface between the zircon and glass. N.A. – not analyzed. Standard deviations are expressed for Z1 and Z10 based on the first 4 to 6 measurements nearby zircon crystal.