Zircon survival in shallow asthenosphere and deep lithosphere 

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ABSTRACT

Zircon (ZrSiO₄) is the most frequently used geochronometer of terrestrial and extraterrestrial processes. To shed light on question of zircon survival in the Earth’s shallow asthenosphere, high-temperature experiments of zircon dissolution in natural mid-ocean ridge basaltic (MORB) and synthetic haplobasaltic melts have been performed at temperatures of 1250–1300 °C and pressures from 0.1 MPa to 0.7 GPa. Zirconium measurements were made in situ by electron probe microanalyses (EPMA) at high current. Taking into account secondary fluorescence effects in zircon-glass pairs during EPMA, a zirconium diffusion coefficient of 2.87E-08 cm²/s was determined at 1300 °C and 0.5 GPa. When applied to the question 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 reaction with basaltic melt at pressures of 0.2–0.7 GPa. We observed incongruent (to crystal ZrO₂ and SiO₂ in melt) dissolution of zircon in natural mid-ocean ridge the basaltic melt at low pressures <0.2 GPa and in the haplobasaltic melt at 0.7 GPa pressure. Our 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 meaning of the zircon-based ages estimated from these minerals. The origin of zircon in shallow (ultra-) mafic chambers is likely related to the crystallization of intercumulus liquid. Large zircon megacrysts in kimberlites, peridotites, alkali basalts, and carbonatite magmas suggest fast transport and short interaction durations between zircon and melt. 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.

Keywords: Zircon, mineral dissolution, asthenosphere, lithosphere, basaltic melt, experiment

INTRODUCTION

Zircon is the most frequently used mineral for dating terrestrial and extraterrestrial rocks (e.g., Valley et al. 2014a) using a variety of isotopes in the U-Th-Pb system (Schmitt et al. 2014). Furthermore, zircon has high closure temperatures for a wide range of elements (and their 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) while O and Hf isotopic compositions and trace element contents are commonly employed to provide insight into the source of zircon crystals and their magmatic or hydrothermal protoliths (e.g., Iizuka et al. 2015; Valley et al. 2014a).

The use of zircon as a petrogenetic tool requires knowledge of the stability field of this mineral, in addition to quantification of solubility limits and crystallization/dissolution rates at relevant P-T conditions and fields of melt composition. Experimental work to determine zircon solubility, dissolution rates and diffusion coefficients of Zr in silicate liquids began in the early 1980’s, but was concentrated on felsic and intermediate compositions of variable H₂O contents at high temperatures and pressures (Watson 1982; Harrison and Watson 1983; Ellison and Hess 1986; Baker and Watson 1988; Baker et al. 2002; LaTourrette et al. 1996; Nakamura and Kushiro 1998; Mungall et al. 1999; Koepke and Behrens 2001; Lundstrom 2003; Watson et al. 2006; Rubatto and Hermann 2007; Behrens and Hahn 2009; Burnham and Berry 2012; Boehnke et al. 2013; Zhang and Xu 2016; Holycross and Watson 2016, 2018; Shao et al. 2018; Borisov and Aranovich 2019). In contrast, there are few experimental studies on basaltic systems, an exception be-
ing the study of Dickinson and Hess (1982) on lunar systems, and more recent studies of synthetic terrestrial basaltic melts (Boehnke et al. 2013; Holycross and Watson 2016; Shao et al. 2018; Borisov and Aranovich 2019) and dunes (Anfilogov et al. 2015).

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

However, current experimental data in mafic systems are sparse and sometimes contradictory, and generally insufficient to distinguish between these different formation scenarios. For example, reaction with fluids, silicate melts and/or other minerals (e.g., olivine, chromite), may lead to modifications of the primary zircon elemental and isotope signatures through diffusion or dissolution-precipitation (Geisler et al. 2007; Bea et al. 2018), but there are no experimental data on the survival of zircon in silicate melts, e.g., Harrison and Watson 1983; Gervasoni et al. 2016 and references therein, Supplementary Material) glassy tholeiitic basalt (number 3786/3) from Knapovich ridge of the Mid-Atlantic Ridge sampled by dredging during 38th Research Vessel Academik Mstislav Keldysh expedition (Suschevskaya et al. 2000). The MORB glass (that contains no traces of olivine and/or chromite phenocrysts) has been crushed to powder (<100 µm grain size).

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

### 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 crystall 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 chip was placed at the bottom, the upper part of the capsule being filled with basaltic glass powder. Starting materials were weighed carefully to control zircon/melt ratio. Distilled water was added in one experiment (Z7) to study the effect of hydrous basalt (Table 1). This water was introduced with a micro-syringe to the basaltic powder when the sample was already loaded into the capsule. Because of the fast kinetics of zircon dissolution at high temperatures and to avoid the complete dissolution of zircon crystal, run durations had to be shorter than the time necessary to reach oxygen fugacity equilibrium with piston-cylinder double-capsule techniques using mineral buffers (48 h; Matjuschkin et al. 2015). The redox conditions in our experiments are thus controlled by the initial Fe2+/Fe3+ ratios of the natural samples used as starting materials (MORB glass), possibly affected by partial exchange of Al2O3 with pressure media (in piston-cylinder experiments). The redox conditions established were estimated to range from FMQ(+1.5) to FMQ(+3.6) (where values indicate logarithmic units compared to the FMQ, fayalite-magnetite-quartz buffer) (Borisov et al. 2020). These redox conditions were estimated from

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

| Sample number | Techniques | Conditions (pressure, temperature, redox conditions) | Duration (hours) | Type of basalt and initial mass of Zrn to basalt to water | Observed final phases (Bdy zone thickness in µm) | Interface melt Ç content Zr (ppm) |
|---------------|------------|------------------------------------------------------|------------------|----------------------------------------------------------|------------------------------------------------|----------------------|
| Z1            | BGI, PC    | 1300 °C, 0.5 GPa                                       | 5h               | Zrn to BAS 0.075                                        | Partially dissolved zircon (PDZ) Zrn, bas |
| Z2            | IRAP, G    | 1300 °C, 0.1 MPa, FMQ                                  | 1h 15min         | Zrn to BAS 0.086                                        | PDZ, Bdy, Lm (80 ± 20 µm) | N.A.                |
| Z3            | IRAP, G    | 1300 °C, 0.1 MPa, FMQ                                  | 15 min           | Zrn to BAS 0.142                                        | PDZ, Bdy, Lm (10 µm)  | N.A.                |
| Z4            | KIEM, PC   | 1300 °C, 0.7 GPa                                       | 5h               | Zrn to BAS 0.037                                        | -                                             | -                    |
| Z6            | KIEM, PC   | 1300 °C, 0.7 GPa                                       | 5h               | Zrn to Andi 0.157                                       | PDZ, Bdy, Lm (100 ± 30 µm) | N.A.                |
| Z7            | KIEM, PC   | 1300 °C, 0.7 GPa                                       | 5h               | Zrn to Andi 0.097; H2O = 7.0 wt%                        | PDZ, Bdy, Lm (10 µm)  | N.A.                |
| Z10           | KIEM, HVP  | 1250 °C, 0.2 GPa                                       | 5h               | Zrn to BAS 0.155                                        | PDZ (n.a.)                                      | 2343 ± 554           |

* 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; PC = piston cylinder; G = gas-mixing furnace at one atmosphere pressure; HVP = 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; Lm = basaltic glass.
* Interface melt concentration in parts per million (ppm) (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 four to six measurements nearby zircon crystal.
Figure 1. (a) Backscattered electron image of Z1 sample, demonstrating congruent dissolution of zircon (Zrn) in natural basaltic melt at 0.5 GPa. (b and c) Backscattered electron image of Z2 sample illustrating incongruent zircon dissolution in natural basaltic melt. A reaction with basaltic melt at 0.1 MPa causes zircon replacement by baddeleyite and SiO₂-rich melt. (d and e) Backscattered electron image of Z3 sample demonstrating incongruent zircon dissolution in natural basaltic melt. A reaction with basaltic melt at 0.1 MPa causes zircon replacement by baddeleyite (Bdy) and liberation of SiO₂-rich melt (L_{SiO₂}). (f) Z4 sample: the bulk zircon dissolution in natural basaltic melt at 0.7 GPa according to the congruent mechanism. (g) Backscattered electron image of Z6 sample illustrating incongruent zircon dissolution in haplobasaltic melt. A reaction with the melt at 0.7 GPa causes zircon replacement by baddeleyite and liberation of SiO₂-rich melt. (h) Backscattered electron 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) Backscattered electron image of Z10 sample, demonstrating congruent dissolution of zircon (Zrn) in natural basaltic melt at 0.2 GPa.
the olivine-chromite assemblages using the equations of Ballhaus et al. (1991) and from the mole fraction of ferric iron Fe³⁺ obtained in the basaltic glass by XANES (X-ray absorption near edge structure).

Two piston-cylinder systems were used in our experiments. The experiment (Z1) used the Max Voggemeier end-loaded Boyd-England piston-cylinder apparatus at the Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI), Bayreuth, Germany. Talc cells 3/4 inch in diameter with Pyrex sleeves were used. A tapered graphite furnace was inserted in each cell (Fig. 2a). Alumina (Al₂O₃) spacers were used as pressure-transmitting medium. An Al₆O₉P₃O₅ capsule loaded with starting materials was set in the central part of the assembly. A 20% pressure correction was applied for the friction between the talc cell and pressure vessel. A molybdenum disulfide (MoS₂) lubricant was introduced to minimize the friction. The temperature in the upper part of the capsules was controlled by a EUROTERM (2404) controller via either W₁₇Re₅/W₁₇Re₅ (type D) or Pt₁₀Rh₇/Pt₁₃Rh₃ (type B) thermocouple accurate to ±0.5 °C. The uncertainty on pressure was estimated to be ±0.04 GPa. The sample was compressed to 0.5 GPa during a period of 20 min and then 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 quenched by switching off the power supply. Decompression then lasted 20 min to 2 h. The quench rate to room temperature was up to 80 °C/min.

Experiments (Z4, Z6, Z7) used the end-loaded Boyd-England piston-cylinder apparatus at the Korchinskii Institute of Experimental Mineralogy, Chernogolovka, Russia. Standard talc-Pyrex cells ⅜ inch in diameter, equipped with tube graphite heaters and inserts made of MgO ceramics were used as pressure-transmitting medium (Fig. 2b). The pressure at elevated temperatures was calibrated against two reactions of brucite = periclase + H₂O and albite = jadeite + quartz equilibria. A pressure correction (12%) was introduced for the friction between the cell and hard-alloy vessel. To minimize friction, a Pb foil and molybdenum disulfide (MoS₂) lubricant were used. Al₂O₃P₃O₅ capsules with starting mixtures were mounted in the central parts of the cells. The temperature in the upper part of the capsule was controlled to ±1 °C using a MINITHERM controller via a W₁₇Re₅/W₁₇Re₅ thermocouple insulated by mullite and Al₂O₃ without pressure correction. For the Pyrex-bearing assemblies, the sample was heated to 550–600 °C at low confining pressure (0.15–0.2 GPa) for a few minutes to soften the Pyrex glass, then both temperature and pressure were increased simultaneously up to the desired run conditions. The uncertainty on pressure was estimated to be ±0.04 GPa. Samples were maintained at run conditions for desired durations then quenched by switching off the power supply. The quench rate was 100–200 °C/min.

Experiments Z2–Z3 used a vertical gas-mixing furnace at one atmosphere pressure, 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 Fayalite-Magnetite-Quartz (FMQ) buffer. The closed, but unsealed, Au₈₀Pd₂₀ capsules loaded with starting materials were held on a Pt wire (0.3 mm in diameter) and introduced into the hot spot of the gas-mixing furnace. Samples were rapidly quenched (~1000 °C/s) by dropping the sample into the cold zone of the furnace, in the CO-CO₂ atmosphere, by melting a thin Pt suspension wire with an electric shortcircuit. After evacuation of the CO, the samples were recovered and mounted in epoxy and polished with SiC papers.

For the experiment Z10, we used an internally heated gas pressure vessel at the Korchinskii Institute of Experimental Mineralogy, Chernogolovka, Russia. The pressure in the system was created by pure Ar gas. The system was heated by a furnace with two windings (to minimize the thermal gradient). The temperature was controlled by a TRM-101 OVEN controller through two S-type (Pt90Rh10 vs. Pt100) thermocouples. The 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 quenched by switching off the furnace. The pressure during the quench was maintained 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 papers and diamond pastes.

**Microanalytical methods**

To study the trace element profile of Zr in the reaction zones we used electron probe microanalysis ( Cameca SX-Five). Major element analyses of minerals and glasses (Fig. 3, Supplementary Material) and sample imaging were made at the Géosciences Environnement Toulouse (GET, Toulouse, France) laboratory and at the Centre de Microcaractérisation Raimond Castraing (Toulouse, France). The main experimental phases (baddeleyite, zircon, and glasses) in the samples were identified by the EDS technique using a scanning electron microscope (SEM) JEOL JSM-6360 LV with energy-dispersive X-ray spectroscopy (EDS) in GET, Toulouse, France.
Correcting for secondary fluorescence effects measured between zircon and the same (MORB) basaltic glass (Borisova et al. 2018). The corrected profile taking into consideration of the effect was obtained by linear interpolation of the secondary fluorescence effect with the function “numpy.interp” of Python language (ver. 1.17), (e.g., Oliphant 2006) and by simple subtraction from the measured Zr concentration. The mathematic transformation of the corrected Zr contents in the profiles to the error function \(\text{erf}(\cdot)\) correlates linearly with the distance from the interface with a slope of 0.0022 (Fig. 3, Supplementary Material1), suggesting diffusional control of the Zr distribution due to zircon dissolution in the basaltic melt according to the criterion given by Harrison and Watson (1983). Unfortunately, there is no way to extract the diffusion coefficient values from experiments where zircon dissolves incongruently, compared to congruent dissolution in natural basaltic system at ≥0.2 GPa.

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 \(D_{Zr} = 2.87E-08\ \text{cm}^2/\text{s}\) at 1300 °C and 0.5 GPa (Supplementary Material1). 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).

RESULTS

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.

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

A summary of the phase relations associated with zircon dissolution at 1250 to 1300 °C in (haplo-) basaltic melts (Fig. 4) shows that at 0.1 MPa, zircon dissolves incongruently to form baddeleyite (ZrO2) and a SiO2-rich melt. Baddeleyite is also formed at 0.7 GPa in the synthetic haplobasaltic (low \(d_{\text{fO2}}\)) melt, but no baddeleyite precipitation is observed in the pressure range 0.2 to 0.7 GPa in natural terrestrial tholeiitic basalt melt. The favorable experiment Z1 has been used to extract the diffusion coefficient of Zr, as described above, providing a value of \(D_{Zr} = 2.87E-08\ \text{cm}^2/\text{s}\) at 1300 °C and 0.5 GPa (Supplementary Material1). For the question of the interface concentration of Zr, zircon solubility is higher at 0.2 GPa pressure (Z10 run, Table 1) compared to that at 0.5 GPa (Z1 run), suggesting possible stabilization of zircon at high pressures. For modeling purposes, a value of 20,840 ± 104 ppm Zr was used (corresponding to zircon solubility in MORB melt at 0.5 GPa and 1300 °C), and combined with the initial Zr concentration of 94.3 ppm measured in the starting MORB glass (Borisova et al. 2020).

DISCUSSION

Zircon vs. baddeleyite stability during dissolution

In general terms the relative stability of zircon and baddeleyite in terrestrial and extraterrestrial systems can be rationalized in terms of the silica activity of the silicate melt associated with the reaction:
**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.**

**Zr diffusivity and zircon solubility in silicate melts**

Most existing models considering zircon solubility and dissolution are based on felsic and intermediate and synthetic systems (zircon in felsic and intermediate silicate liquids, e.g., Harrison and Watson 1983; Boehnke et al. 2013; Zhang and Xu 2016; and references therein). In those cases, zircon is apparently less soluble and stable compared to the natural mafic and ultramafic systems. The main factors controlling solubility of zircon in silicate melts are temperature and the melt composition expressed in terms of ratio of nonbridging O atoms per tetrahedrally coordinated cations (NBO/T), which is a simple measure of silicate melt structure based on the ratio between network formers and network modifiers. For example, the factors such as M [([Na + K + 2 Ca]/(Al-Si)) (all in cation ratio)], G (where numerator (3 Al, O, Si) represents the network formers, while the denominator (Na, O + K, O + CaO + MgO + FeO) represent the network modifiers of the melt) or B expressed in oxide mole fractions in the melts [0.14(X_{SiO2}/X_{SiO2}) + 1.3(X_{CaO}/X_{SiO2}) + 1.5(X_{Na2O}/X_{SiO2}) - 4.5(X_{TiO2}/X_{SiO2}) - 2.7(X_{Al2O3}/X_{SiO2})^2 + (X_{MgO}/X_{SiO2})^2 - 3.7(X_{Fe2O3}/X_{SiO2})^2 + 75(X_{K2O}/X_{SiO2})] as well as the melt water contents have been proposed as factors controlling solubility of zircon in silicate melts (e.g., Harrison and Watson 1983; Gervasoni et al. 2016, 2017; Borisov and Aranovich 2019 and references therein). It is expected that the synthetic (Fe- and Ti-absent) and natural Fe- and Ti-containing basaltic melts would not be similar in respect to zircon solubility. Our natural basaltic liquid (8.2 wt% of MgO, M = 3.3; G = 2.5, B = 0.15) provides a theoretical zircon solubility of 23 078 ppm (or 2.3 wt% of Zr) according to model of Borisov and Aranovich (2019), which is in a very good accordance with the experimentally measured solubility of 20 840 ± 104 ppm. The theoretical solubility of zircon in MORB melts is thus comparable to experimental ones (2.2–3.6 wt% of Zr) obtained by Boehnke et al. (2013) for basaltic liquids at 1225°C and 1 GPa. The factors such as M, G, and B are indicators of zircon solubility in silicate melts but may be also used for prediction of Zr diffusivity, although the most efficient factor controlling the elemental diffusivity in silicate melts besides temperature remains the melt viscosity controlled primarily by the melt SiO2 content (e.g., Mungall 2002).

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/s) and the kinetic model of Bindeman and Melnik (2016), it is predicted that a sphere of zircon 100 μm in diameter will survive for ~10 h, a sphere of 50 μm diameter for ~3 h and a grain 10 μm in diameter for only ~10 min. At the other extreme, the dissolution of a 1 cm crystal such as Mud Tank zircon, would require ~96 000 h (~11 yr).

However, before reaching firm conclusions concerning the timescales of zircon dissolution, we note that literature data on Zr diffusion in synthetic melts (Fig. 5) vary over more than 5 orders
of magnitude. Despite this diversity, Zhang and Xu (2016) have proposed 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 diffusivity has been compared to Equation 9 of Zhang and Xu (2016) for our studied melt composition and experimental conditions (Supplementary Material1) as well as to the measured and calculated values from the other experimental works (Fig. 6). We note that our measured Zr diffusivity in natural tholeiitic basalt is comparable to those of synthetic haplobasalt (LaTourrette et al. 1996) and synthetic basalt (Holycross and Watson 2016), close to the line 1:1 on Figure 6, suggesting a good fit between the experiments for dry basaltic systems and the theoretical model for the basaltic systems. Additionally, other experimental data (except for those of Koepke and Behrens 2001) broadly spread along the line 1:1. We thus conclude that the model of Zhang and Xu (2016) may be used to predict Zr diffusivity in volatile-poor natural basaltic melts such as those studied here.

**Implications**

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 and 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 yr to disappear.

To explain the presence of zircon in tholeiitic basaltic melts at upper mantle temperatures of 1300 °C, Zr concentrations in melts have to reach 20000–30000 ppm (Table 1). Thus, zircon crystallization directly from basaltic melt with common Zr concentration of tens to hundreds of parts per million is virtually impossible. The presence of zircon in mafic and ultramafic rocks may thus be related to some other processes that led to Zr enrichment. Such processes include partial melting of hydrated peridotite (Borisova et al. 2017, 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, 2020).

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 and Aranovich 2019), total zircon dissolution and reprecipitation (Bea et al. 2001) and/or a contribution of metasomatic Si-F-rich fluid (e.g., Louvel et al. 2013). It is also possible that the final differentiates of metasomatized mafic/ultramafic magmas in the mantle, with “special” peralkaline chemistry, and involving fluorine can lead to “pegmatitic” zircon megacryst growth. Zircon solubility strongly depends on temperature, thus relatively

**Figure 5.** All available and new (this work) experimental data on Zr diffusivity (D) in dry and hydrous silicate melts [in log(D), D in cm²/s] vs. temperature (10000°T in K⁻¹). The (haplo-) basaltic systems are represented by data of 1996 LaT = LaTourrette et al. 1996, 2016HW = Holycross and Watson 2016, and this work. The other systems, such as 1983HW representing data of Harrison and Watson 1983, 1998NK = Nakamura and Kushiro 1998, 1999M = Mungall et al. 1999, 2001KB = Koepke and Behrens 2001, 2002B = Baker et al. 2002, 2016ZX = Zhang and Xu 2016, 2018HW = Holycross and Watson 2018. This work is dry to hydrous intermediate to felsic systems.

**Figure 6.** All available and new data on the measured Zr diffusivity [log(D), D in cm²/s] in dry and hydrous silicate melts vs. calculated Zr diffusivity [log(D), D in cm²/s] after Zhang and Xu (2016) (calculated on hydrous basis). The (haplo-) basaltic systems are represented by data of 1996 LaT = LaTourrette et al. 1996, 2016HW = Holycross and Watson 2016, and this work. The other systems, such as 1983HW representing data of Harrison and Watson 1983, 1998NK = Nakamura and Kushiro 1998, 1999M = Mungall et al. 1999, 2001KB = Koepke and Behrens 2001, 2002B = Baker et al. 2002, 2016ZX = Zhang and Xu 2016, 2018HW = Holycross and Watson 2018 are dry to hydrous intermediate to felsic systems.

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cold lithospheric roots with temperatures <1000 °C are possible environments for these processes.

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, 2019b), 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 the Granophyre 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 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 fluid-rock interaction. For example, isotopically homogeneous megacrysts such as Mud Tank zircon (Valley 2003; Gain et al. 2019) might be associated with such metasomatism involving fluids rather than incompatible element-rich silicate melts. These zircon crystals may have been formed at mantle conditions from some type of ultramafic melts/fluids. However, the presence of these zircon megacrysts in carbonatite rocks is in contradiction to the recent experimental data by Geravasoni et al. (2016, 2017), suggesting that zircon is not stable in a low-silica carbonatite melt and that zircon may not be a primary mineral in low-silica (carbonatite) melts. Kinetic constraints (i.e., slow reaction rates and incongruent dissolution) may help to preserve metastable zircon, but this idea cannot be tested in the absence of experimental data concerning zircon dissolution/precipitation rates and mechanisms at relevant conditions.

Reconstructing the detailed formation history of Mud Tank zircon is beyond the scope of this contribution, but it was clearly not in equilibrium with mafic-ultramafic melts at magmatic temperatures. On the other hand, Mud Tank zircon has a strong mantle signature of Hf isotope composition (the average εHf at 731 Ma is +7.0 based on recent data of Gain et al. 2019 and CHUR 176Hf/177Hf = 0.282785 and 176Lu/177Hf = 0.0336 of Vervoort 2014), despite elemental and isotopic diffusion that are extremely sluggish (Cherniak 2010) and 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 to mantle metasomatism with little or no crustal contribution, in agreement with conclusions of Currie et al. (1992) concerning the origin of the Mud Tank Carbonatite complex as a whole and a detailed geochemical study of Mud Tank zircon crystals and the zircon-hosted inclusions (Gain et al. 2019).

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-known strong Zr and Hf depletions in composition of the carbonatite rock and glasses from the oceanic settings (e.g., Hauri et al. 1993). This fact implies that a deep magmatic process (e.g., liquid immiscibility or and fractional crystallization of a mineral phase) might have been responsible for the formation of the strong negative Zr and Hf anomalies at high pressures (perhaps, at ~9 GPa), due to differentiation of the primary carbonatite melts. Perhaps, zircon, reidite or another high-pressure Zr-rich mineral phase (e.g., Timms et al. 2017) might be such phase responsible for the Zr and Hf depletions and might be formed from the carbonatite melts at deep asthenospheric conditions (>1.0 GPa). However, zircon stability and solubility have never been investigated experimentally yet at these high- to ultrahigh-pressure conditions.
CONCLUDING REMARKS

(1) Our data confirm high solubility of zircon in basalt of 20000–30000 ppm Zr, and establish very fast congruent dissolution of zircon in natural basaltic melt at pressures of 0.2 to 0.7 GPa and a temperature of 1300 °C.

(2) We have calculated timescales of zircon survival in natural mafic liquids of tholeitic basalt composition (M = 3.3; G = 2.5; B = 0.15). For example, spherical zircon of 1 cm in diameter will be completely dissolved at 1300 °C and 0.5 GPa in tholeitic basaltic liquid in ~11 years, 100 μm zircon in ~10 h, a zircon sphere of 50 μm in ~3 h and a 10 μm sphere in ~10 min.

(3) Zircon in natural ultramafic (carbonatite) and mafic (hapol-basaltic) 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 µm/min) may be used as a kinetic indicator to calculate approximate timescales of the zircon megacryst transport to the surface.

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

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