Zircon survival in shallow asthenosphere and deep lithosphere

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Zircon (ZrSiO$_4$) 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 pressure 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 cm$^2$/sec has been 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 mantle pressures of 0.2 – 0.7 GPa. We observed incongruent (to crystal ZrO$_2$ and SiO$_2$ in melt) dissolution of zircon in natural mid-ocean ridge basaltic melt at low pressures < 0.2 GPa and in haplobasaltic melt at elevated 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 the composition of these minerals. The origin of zircon in shallow (ultra-) mafic chambers is likely related to crystallization of intercumulus liquid. Large size zircon megacrysts in kimberlites, peridotites, alkali basalts and carbonatite magmas suggest fast transport and short interaction 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.
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/and hydrothermal protoliths (e.g., Iizukaa 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 has concentrated on felsic and intermediate compositions of variable H₂O contents at high temperatures and pressures (Watson, 1982; Harrison & Watson, 1983; Ellison & Hess, 1986; Baker & Watson, 1988; Baker et al., 2002; LaTourrette et al., 1996; Nakamura & Kushiro, 1988; Mungall et al., 1999; Koepke & Behrens, 2001; Lungstrom 2003; Watson et al., 2006; Rubatto & Hermann, 2007; Behrens & Hahn, 2009; Burnham & Berry, 2012; Boehnke et al., 2013; Zhang & Xu, 2016; Holycross & Watson, 2016; 2018; Shao et al., 2018; Borisov & Aranovich, 2019). In contrast, there are few experimental studies on basaltic systems, an exception being the study of Dickinson & Hess (1982) on lunar systems, before more recent studies of synthetic terrestrial basaltic melts (Boehnke et al.,...
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 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, dolerites, 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,b; Bea et al., 2020 and references therein) as well as in basaltic meteorites (Ireland & Włoziak, 1992; Humayun et al., 2013, Valley et al., 2014b, Iizukaa et al., 2015; Bellucci et al., 2019). However, there is 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-lasting 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 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 and preservation of Pb-U-Th-O-Ti-REE signatures at high temperature-pressure-volatile content conditions in mafic and ultramafic systems. These gaps in knowledge prevent robust interpretation of the ages derived from zircon in terrestrial and extraterrestrial rocks.
In light of the fact that interaction of zircon with natural terrestrial basaltic liquid has never been studied experimentally, and with the overall aim of providing constraints for a general model of zircon stability in natural shallow asthenospheric melts of basaltic composition, an experimental program has been initiated to constrain the solubility limit and dissolution kinetics of zircon at high pressure and temperature in mafic systems. In this first contribution we present the results of interaction between natural Mud Tank zircon and natural and synthetic basaltic and haplobasaltic melts at 1250 - 1300°C at pressures from 0.1 MPa to 0.7 GPa.

METHODS

Starting materials

The zircon crystals used in this study are from the ~730 Ma Mud Tank carbonatites (Crohn and Moore, 1984; Gain et al., 2019) provided as crystals ~1cm in size by Sebastien Meffre (UTAS, Hobart, Australia). These crystals were first prepared as doubly polished ~1000 µm-thick sections, then made into smaller double-polished chips by slight pressing of the section. 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 tholeiitic basalt (number 3786/3) from Knipovich ridge of the Mid Atlantic Ridge sampled by dredging during 38th Research Vessel Adademic Mstislav Keldysh expedition (Sushchevskaya et al., 2000). The MORB glass (that contains no traces of olivine and/or chromite phenocrysts) has been crushed to powder (<100 µm glass size).

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).
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 Au$_{80}$Pd$_{20}$ 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$^{\text{MQ}}$ has been 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 fast kinetics of zircon dissolution at high 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 double-capsule techniques using mineral buffers (48 hours: Matjuschkin et al., 2015). The redox conditions in our kinetic experiments are thus considered to be controlled by the initial Fe$^{2+}$/Fe$^{3+}$ ratios of the natural samples used as starting materials (MORB glass), possibly affected by partial exchange of Al$_2$O$_3$ 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) (Borisova et al., 2020). These redox conditions were estimated from the olivine-chromite assemblages using equations of Ballhaus et al. (1991) and from mole fraction of ferric iron Fe$^{\text{III}}$ obtained by XANES (X-ray absorption near edge structure).
Two piston-cylinder systems have been used in our experiments. The experiment (Z1) used the Max Voggenreiter© 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 Au₈₀Pd₂₀ 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 W₅Re₉/W₂₅Re₇₅ (type D) or Pt₆Rh₉₄/Pt₃₀Rh₇₀ (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 minutes 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 minutes to 2 hours. 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 Korzhinskii Institute of Experimental Mineralogy, Chernogolovka, Russia. Standard talc-Pyrex cells 3/4 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. Au₈₀Pd₂₀ capsules with starting mixtures were mounted in the central parts of the cells. The temperature in the upper part of the
capsules was controlled to ±1°C using a MINITHERM controller via a W\textsubscript{95}Re\textsubscript{5}/W\textsubscript{80}Re\textsubscript{20} thermocouple insulated by mullite and Al\textsubscript{2}O\textsubscript{3} 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 in order 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 CO\textsubscript{2} corresponding to the fayalite-magnetite-quartz (FMQ) buffer. The closed, but unsealed, Au\textsubscript{80}Pd\textsubscript{20} 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-CO\textsubscript{2} atmosphere, by melting a thin Pt suspension wire with an electric shortcut. After evacuation of the CO, the samples were recovered and mounted in epoxy and polished with SiC sandpapers.

For the experiment Z10, we have used an internally heated gas pressure vessel at the Korzhinskii 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 set and measured by a TRM-101 OVEN controller through two S-type (Pt\textsubscript{90}Rh\textsubscript{10} vs Pt\textsubscript{100}) 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 sand papers and diamond pastes.

Microanalytical methods

To study the trace element profile of Zr in the reaction zones we have used electron probe microanalysis (CAMECA SX-Five). Major element analyses of minerals and glasses (Fig. 3, Supplementary Material) and the sample imaging were made at the Géosciences Environnement Toulouse (GET, Toulouse, France) laboratory and at the Centre de Microcaractérisation Raimond Castaing (Toulouse, France). The main experimental phases (baddeleyite, zircon and glasses) in the samples have been identified by EDS microprobe technique using a scanning electron microscope (SEM) JEOL JSM-6360 LV with energy-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 Centre Castaing, Toulouse, France. For the electron microprobe CAMECA SX Five, operating conditions were: an accelerating voltage 15 kV, currents of 20nA for the major elements depending on the resistance of the material under the electron beam, and 100 nA for the minor Zr. Focused (~2 µm) beam conditions were used for the major and trace (Cr, Zr) element analyses of the glass phases. The following synthetic and natural standards were used for calibration: natural albite (for Na), natural corundum (Al), natural wollastonite (Si, Ca), natural sanidine (K), synthetic pyrophanite (Mn, Ti), natural hematite (Fe), natural periclase (Mg), synthetic Cr₂O₃ (Cr), and reference natural zircon (Zr) provided by the Micro-Analysis Consultants© Ltd.. Element and background counting times were 5 s for Na and K and 10 s
for other major elements, whereas, peak counting times were 120 s for Cr, and 240 s for Zr.
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
glasses of mafic and ultramafic composition (KL2-G, ML3B-G, GOR132-G, GOR128-G,
Jochum et al., 2006) obtained from natural rock powders were analyzed as unknown samples
to monitor the accuracy of the major and trace element analyses. The accuracy estimated on
the reference glasses ranges from 0.5 to 5 % (1σ RSD = relative standard deviation),
depending on the element contents in the reference glasses. The starting MORB glass
containing 0.56 wt% H₂O was analyzed according to the method of Bindeman et al. (2012).

Secondary fluorescence effect and kinetic modeling

Given that our overall aim is to model the behavior of zircon in ad-hoc natural systems, we
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
control mineral dissolution: 1) the composition of liquid that is saturated in the phase of
interest (that can be simplified to the concentration of a limiting element, in our case Zr, at the
crystal-liquid interface), and 2) the diffusion coefficient of that limiting element in the liquid.
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
around host crystals (Borisova et al., 2018). Particular attention must thus be paid to eliminate
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
from one diffusion profile of the sample Z1 following the method of Harrison and Watson (1983). For that, Zr (ppm) profiles perpendicular to the zircon-glass interface in the Z1 sample have been measured, correcting for secondary fluorescence effects measured between zircon and the same (MORB) basaltic glass (Borisova et al., 2018). The corrected profile taking into consideration the effect has been obtained by linear interpolation of the secondary fluorescence effect with the function 'numpy.interp' of Python language (version 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 \((\text{erf}^{-1})\) correlates linearly with the distance from the interface with a slope of 0.022 (Fig. 3, 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). 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 \(\geq 0.2\) 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 \(D_{Zr}=2.87\times10^{-8}\) cm\(^2\)/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).

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 SiO$_2$-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 SiO$_2$-rich glass (Fig. 1).

A summary of the phase relations associated with zircon dissolution at 1250°C to 1300°C in (haplo-) basaltic melts (Fig. 4) shows that at 0.1 MPa, zircon dissolves incongruently to form baddeleyite (ZrO$_2$) and a SiO$_2$-rich melt. Baddeleyite is also formed at 0.7 GPa in the synthetic haplobasaltic (low a$_{SiO2}$) 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 $D_{Zr} = 2.87E-08$ cm$^2$/sec at 1300°C and 0.5 GPa (Supplementary Materials). 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 the value at 0.5 GPa and 1300°C),...
and combined with the initial Zr concentration of 94.3 ppm measured in the starting basaltic melt (Borisova et al., 2020).

**DISCUSSION**

**Zircon versus 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:

\[
\text{Zr(SiO}_4\text{)}^{Zm} = \text{ZrO}_2^{Bdy} + \text{SiO}_2^L
\]  

(eq. 1),

where Zm is zircon, Bdy - baddeleyite and L is silicate melt. Equation (1) implies that melts of higher silica activity will favor zircon stability, consistent with the fact that zircon prefers to crystallize in felsic, intermediate and silica-saturated (high \(a_{\text{SiO}_2}\)), rather than mafic and ultramafic systems (low \(a_{\text{SiO}_2}\)). Indeed, equation (1) predicts baddeleyite stability in low \(a_{\text{SiO}_2}\)-systems, such as ultramafic (e.g., carbonatite, kimberlite), and mafic (haplobasaltic) systems.

For example, Gervasoni et al. (2017) has investigated the system of zircon in low-\(a_{\text{SiO}_2}\) carbonanite melt at 0.7 GPa and these authors have described stability of baddeleyite and incongruent dissolution of zircon crystals with formation of corona of baddeleyite. In contrast, no baddeleyite crystallization has been observed by Shao et al., (2018) in a synthetic basalt system at pressures 0.5 – 1.5 GPa, implying baddeleyite stability only at lower pressures (< 0.5 GPa) in their basaltic systems. The observed effect of pressure on the relative stability of
zircon and baddeleyite is consistent with the fact that increasing pressure tends to increase
silica activity of mafic silicate melts, as illustrated by the displacement of the olivine-
orthopyroxene cotectic. In any case, decompression will favor incongruent rather than
congruent dissolution. We also note that comparison of Z2 and Z3 samples from the same
time series experiments implies an approximately constant rate of baddeleyite rim formation
of 0.9 ± 0.2 µm/min at constant temperature, pressure and water contents. This rate may be
used as a kinetic indicator to calculate approximate timescales of the zircon megacryst
transport to the surface.

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 - felsic and intermediate silicate liquids, e.g.,
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
and ultramafic systems. The main factors controlling solubility of zircon in silicate melts are
temperature, the melt composition expressed in terms of ratio of nonbridging oxygens 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 · Al₂O₃ +
SiO₂) represents the network formers, whilst the denominator (Na₂O + K₂O + CaO + MgO +

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FeO) represent the network modifiers of the melt) or B expressed in oxide mole fractions in the melts \((0.14(X_{\text{TiO}_2}/X_{\text{SiO}_2}) + 1.3(X_{\text{CaO}/X_{\text{SiO}_2}}) + 1.5(X_{\text{Na}_2\text{O}/X_{\text{SiO}_2}}) - 4.5(X_{\text{K}_2\text{O}/X_{\text{SiO}_2}}) - 2.7(X_{\text{Al}_2\text{O}_3/X_{\text{SiO}_2}})^2 + (X_{\text{MgO}/X_{\text{SiO}_2}})^2 - 3.7(X_{\text{CaO}/X_{\text{SiO}_2}})^2 + 75(X_{\text{K}_2\text{O}/X_{\text{SiO}_2}})^2)\) as well as the melt water contents have been proposed as factors controlling solubility of zircon in silicate melts (e.g., Harrison & Watson, 1983; Gervasoni et al., 2016; 2017; Borisov & Aranovich, 2019 and references therein). It is expected that the synthetic (Fe- and Ti-poor) 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 & 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 SiO\(_2\) 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 cm\(^2\)/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
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 CO$_2$ 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 Material) 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 & 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 & 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 & 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.
To explain the presence of zircon in tholeiitic basaltic melts at upper mantle temperatures of 1300°C, Zr concentrations in melts have to reach 20,000 – 30,000 ppm (Table 1). Thus, zircon crystallization directly from basaltic melt with common Zr concentration of 10s to 100s ppm 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; Borisova et al., 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 & 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 metasomatised 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 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,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 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, 1998; 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/fluuids. 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 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 $\varepsilon_{\text{Hf}}$ at 731 Ma is $+7.0$ based on recent data of Gain et al., 2019 and CHUR $^{176}\text{Hf}/^{177}\text{Hf}_0 = 0.282785$ and $^{176}\text{Lu}/^{177}\text{Hf}_0 = 0.0336$ 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 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 other 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.

CONCLUSIONS

1) Our data confirm high solubility of zircon in basalt of 20,000 – 30,000 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 tholeiitic 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 tholeiitic basaltic liquid in ~11 years,
100 microns zircon in ~10 hours, a zircon sphere of 50 microns in ~3 hours and a 10 micron 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 SiO$_2$-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 SiO$_2$-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 megacrust 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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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 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 SiO$_2$-rich melt. (D,E) Back-scattered 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 SiO$_2$-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) Back-scattered 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 SiO$_2$-rich melt. (H) Back-scattered 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 SiO$_2$-rich melt ($L_{SiO_2}$). (I) Back-scattered electron image of Z10 sample, demonstrating congruent dissolution of zircon (Zrn) in natural basaltic melt at 0.2 GPa.
**Figure 2(a)** Principal schema of assemblage of piston cylinder applied at BGI (Germany).

**Figure 2(b)** Principal schema of assemblage of piston cylinder applied at KIEM (Russia).
Figure 3. (A) The measured Zr contents versus distance (in µm) 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 \( \text{erf}^{-1} (1-C_x/C_o) \) versus distance (in µm) 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).
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 pressure-loading 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.
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) – (LaTourette et al., 1996), (2016HW) – (Holycross & Watson, 2016) and this work. The other systems, such as (1983HW) representing data of (Harrison & Watson, 1983), (1998NK) – (Nakamura & Kushiro, 1998), (1999M) – (Mungall et al., 1999), (2001KB) – (Koepke & Behrens, 2001), (2002B) – (Baker et al., 2002), (2016ZX) – (Zhang & Xu, 2016), (2018HW) – (Holycross & Watson, 2018) are 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 versus calculated Zr diffusivity (log(D), D in cm²/s) after Zhang & Xu (2016) (calculated on hydrous basis). The (haplo-) basaltic systems are represented by data of (1996 LaT) – (LaTourette et al., 1996), (2016HW) – (Holycross & Watson, 2016) and this work. The other systems, such as (1983HW) representing data of (Harrison & Watson, 1983), (1998NK) – (Nakamura & Kushiro, 1998), (1999M) – (Mungall et al., 1999), (2001KB) – (Koepke & Behrens, 2001), (2002B) – (Baker et al., 2002), (2016ZX) – (Zhang & Xu, 2016), (2018HW) – (Holycross & Watson, 2018) are dry to hydrous intermediate to felsic systems.
Figure 7. The calculated time of zircon dissolution in tholeiitic basaltic melt at 1300°C according to the kinetic model of Bindeman & Melnik (2016) versus zircon size (in μm). The shaded light grey field corresponds to the dissolution timescales from hours to years 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 mantle (from $10^{-4}$ to $10^{2}$ years) according to Turner and Costa (2007), suggesting high percentage of the zircon crystals and megacrysts to be dissolved upon their transport to the surface.
Figure 8. H, m - height in meters versus Zr in ppm contents in rocks of the Kivakka mafic-ultramafic 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.
Table 1. Pressure-temperature-redox conditions of experiments on zircon dissolution in natural basaltic and synthetic haplobasaltic melt

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Techniques</th>
<th>Conditions (pressure, temperature, redox conditions)</th>
<th>Duration (hours)</th>
<th>Type of basalt &amp; initial mass of Zrn to basalt to water**</th>
<th>Observed final phases (Bdy zone thickness in µm)</th>
<th>Interface melt C₀ content Zr (ppm)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>BGI, PC</td>
<td>1300°C, 0.5 GPa</td>
<td>5h</td>
<td>Zrn to BAS 0.075</td>
<td>Partially dissolved zircon (PDZ) Zrn, L&lt;sub&gt;bas&lt;/sub&gt;</td>
<td>20,840 ± 348</td>
</tr>
<tr>
<td>Z2</td>
<td>IRAP, G</td>
<td>1300°C, 0.1 MPa, FMQ</td>
<td>1h 15min</td>
<td>Zrn to BAS 0.086</td>
<td>PDZ, Bdy, L&lt;sub&gt;bas&lt;/sub&gt; (80 ± 20 µm)</td>
<td>N.A.</td>
</tr>
<tr>
<td>Z3</td>
<td>IRAP, G</td>
<td>1300°C, 0.1 MPa, FMQ</td>
<td>15 min</td>
<td>Zrn to BAS 0.142</td>
<td>PDZ, Bdy, L&lt;sub&gt;bas&lt;/sub&gt; (10 µm)</td>
<td>N.A.</td>
</tr>
<tr>
<td>Z4</td>
<td>KIEM, PC</td>
<td>1300°C, 0.7 GPa</td>
<td>5h</td>
<td>Zrn to BAS 0.037</td>
<td>L&lt;sub&gt;bas&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>Z6</td>
<td>KIEM, PC</td>
<td>1300°C, 0.7 GPa</td>
<td>5h</td>
<td>Zrn to AnDi 0.157</td>
<td>PDZ, Bdy, L&lt;sub&gt;bas&lt;/sub&gt; (100 ± 30 µm)</td>
<td>N.A.</td>
</tr>
<tr>
<td>Z7</td>
<td>KIEM, PC</td>
<td>1300°C, 0.7 GPa</td>
<td>5h</td>
<td>Zrn to AnDi 0.097; H&lt;sub&gt;2&lt;/sub&gt;O = 7.0 wt%</td>
<td>PDZ, Bdy, L&lt;sub&gt;bas&lt;/sub&gt; (10 µm)</td>
<td>N.A.</td>
</tr>
<tr>
<td>Z10</td>
<td>KIEM, IHPV</td>
<td>1250°C, 0.2 GPa</td>
<td>5h</td>
<td>Zrn to BAS 0.115</td>
<td>PDZ, L&lt;sub&gt;bas&lt;/sub&gt;</td>
<td>23,438 ± 554</td>
</tr>
</tbody>
</table>
** 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 SiO$_2$-rich glass; L$_{bas}$ – basaltic glass.

*** - Interface melt concentration in ppm ($C_0$) (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.