

Supplementary Material

for article ‘In situ probing of the present-day zircon-bearing magma chamber at Krafla, Northeastern Iceland’ by Borisova et al.

Detailed description of the rock and glass materials and analytical, dating and imaging procedures applied in this study

Compositions of the granophyre rock material and the Krafla rhyolite sampled by Iceland Deep Drilling Project well 1 (IDDP-1) are given in Table 1. The rhyolite material (Viti crater granophyre, IC-82, Krafla volcano) is a fine grained granophyre with crystal sizes of up to ~1 mm. The Viti Crater (65°43'03.37" N and 16°45'17.59" O, 595 m) granophyre rock samples consist of such felsic minerals as quartz, plagioclase, alkali-feldspar, clinopyroxene, and accessory zircon, apatite, magnetite, ilmenite, and zircon, chevkinite (Ca-REE silicate) and Nb-Y silicate minerals. The IDDP-1 (brown) rhyolite (Table 1) glass investigated in this work consists of felsic glass (up to 95%), plagioclase, two pyroxenes, titanomagnetite and/or apatite and zircon are also forming glomerocrysts; quartz and alkali feldspar show textural evidence for resorption, and were interpreted by Zierenberg et al. (2013) as xenocrysts. All granophyre and basaltic rocks were sampled during the USA-Iceland and French-Iceland expeditions in 2018 – 2019.

The glassy shards of the IDDP-1 samples were mounted in epoxy. Ten thick sections of the Viti granophyre were examined. We identified and analyzed ~60 zircons and one baddeleyite by scanning the sections. Identification of glass and zircon phases and the sample imaging was performed at Géosciences Environnement Toulouse (GET, Toulouse, France) laboratory (Borisova et al., 2012; 2020; 2021) using a Bruker TESCAN scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) (Toulouse, France) (Borisova et al., 2021) and a JEOL JSM 7100F TTLS LV field-emission gun (FEG) SEM at the Centre de Microcaractérisation Raimond Castaing, Toulouse (France). Major and trace element concentrations of sample phases were analyzed using a CAMECA SX-Five electron microprobe at the Centre de Microcaractérisation Raimond Castaing (Toulouse, France). The trace Ti and Hf contents in zircons were analyzed using accelerating voltages of 15 to 25

kV, and beam currents of 200 to 300 nA, allowing detection limits down to 9 ppm (Ti) and 160 ppm (Hf), and precisions of 8 ppm (Ti) and 230 ppm (Hf). The Ti-in-zircon contents of the IDDP-1 zircons (Eugene, USA) were analyzed at 15 kV and 50 nA (3 μm beam size), with a detection limit of 40 ppm. Analyses of such reference materials as 91500 and Plesovice zircons and NIST 610 and 612 and ATHO-G glasses were used to check the Ti-in-zircon accuracy. Major elements of zircon minerals were analyzed using a 15 kV accelerating voltage and a 20 nA beam current. The following synthetic and natural standards were used for calibration: albite (Na), corundum (Al), wollastonite (Si, Ca), sanidine (K), pyrophanite (Mn, Ti), hematite (Fe), periclase (Mg), zircon (Zr, Hf). Peak and background counting times for most analyzed elements were 10 s and 5 s, respectively. Detection limits of zircon analyses were: 300 ppm (Al), 330 ppm (Si), 700 ppm (Ca), 1000 ppm (Fe), 800 ppm (Y), 1600 ppm (Zr), 2250 ppm (Ce), 5000 ppm (Gd), 2700 ppm (Dy), 1200 ppm (U), 4000 ppm (Th) and 350 ppm (P). Silicate reference glasses of MPI-DING of felsic composition (ATHO-G of Jochum et al., 2006; Borisova et al., 2010) were analyzed to additionally monitor the accuracy of results. Analyses of these reference materials allowed major element precisions to be within the limit of the analytical uncertainty (e.g., 8 ppm Ti, obtained from counting statistics). The accuracy of EPMA data estimated from the analyses of the reference glasses ranges from 0.5 to 3% (1σ RSD = relative standard deviation), depending on the element contents of the reference glasses. To avoid the secondary fluorescence contribution in the Ti-in-zircon concentrations, zircon analyses were collected at $\geq 50 \mu\text{m}$ from the interface with titanomagnetite and at $\geq 100 \mu\text{m}$ from the interface with ilmenite (calculations using the program FANAL (Llovet et al., 2012) yielded an apparent Ti concentration due to secondary fluorescence of ~ 6 ppm at $50 \mu\text{m}$ from titanomagnetite and ~ 9 ppm at $100 \mu\text{m}$ from ilmenite at 15 keV, values which are lower than the detection limits for this element). Finally, the obtained Ti-in-zircon data were filtered for effects from possible invisible Al- and Fe-bearing micro-inclusions.

In the geochemical modeling, we used the Zr contents in glass surrounding zircons analyzed by EPMA (Eugene, USA) at the interface with the zircon crystals (at 15 kV and 400 nA, with a focused beam). Analyses were conducted on a CAMECA SX-100 electron microprobe equipped with 5 wavelength dispersive spectrometers. Energy dispersive (EDS) spectra were acquired and processed

using a Thermo NSS EDS system. Operating conditions were 15 kV and 400 nA for Zr, and 15 kV accelerating voltage, 50 nA electron beam and a beam size of 3 microns for the rest of elements. Analyzing crystals and X-ray lines were as follows: LiF for Ca K α and Fe K α , LLiF for Ti K α , LPET for Zr L α , TAP for Al K α , Mg K α , and Si K α . The EDS was used for the analysis of Na K α and K K α . Standards were synthetic MgO for Mg, synthetic SiO₂ for Si, synthetic TiO₂ for Ti, Zircon crystal (synthetic) for Zr, Nepheline for Al and Na, Diopside (Chesterman) for Ca, Orthoclase MAD-10 for K, and Magnetite U.C. #3380 for Fe. Additionally, to study Zr element profiles, we have used an electron probe microanalysis (CAMECA SX-Five) at the Centre de Microcaractérisation Raimond Castaing (Toulouse, France). For the CAMECA SX Five, we have applied the following conditions for the electron beam: an accelerating voltage 15 kV, currents of up to 200 nA for Zr (e.g., Borisova et al., 2020). To avoid damage on such less resistant materials as hydrous glasses, defocused conditions were used up to 10 μ m for the beam diameter on the surface of the glass phases. The following synthetic and natural standards were used for calibration: albite (for Na), corundum (Al), wollastonite (Si, Ca), sanidine (K), pyrophanite (Mn, Ti), hematite (Fe), periclase (Mg), Cr₂O₃ (Cr), nickel metal (Ni) and reference zircon (Zr). All Zr profiles in glass adjacent to zircon were corrected for secondary fluorescence effects across phase boundaries. To this end, apparent Zr k-ratio profiles due to secondary fluorescence, where the k-ratio is defined as the ratio of the characteristic X-ray intensity emitted by an element in the specimen to that emitted by the same element in the standard, were calculated for the measured samples using the program FANAL (Llovet et al., 2012), they were converted into apparent Zr concentration profiles (in wt.%) by applying a ZAF correction factor, and they were subtracted from the measured profiles. The ZAF factor was obtained using the program CALCZAF (see e.g., Borisova et al, 2018).

In-situ ²³⁸U-²³⁰Th dating of zircons from the IDDP-1 and the host granophyre samples was conducted using the Stanford-USGS SHRIMP-RG ion microprobe following the analytical protocol described in Burgess et al. (2021) using MAD-1 (Coble et al., 2018) and z6266 (Stern and Amelin, 2003) zircons as standards for U/Th relative sensitivity (e.g., Schmitt, 2011).

Ultraviolet femtosecond laser (235 fs, 257 nm, New Wave Research, USA) coupled to the HR-ICP-MS Elements (Thermo Fisher Scientific) was applied to analyze major and trace element concentrations in the IDDP-1 rhyolite glasses and trace elements in the dated zircons (Toulouse, France). The applied ultraviolet femtosecond (fs) laser (280 fs) was fired with a frequency of 6 to 7 Hz, 20 to 40% energy, 2.7 to 3.4 J/cm², producing a nominal crater of 15 to 33 μm in diameter. The fs LA-ICP-MS signals on the following isotopes were detected: ⁷Li, ¹¹B, ²³Na, ²⁵Mg, ²⁷Al, ²⁹Si, ³¹P, ³⁹K, ⁴³Ca, ⁴⁹Ti, ⁵⁵Mn, ⁵⁷Fe, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹²¹Sb, ¹³³Cs, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁸⁰Hf, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th, ²³⁸U. The external reference material used was SRM NIST 610 or 612 and the analysis accuracy was monitored by analyses of SRM NIST 610 and MPI-DING ATHO-G rhyolite glasses as well as reference zircons (91500, Plesovice and GJ1). Software used for processing the quantification of the analyses were SILLS and IOLITE 2.5 (Guillong et al., 2008; Paton et al., 2011).

To estimate the glass (quenched melt) fraction in the IDDP-1 fragments containing zircons, the contrast of the BSE images was optimized to distinguish each mineral and glass phase by their greyscale contrast (**Fig. 3**). As the brightness is related to the mean atomic number (*Z*) of the phase, white phases correspond to oxides and zircons (higher mean *Z*), while dark phases correspond to quartz and feldspar (lower mean *Z*). The remaining phases in light grey correspond to rhyolitic glass and they were selected using the ImageJ software. Each area with this grayscale range was selected, changed to red and the glass area was measured. To obtain the glass fraction, the glass area was divided by the sample's area. The same methodology was applied to obtain the average zircon size and radius (in μm). All numerical data are given in the **Supplemental Tables S1 – S8**.