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Low-temperature dissociation of zircon in highly alkaline conditions: A cautionary note for studies on natural glasses of debated origin

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Abstract—Dissociated zircon is largely used as a robust indicator of glasses generated by impact cratering and airbursts. The reaction of zircon dissociation, i.e. ‘ $\text{ZrSiO}_4 \rightarrow \text{ZrO}_2 + \text{SiO}_2$ ’, requires high temperatures ($>1670^\circ\text{C}$) only reached by extreme geological processes. Using high-temperature experiments, this study shows that zircon can dissociate and form ZrO_2 -rich coronitic rims at temperatures of $900\text{--}1000^\circ\text{C}$ ($P = 1$ bar), in the presence of a specific chemical environment made of NaCl or a mixture of NaCl and caliche soil (Ca-sulfates). The use of silica glass vessels provides a SiO_2 -rich environment during the experiments. We observe that the dissociation is strongly related to the complexity of the surrounding system (e.g. the presence of other minerals that act as a flux) in which the reaction occurs. For these reasons, we suggest considering a more careful approach in using dissociated zircon as indicative of very high temperatures in glass-forming processes.

INTRODUCTION

Impact melts generated by hypervelocity impacts have experienced temperatures well above the maximum temperatures recorded in volcanic or ancient anthropogenic glasses ($<1200^\circ\text{C}$; Dressler & Reimold, 2001; Osinski et al., 2018; Cicconi et al., 2022). Evidence for such high temperatures may be gained from the following observations: (1) loss of volatiles including water, (2) presence of inclusions of a pure SiO_2 glass, also known as lechatelierite, (3) dissociation of zircon (ZrSiO_4) (e.g., Glass, 1990; El Goresy, 1965; Glass & Simonson, 2012). The $\text{ZrO}_2\text{--SiO}_2$ phase diagram determines that crystalline zircon dissociates at $\sim 1670^\circ\text{C}$ into tetragonal or cubic zirconia and liquid silica, depending on temperature conditions. During cooling, due to martensitic phase transformation from

high-temperature zirconia polymorphs, monoclinic ZrO_2 forms, i.e., baddeleyite (e.g., Kaiser et al., 2008; Timms, Erickson, Pearce, et al., 2017). The identification of preexisting cubic zirconia, which can be achieved using EBSD phase heritage/reconstruction (Cayron, 2007; Cayron et al., 2010), is an important geothermometer as cubic zirconia is stable at temperatures $>2370^\circ\text{C}$, indicating the formation of superheated melts (Chinchalkar et al., 2024; Timms, Erickson, Zanetti, et al., 2017; Tolometti et al., 2022). Under reflected light and backscattered electrons (BSE) imaging in a scanning electron microscope (SEM), dissociated zircon in glasses is easily recognized by the presence of bright coronitic rims of baddeleyite surrounding the primary crystal core of zircon (e.g., Timms, Erickson, Pearce, et al., 2017, their figures 4 and 9). Dissociation can also locally affect the border and fractures of the crystal. Dissociated zircon

crystals have been observed in tektites (Australites [Cavosie, Timms, Erickson, et al., 2018] and Georgiites [Glass et al., 1995]), Libyan desert glass (Cavosie & Koeberl, 2019; Kleinmann, 1968) and impact glasses and related rocks from the following impact structures: Acraman (Schmieder et al., 2015), Aouelloul (El Goresy, 1965), Chixculub (Wittmann et al., 2005), Luizi (Cavosie, Timms, Ferrière, et al., 2018), Meteor crater (Cavosie et al., 2016), Mien (Martell et al., 2021), Mistastin (Timms, Erickson, Zanetti, et al., 2017; Tolometti et al., 2022; Zanetti et al., 2015), Pantasma (Rochette et al., 2019), Ries (El Goresy, 1965; Wittmann et al., 2006), Yarrabubba (Erickson et al., 2020), Vredefort (Kovaleva et al., 2021), and West Clearwater Lake (Chinchalkar et al., 2024). Zircon dissociation is also observed in the lunar Apollo 14 and 15 breccias and soils (Crow et al., 2019), the lunar meteorite Dhofar 458 (Zhang et al., 2011), and Howardite-Eucrite-Diogenite (HED) meteorites from the asteroid Vesta (Barboni et al., 2024). Although it does not correspond to the stringent diagnostic criteria for impact (high pressure or extraterrestrial contamination evidence), the presence of dissociated zircon in a glass of disputed origin has been presented as evidence for impact or airburst (Bunch et al., 2021; Schultz et al., 2022a).

The case of airbursts differs from that of cratering impacts by their P–T conditions: both create very high temperatures (up to 10,000°C; French, 1998) but airbursts are characterized by lower pressures (~1–10 kPa, e.g., Aftosis et al., 2019) than cratering impacts at the Earth's surface (~7 to >100 GPa; Cavosie & Koeberl, 2019). However, the pressure generated by an airburst event is debated, with some models suggesting that pressures up to ~30 GPa can occur (West et al., 2024). The process of airburst is still not well documented, due to the lack of clear geological evidence (e.g. the presence of a crater) which makes their (eventual) products even more difficult to recognize (Boslough & Crawford, 2008). The only other known natural process that can cause zircon dissociation is lightning (Essene & Fisher, 1986; Kenny & Pasek, 2021). However, the distinct shape and internal structure of fulgurites usually make them readily identifiable.

The use of zircon dissociation as a strong criterion to identify impact glasses (in the following, the term will be used as comprehensive of impacts and airburst products) fails to acknowledge that the temperature prediction from the zircon phase diagram is valid only in the absence of chemical reactivity with other compounds than ZrO_2 and SiO_2 . In the mineral processing industry, it is known that there are ways to obtain the dissociation of zircon at much lower temperatures, e.g. using alkaline fusion (Abdelkader et al., 2008; West, 1954). Zircon dissociation to baddeleyite (and other Ca-rich phases) can be achieved

at temperatures as low as 600°C–900°C at pressures of 400–1000 MPa (Lewerentz, 2011; Lewerentz et al., 2019). The dissociation of zircon is also strongly dependent on its structural state, as it often suffers structural damage induced by radiation (due to the decay of U and Th included in the crystals). Amorphous (metamict) zircon has been experimentally shown to decompose into $\text{ZrO}_2 + \text{SiO}_2$ at ~1000°C at room pressure (Nasdala et al., 2002). Both hydrothermal alteration experiments (Geisler et al., 2001, 2003, 2004, 2007) and natural samples case studies (e.g., Nasdala et al., 2009, 2010; Seydoux-Guillaume et al., 2015) have also shown that metamict zircon is more easily subjected to alteration (e.g., decreased stability when subjected to hydrothermal solutions, forming micrometer-thick reaction rims, nanoscale pores, accumulating solvent element in the structure [Ca, Al, Fe]).

This work investigates the possibility that crystalline zircon dissociation to baddeleyite can occur at atmospheric pressure and under dry conditions at $T \leq 1000^\circ\text{C}$, suggesting that this reaction should not be considered, alone, as indisputable evidence of extreme geological conditions. The study is primarily intended for glasses of debated origin, where there is no other clear evidence of shock and high-temperature conditions. Specifically, we explored highly alkaline conditions, such as those that could occur in the presence of evaporitic soils. Our aim is also to emphasize how crucial it is to constrain the conditions under which this reaction occurs, as it is fundamental for understanding the formation of certain natural glasses whose origins are still debated. One case is that of Pica glass, whose geological context was considered for the design of our experiments. Pica glass is an unusual surface glass layer found in different locations of the Atacama Desert (Chile), whose origin has been attributed to different processes: surface vitrification due to biomass fires in soils (Roperch et al., 2017, 2022) and cometary airburst (Schultz et al., 2022a, 2022b). The extended areal distribution of Pica glass and the lack of evidence of remagnetization by strong fields excluded the hypothesis of lightning strikes for their formation (Roperch et al., 2017). The presence of dissociated zircon in Pica glass is seemingly robust evidence for impact produced by Schultz et al. (2022a). Whatever the source of the high temperatures, Pica glass has been generated from the melting of the Atacama Desert surface soil, which is rich in *caliche*, i.e. crusts made of salts, mostly NaCl and Ca-sulfates (Voigt et al., 2020). The soil itself may thus provide the necessary reagents to lower the temperature of zircon dissociation. To demonstrate this, we conducted an experimental study to determine the temperature range for zircon dissociation in the presence of salts at atmospheric pressure.

MATERIALS AND METHODS

Experimental Technique

The zircon crystals used for the experiments come from a homogeneous batch of crystals extracted from granitoids from the Kaapvaal Craton, South Africa (Poujol et al., 2021), with grain sizes of $\sim 100\ \mu\text{m}$ (Figure 1a). The experiments were conducted inside silica glass vessels ($V \sim 1.5\ \text{cm}^3$) covered with a silica glass lid. The zircon crystals were laid at the bottom of the vessel, in direct contact with the glass. The reagents used to investigate the dissociation temperature are (i) caliche soil collected in the Atacama Desert, composed of Ca sulfates—primarily gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with minor anhydrite CaSO_4 (Figure S1), and grain size of $10\text{--}20\ \mu\text{m}$, and (ii) NaCl crystals, with grain sizes between $100\text{--}500\ \mu\text{m}$ (Figure 1b,c). Some experiments were conducted using a mixture of halite and caliche. The addition of NaCl is justified by its widespread presence in the Atacama Desert, where it is often found mixed with gypsum (Voigt et al., 2020). In the case of impact or airburst in hot deserts, zircon can be present as single crystals surrounded by sand. To ensure that the zircon crystals would be completely surrounded by the reagents, and to have a sufficient number of zircon crystals to investigate after the experiments, we chose the following proportion of zircon to reagent. For each portion of zircon crystals ($\sim 1\text{--}2\ \text{mg}$), about ten portions of reagents are used ($10\text{--}20\ \text{mg}$). Since gypsum and anhydrite are the most common salts in the Atacama Desert, the ratio of caliche to NaCl chosen for experiments where both are present is approximately 5:1. Precise proportions of the reagents used are arbitrary, due to the wide variation in the distribution and concentration of salts in the desert (Voigt et al., 2020). Using silica glass vessels ensures the presence of an SiO_2 -rich environment during the experiments, which is necessary to simulate zircon dissociation in a silicate glass. A droplet of pure H_2O is added to each experiment to make the components adhere to each other. Once filled, the vessel is covered by the lid (not sealed, used to limit the escape of volatile elements) and put in a WiseTherm oven for six hours at temperatures from 800°C to 1000°C , at atmospheric pressure. A preliminary experiment has been conducted at 1000°C for 30 min, which is reported among the other results in Table 1. At the end of the six hours, after cooling, the vessels are embedded in resin and polished down to expose zircon interiors and obtain a section of numerous zircon crystals. The area analyzed for each experiment is $\sim 0.1\ \text{cm}^2$.

Analytical Techniques

The zircon crystals were analyzed using a Hitachi S-3000N SEM with a Bruker Energy Dispersive X-ray

Spectrometer (EDS) at the Centre de Recherche et d'Enseignement de Geosciences de l'Environnement (CEREGE) and a Zeiss Gemini 500 Field-Emission Gun Scanning Electron Microscope (FEG-SEM) with an EDAX EDS system at Centre Pluridisciplinaire de Microscopie Electronique et de Microanalyse (CP2M) in Marseille, France. BSE images were acquired at a voltage of 15 kV.

The age of the zircon crystals has been determined to better characterize their properties. Forty zircon crystals were dated via U–Pb at the Envitop analytical facility at CEREGE using an Element XR ICP-MS connected to a NWR193 laser (ArF 193 nm) ablation system. Zircon crystals were ablated with a 25-micron spot diameter, a 15 Hz pulse repetition rate, an energy fluence of $1.5\ \text{J}/\text{cm}^2$, and a carrier gas flow of $0.975\ \text{L}/\text{min}$. Data reduction, date, and date uncertainty calculations were conducted with an in-house MATLAB script. Details about our U–Pb dating workflow, data reduction steps, and discordance filter are given in Licht et al. (2024). The three zircon validation reference materials used during these sessions yielded offsets around TIMS ages $<1\%$ in most cases, and $<2\%$ otherwise. Out of the 40 analyzed zircon crystals, 27 yield concordant U–Pb ages (see Table S1). The final Concordia age was calculated with concordant ages only using IsoPlotR (Vermeesch, 2018).

X-ray diffraction on a powdered sample of caliche was conducted with an X'Pert Pro (Panalytical) equipped with a ray X cobalt tube ($\lambda = 1.79\ \text{\AA}$), operating at 40 kV and 40 mA. The analysis was conducted between 5° (2θ) et 75° (2θ) with a step size of 0.026° and a total counting time of 3 h. The sample was powdered in an agate mortar and deposited with ethanol on a low-background silicon support. The sample rotates on a horizontal plane at a velocity of 15 rotations per minute to improve the statistics. The phase identification has been conducted using the software X'Pert Highscore Plus, using the database ICDD PDF2.

For Raman spectroscopy, we used a Renishaw inVia Raman Microscope with a 100x objective at Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), France. The samples were excited by a 633 nm laser at 100% power or attenuated to 50% to 5%. The spectra were collected with multiple acquisitions ($n = 6$) with counting times of 10 s and with a 1200 lines/mm grating (therefore a resolution of $1.35\ \text{cm}^{-1}$). The spectrum range was $50\text{--}1200\ \text{Raman}/\text{cm}^{-1}$. Raman spectroscopy was used for the identification of phases in the rims (after the experiment) and to investigate the crystallinity of the zircon crystals used (before the experiments). In both cases, the analysis was performed on polished samples embedded in resin.

Two electron-transparent lamellae of the mineral interface (zircon/rim/matrix) were prepared using a Thermo Fisher Scientific FEI 125 Helios Nanolab 600i

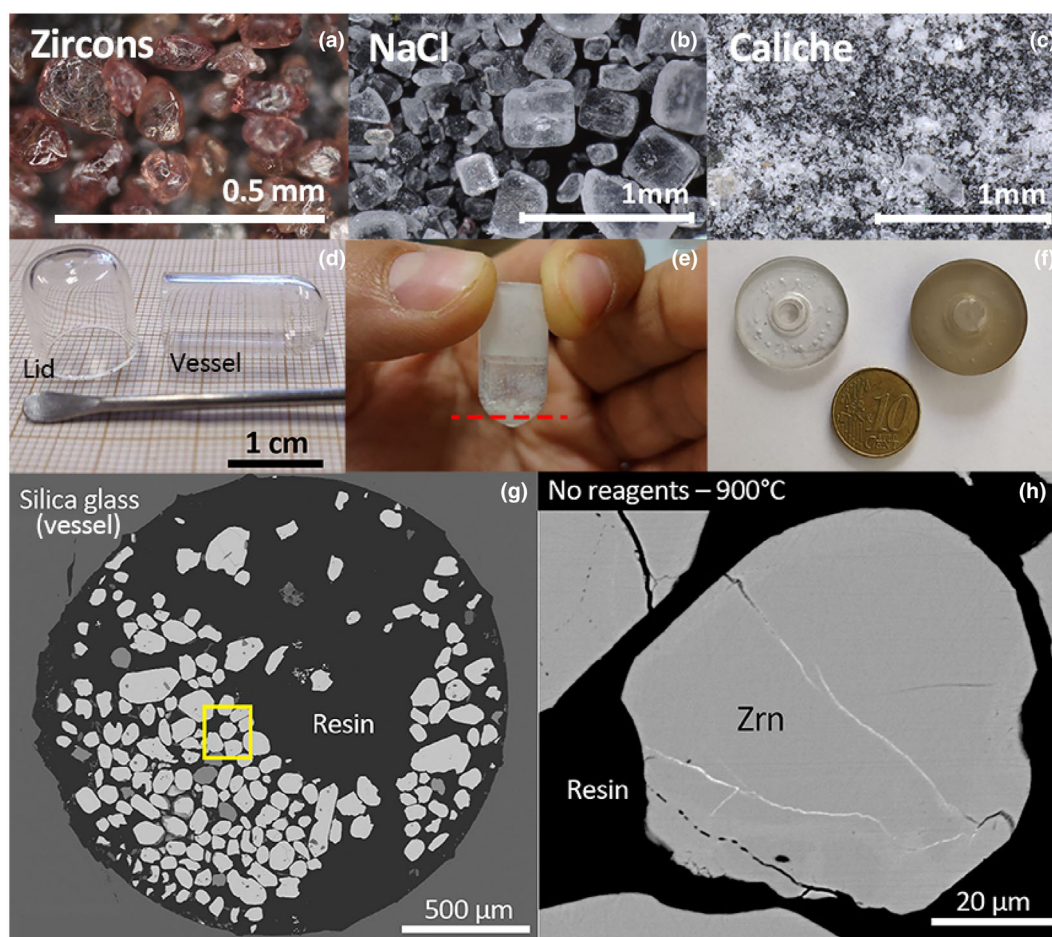


FIGURE 1. (a) Optical images of the zircon crystals used for the experiments (granulometry $\sim 100\ \mu\text{m}$). (b, c) Optical image of NaCl ($100\text{--}500\ \mu\text{m}$) and caliche (gypsum, $10\text{--}20\ \mu\text{m}$) crystals used as reagents for the experiments. (d) Picture of the SiO_2 vessel and lid used for the experiments. (e) Vessel (after removal of the lid) after one experiment, ready for the embedding in resin and polishing (red dashed line is a typical section obtained after the polishing). (f) Samples embedded in resin uncoated and C-coated. (g) BSE image of the whole section from the experiment at 900°C where zircon crystals are exposed to high temperature with no reagents (yellow box indicates the position of the zircon in h). Minor apatite and quartz grains are unintentionally present (darker crystals). (h) BSE image of typical unreacted zircon: fractured, often filled with bright phases (Zr-rich), no signs of dissociation. The fractures observed could be due to thermal breakdown or they may have already been present.

Focused-Ion Beam Scanning Electron Microscope (FIB/SEM) at MANUTECH USD platform in Saint-Etienne, France. A lamella was taken from each experiment showing dissociated rims. One lamella, where zircon has a very porous rim, was kept thicker to avoid its destruction. Nanoscale characterization was performed at 200 kV with a NeoARM200F (scanning) Transmission Electron Microscope (TEM/STEM) operated by the Consortium Lyon Saint-Etienne de Microscopie (CLYM) and hosted within the Hubert Curien Laboratory, Saint-Etienne, France. The NeoARM200F is equipped with a cold field-emission gun and a sixth-order aberration corrector (ASCOR). Images were obtained using a bright field and dark field detector for TEM and a high-angle annular dark field (HAADF) in STEM mode. A JEOL large angle silicon drift EDS

detector ($0.96\ \text{sr}$) was used to acquire X-ray maps with $0.1\ \mu\text{s}$ dwell time and a real time of 15 min to 2 h. Quantification was achieved using theoretical k-factors provided by JEOL®, the Cliff-Lorimer method (Cliff & Lorimer, 1975), and an absorption correction procedure (Horita et al., 1987; Morris, 1980; Zanetta et al., 2021, 2022). EDS data were processed using Hyperspy library (De La Peña et al., 2024).

RESULTS

Pre-Experiment Characterization

The zircon crystals yield a homogenous $2748.3 \pm 6.5\ \text{Ma}$ (2 s) Concordia age (MSWD = 1.1 with 25 out of the 27 zircons, see Figure S2). Their chemical composition is

TABLE 1. All experiments conducted are listed along with their running conditions: duration, temperature (T), and reagents.

Time (h)	T(°C)	Reagents	Reacted grains (%)	Rims	Bdy	Fig. (ref)
6	800	NaCl	None	n	n	3a
	800	Caliche + NaCl	None	n	n	3b
	900	None (blank)	None	n	n	1g
	900	Caliche	None	n	n	–
	900	NaCl	None	n	n	3c
	900	Caliche + NaCl	>50%	y	n	3d
	1000	NaCl	<50%	n	y	3e
0.5	1000	Caliche + NaCl	100%	y	y	3f
	1000	NaCl	<50%	n	y	Inset 3e

Note: All experiments were run at atmospheric pressure. The last four columns report the percentage of reacted grains, the occurrence of rims and baddeleyite (Bdy), and the figure references (Fig. [ref]).

mostly pure ZrSiO_4 , with trace Hf present (averaging 0.7 ± 0.1 wt% when it is present). The crystals are fractured and some have apatite inclusions, but they do not show zoning. The contents of U and Th are 215 ± 90 and 508 ± 229 ppm, respectively (Table S1). Overall, the population is very homogeneous in visual aspect, age, and composition. Their structural state has been inferred using Raman spectroscopy and the calculation of α -doses (Figure S3; Murakami et al., 1991; Nasdala et al., 2001). The α -dose damage can be determined from the U and Th concentrations in zircon and their age (Nasdala et al., 2001). For the zircon crystals used in the experiments, the α -dose damage calculated is equal to 3.84×10^{18} α -doses events/g. Concerning Raman spectroscopy, the peaks are well-defined and show only slight deviations from the $\nu_3(\text{SiO}_4)$ band (from 1005 to 1007 cm^{-1}), with a FWHM of 8.8–13.5 cm^{-1} ($N = 10$) (Figure 2b; Table S2).

Post-Experiment Characterization

One experiment that served as a blank was run with no reagents at $T = 900^\circ\text{C}$, which did not show signs of dissociation in the grains (Figure 1g,h). Three out of nine experiments successfully reproduced coronitic rims, i.e., borders surrounding zircon with symplectitic texture made of micrometer-sized Zr-rich crystals (Figure 3). In all the experiments in which caliche is present, skeletal secondary anhydrite and wollastonite are formed (from 800°C to 1000°C ; right column of Figure 3). Instead, when NaCl is the only reagent, a matrix of Na-rich silicate glass embeds the zircon crystals, progressively more abundant going from 800°C to 1000°C (left column of Figure 3). We obtained the following results (Table 1):

- At $T = 800^\circ\text{C}$, for all the experiments, no zircon crystals showed dissociation (Figure 3a,b).

- At $T = 900^\circ\text{C}$, in the presence of NaCl only, the zircon crystals do not show dissociation (Figure 3c).
- At $T = 900^\circ\text{C}$, in the presence of caliche and NaCl, >50% of the zircon crystals have dissociation rims (Figure 3d).
- At $T = 1000^\circ\text{C}$, in the presence of NaCl, >50% of zircon crystals do not show dissociation. Some grains (<50%) show dissociation in fractures and inclusions, but they do not have dissociated rims (Figure 3e). In the same conditions, but for a duration of half an hour, dissociation occurred in inclusions and fractures, but not forming rims (inset in Figure 3e).
- At $T = 1000^\circ\text{C}$, in the presence of caliche and NaCl, all the zircon crystals are dissociated with rims (Figure 3f).

The rims formed differ by texture and mineralogical composition. At 1000°C with caliche plus NaCl (Figures 3f and 4), all the zircon crystals have dissociation rims, with an average thickness of ~ 15 μm . In this experiment, the rim is characterized by the alternate presence of two textures: (a) highly porous, made only of anhedral ZrO_2 crystals; (b) ZrO_2 crystals cemented by a crystalline Ca-silicate phase. The ZrO_2 phase is identified as baddeleyite by Raman spectroscopy, selected area electron diffraction (SAED) patterns (Figure 4c), and atomic lattice imaging in aberration-corrected STEM mode (Figure 4b, inset). EDS quantification (spot analysis) of the Ca-silicate phase gives Ca = 23.5, Fe = 0.6, O = 56.9, Si = 14.9, and Zr = 4.1 atom%, close to a Ca_2SiO_4 stoichiometry. SAED patterns are best indexed as calcio-olivine, rather than its polymorph larnite (Figure 4d–g). However, the size of the crystals and their superposition with baddeleyite do not allow us to constrain this phase with certainty, either structurally (could correspond to other Ca-, Si- and Zr-rich phases) or chemically (superposition of crystals gives variable elemental ratios depending on sample locality that could account for the low Zr content). This is because the lamella used for TEM/STEM analysis had been kept thick due to the porous nature of the rim which limited the thinning with FIB, thus increasing uncertainties in EDS analyses and SAED indexing.

In the experiment at 900°C (Figures 3d and 5), with caliche plus NaCl, the majority of zircon crystals are dissociated. The rims are ~ 5 μm thick on average and are finer-grained compared to the experiment at 1000°C . The contact between the rim and the unaltered zircon is sharp, and generally, there is an increase in granulometry from the inner to the outer part of the rim. TEM reveals the presence of a single ZrO_2 phase enriched in Ca. Standardless EDS analyses yield a composition of Ca = 8.57, Zr = 33.9, and O = 54.6 atom% which

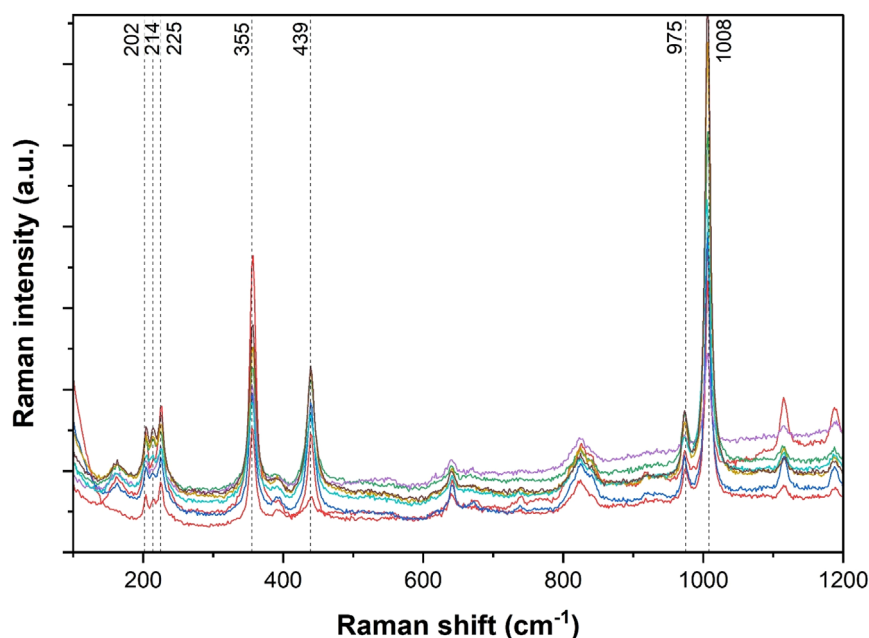


FIGURE 2. Raman spectra of a random selection of zircon crystals used in experiments. The spectra ($n = 8$) are compared to the excitation modes expected for non-metamictic zircon (dashed lines, Zhang et al., 2000).

converts approximately to 90 wt% ZrO_2 and 10 wt% CaO . Selected area electron diffraction (SAED) patterns are consistent with cubic ZrO_2 , rather than baddeleyite (Figure 5d). In this experiment, Raman spectroscopy did not detect baddeleyite in the rim either (orange spectrum in Figure 6a).

DISCUSSION

Pre-Experiment Characterization

The zircon crystals used can be defined as crystalline from their spectroscopical properties (intermediate FWHM and well-defined peaks). Based on spectroscopy results, the zircon crystals used have intermediate characteristics between perfectly crystalline and partly metamict crystals: deviation from 1008 cm^{-1} of the $\nu_3(\text{SiO}_4)$ band, and values of FWHM of 10.9 ± 1.4 (1σ) (when it is $<3\text{ cm}^{-1}$ for very well-ordered ZrSiO_4 and $>30\text{ cm}^{-1}$ for metamict zircon [Zhang et al., 2000; Nasdala et al., 2001]). From the theoretical α -dose calculated for the zircon crystals ($3.84 \times 10^{18}\text{ }\alpha/\text{g}$) it is expected that they exceed the first percolation threshold (around $2.2 \times 10^{18}\text{ }\alpha/\text{g}$; Salje et al., 1999 and Pidgeon, 2014). However, plotting the global theoretical α -dose of zircon crystals ($3.84 \times 10^{18}\text{ }\alpha/\text{g}$) against the measured FWHM values revealed a deviation from the expected curve for unannealed zircon (Palenik et al., 2003). This indicates they underwent annealing and confirms they are not metamict (Figure S3). We thus infer

that the observed low-temperature decomposition cannot be explained by metamictization.

Post-Experiment Characterization

The grain-to-grain variations in observed decomposition can be explained by variable local chemical conditions or by variable individual properties of the crystals. We surmised that the latter did not play a major role in rim formation in our experiments. This conclusion is supported by the fact that no preferential dissociation was observed for inclusion-bearing crystals compared to others, and whenever alteration rims occur, they affect either all the crystals or all those in the same area of the sample. However, the individual properties must be considered whenever dissociation is observed in isolated crystals. Additionally, any possible temperature variation in the same experiment likely did not play a significant role, as the volume of the vessels used is very small ($\sim 0.03\text{ cm}^3$), limiting temperature gradients within the sample. In these experiments, the key factor for dissociation is considered to be the variable distribution of reagents in the volume surrounding zircon.

The dissociation of zircon, forming coronitic rims, is observed starting from a temperature of 900°C when caliche and NaCl are present. With these reagents and an increase in temperature to 1000°C , the reaction observed is more extensive, leading to the formation of thicker and more common rims. Instead, when NaCl is the only reagent, dissociation occurs starting from 1000°C , in

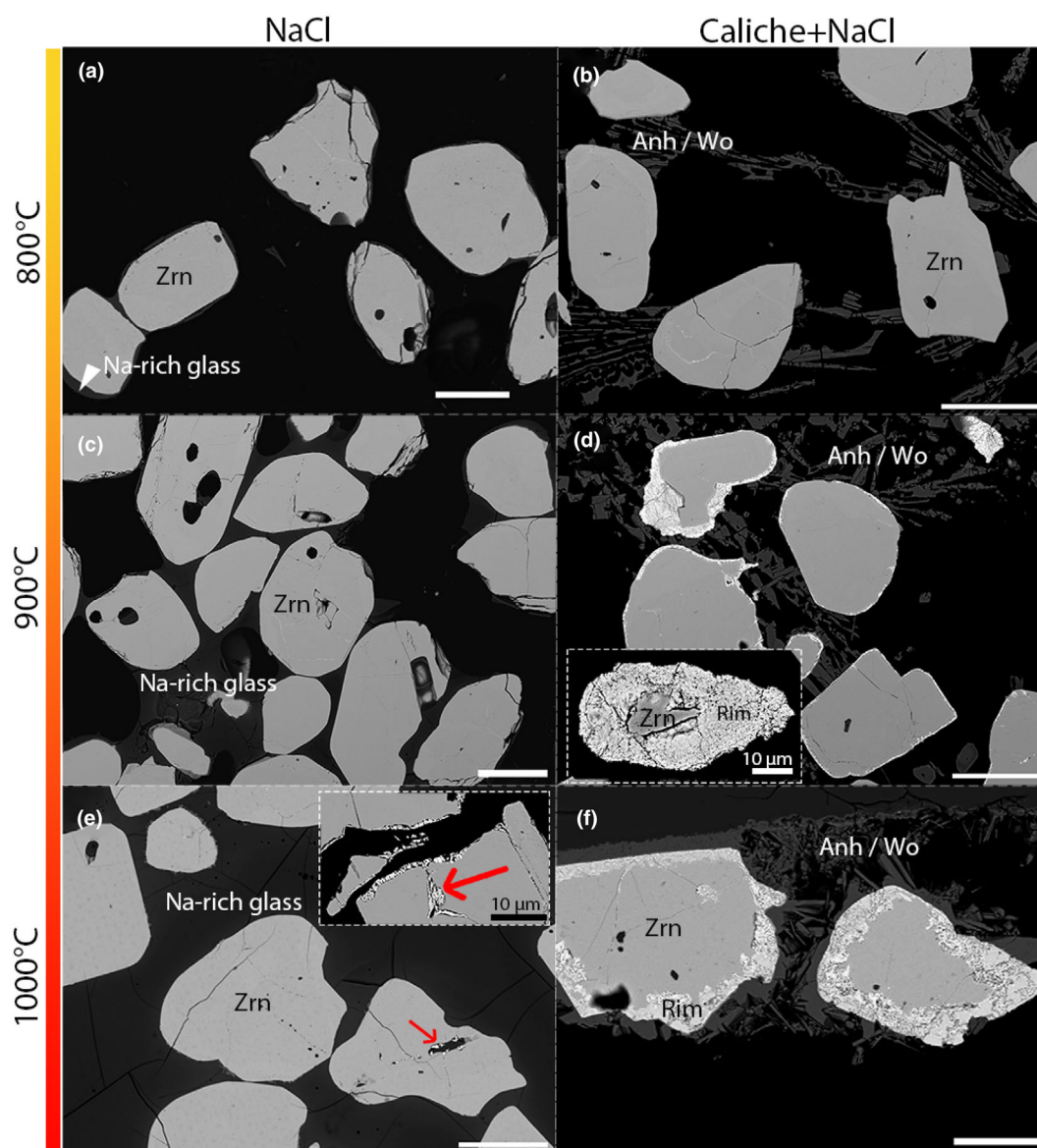


FIGURE 3. Backscattered electron images of the experiments conducted with NaCl (a, c, e) or NaCl + caliche (b, d, f), at $T = 800^{\circ}\text{C}$ (a, b), 900°C (c, d), and 1000°C (e, f). In the inset in (d), there is a zircon that underwent severe dissociation in the same experiment. Zircon dissociation is seen in d, e, and f. Red arrows point to dissociation in cracks and inclusions in the experiment with NaCl at 1000°C (with heating duration of 6 h, and 30 min for the inset image; the greater extent of dissociation at 30 min is not representative of all the grains in the same experiment and could be due to local more favorable conditions). Abbreviations: zircon (Zrn), skeletal crystals of anhydrite and wollastonite mixed (Anh/Wo). All the scale bars indicate $50\ \mu\text{m}$ (unless otherwise stated).

inclusions, fractures, or partly along the border of crystals. Therefore, the dissociation of zircon is highly favored by the occurrence of a more complex reaction environment (caliche + NaCl), even if the favorable conditions for the dissociation reaction can be heterogeneously distributed in the reaction vessel (i.e., not all the zircon crystals behave in different regions of the same experiment and the total area analyzed for each experiment is only $\sim 0.1\ \text{cm}^2$). Finally, the dissociation of ZrSiO_4 in rims is not necessarily associated with the

presence of baddeleyite (ZrO_2). For the experiments where the dissociation of ZrSiO_4 occurs, we propose the following interpretation:

1. **$T = 900\text{--}1000^{\circ}\text{C}$, caliche + NaCl.** Gypsum and NaCl (with melting points of $200\text{--}300^{\circ}\text{C}$ [after a starting release of H_2O at 163°C] and 800°C , respectively) act as fluxes, lowering the temperature at which zircon dissociates. As documented in hydrothermal experiments (Lewerentz et al., 2019), the importance

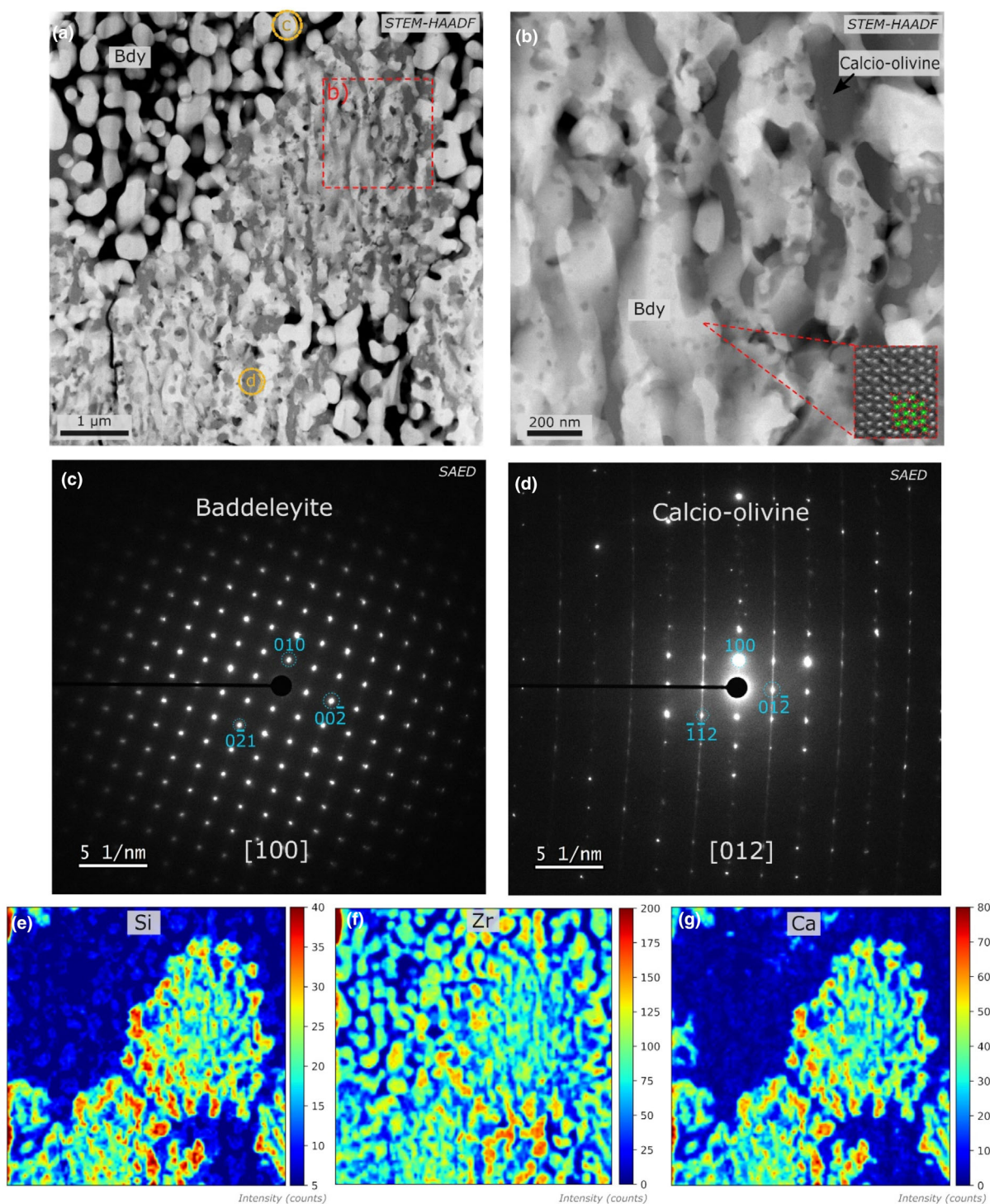


FIGURE 4. (a, b) STEM-HAADF image of a local part of the FIB sampled in the zircon rim in the experiment conducted at 1000°C, with caliche + NaCl. The atomic model of baddeleyite (Bdy) on top of the STEM-HAADF image matches the atomic lattice. (c) Indexed SAED pattern of baddeleyite along the $[100]$ direction. (d) Indexed SAED pattern of calcio-olivine along the $[012]$ direction. Distortion in the SAED pattern is visible. The first-order Laue zone reflections confirm the zone axis. (e–g) Elemental composition of phases in the rim (a): Si, Zr, and Ca, respectively. Two different textures are present: (i) only baddeleyite (Bdy) and (ii) baddeleyite intermixed with the Ca_2SiO_4 phase that potentially contains traces of Zr.

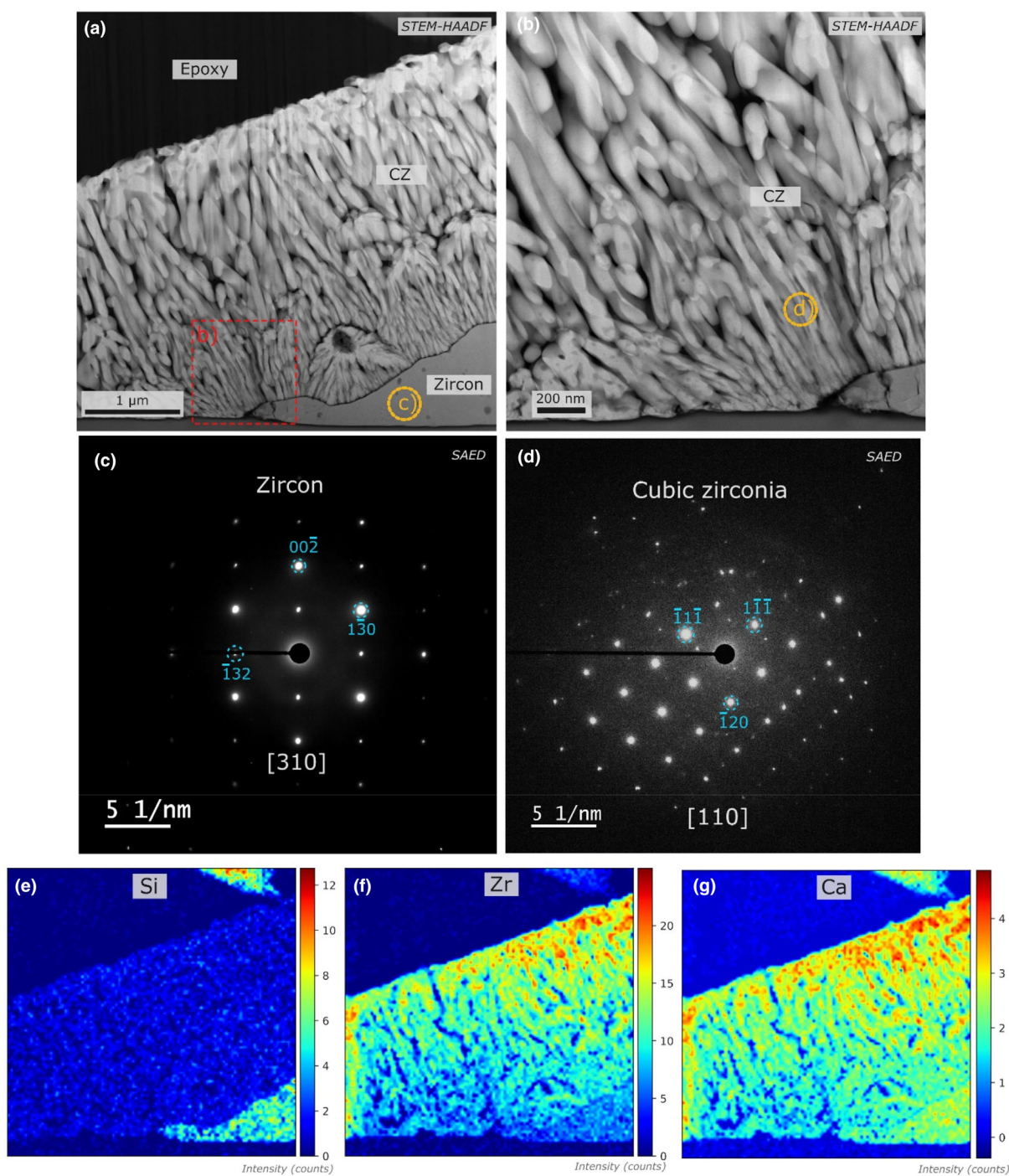


FIGURE 5. (a, b) STEM-HAADF image of dissociated rims in the experiment conducted at 900°C, with caliche + NaCl. (c, d) Diffraction patterns of identified zircon crystal and cubic zirconia (CZ). (e–g) Elemental composition of phases in the rim: Si, Zr, and Ca, respectively. Cubic zirconia (ZrO_2) contains a significant proportion of CaO in its structure ($\sim 10\%$). The zircon rim is homogeneous (only composed of one phase).

of Ca is that it keeps the Si-activity low, forming calcium silicates in the matrix; this way restoring an undersaturated environment in the melt—a condition necessary for ZrO_2 to form. However, in this

experiment, we observe that the ZrO_2 phase in the dissociation rims is not baddeleyite, but rather a cubic CaO-bearing ZrO_2 polymorph. This is due to the high Ca activity in the system, in accordance with

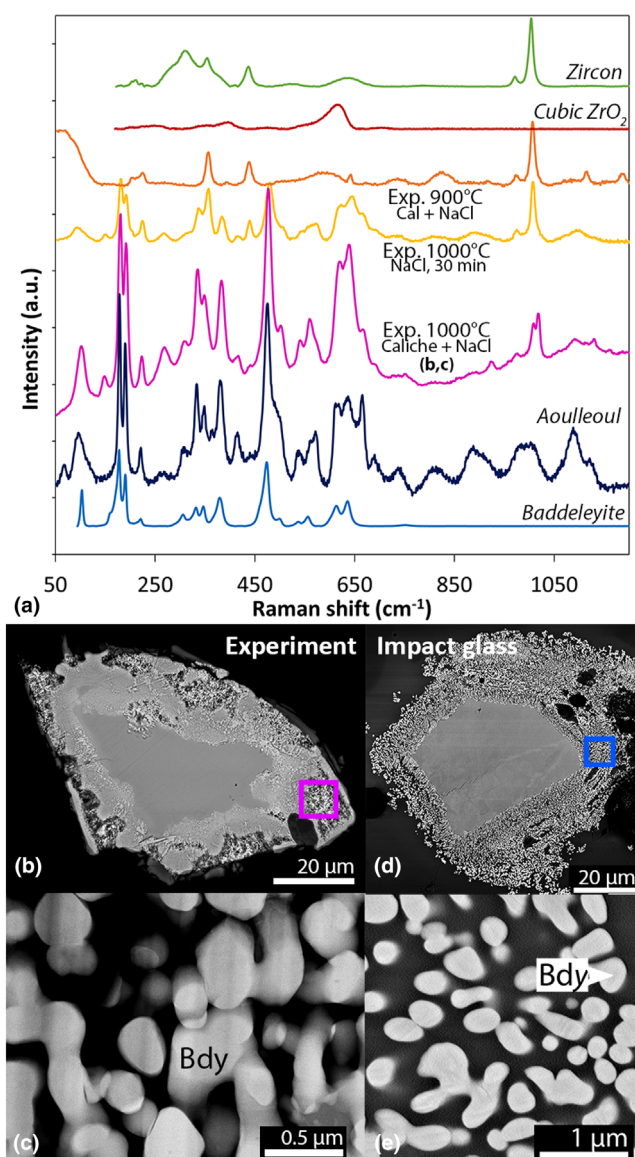


FIGURE 6. (a) Raman spectra of (i) zircon (Zrn) from the RRUFF Database (#R050034)—in green; (ii) cubic ZrO₂ from the RRUFF database (#R040142)—in red; (iii) zircon rim in the experiment at 900°C, caliche + NaCl—in orange; (iv) zircon rim in the experiment at 1000°C, NaCl, 30 min—in yellow; (v) zircon rim of the experiment at 1000°C, caliche + NaCl—in pink; (vi) dissociated zircon in an impact glass (Aouelloul, from Pellegrino, 2021)—in dark blue; and (vii) baddeleyite (Bdy) from the RRUFF Database (#R060078)—in light blue. (b) BSE image of dissociated zircon experimentally formed (1000°C, caliche + NaCl); (c) STEM-HAADF image of baddeleyite crystals in (b). (d, e) BSE images of naturally dissociated zircon in Aouelloul impact glass (Pellegrino, 2021). The colored boxes in (b) and (d) are indicative of the zoomed image in (c) and (e), and on the position in which the Raman spectra were acquired.

the ZrO₂-CaO phase diagram (Duwez et al., 1952; Szczepa & Pędzich, 2010). At this temperature, since less SiO₂ is released from the dissociation of zircon

(and from the vessel), the Ca activity remains high in the melt, destabilizing the formation of baddeleyite at the rim of zircon. Increasing temperatures at 1000°C, more Ca reacts with the melted SiO₂ in the matrix, lowering Ca activity: baddeleyite is stable, and the remaining Ca in proximity to the zircon is retained in the Ca₂SiO₄ phase included between baddeleyite crystals in the rim (Figure 4).

2. **T = 1000°C, NaCl.** In experiments with only NaCl, the melting temperature of the SiO₂ glass of the vessel is also lowered, causing the inner part of the vessel to melt and form a layer of Na-rich glass that embeds zircon crystals, whose abundance is proportional to temperatures—(see Figure 3, left column). For these experiments, dissociation and formation of baddeleyite occur at 1000°C, but to a lesser extent. Baddeleyite forms just in fractures and inclusions of zircon (also documented in natural cases like Pica glass, see figure 3d in Schultz et al., 2022a), which may be due to the high Si activity of the melt (SiO₂ oversaturated system) or facilitated by the presence of weak points in the crystals, i.e., where there are inclusions and fractures.

Experimental and Natural Zircon Dissociation

No phases other than ZrO₂ and SiO₂ are documented in the dissociated rims of zircon found in impact glasses (Cavosie, Timms, Ferrière, et al., 2018; Timms, Erickson, Pearce, et al., 2017), presumed airbursts (e.g., Schultz et al., 2022a) and fulgurites (Kenny & Pasek, 2021). However, a positive identification of baddeleyite is not always presented, e.g. using Raman spectroscopy or diffraction patterns, and the zircon dissociation product is only evidenced as a heavier and Zr-rich compound (e.g., Bunch et al., 2021; Schultz et al., 1994, 2022a). Instead, in hydrothermal experiments (P = 130–1000 MPa, T = 400–900°C), when zircon is reacting with Ca-rich fluids (mainly CaCl₂ and Ca(OH)₂ diluted in H₂O) other Ca- or Ca/Zr-rich phases form together with baddeleyite (Geisler et al., 2001; Lewerentz et al., 2019), similarly to what we observed in our dry experiments (rims of baddeleyite plus Ca₂SiO₄ or cubic ZrO₂ incorporating ~10% CaO). The occurrence of different ZrO₂ polymorphs in zircon rims is documented in naturally dissociated zircon (Chinchalkar et al., 2024; Timms, Erickson, Zanetti, et al., 2017; Tolometti et al., 2022). The significance of cubic zirconia lies in its use as an indicator of temperatures >2370°C, providing evidence of a superheated melt during glass formation, and its identification is achieved through EBSD phase heritage/reconstruction from monoclinic zirconia (baddeleyite) (Cayron, 2007; Cayron et al., 2010). In our experiments, cubic zirconia crystallization at lower

temperatures is possible due to the stabilizing effect of CaO (as documented also for industrial applications by Swab, 2001; Duwez et al., 1952).

Dissociated zircon is documented in different cases of alleged impact or airburst glasses as evidence of extreme temperature conditions, and for this reason, deserves to be revisited, based on re-evaluation of the temperature estimate: Bronze Age archaeological sites (Bunch et al., 2021 and related papers, refuted by Jaret & Scott Harris, 2022); the various Argentinian Pampa glasses, including Rio Cuarto glass (Schultz et al., 1994, 2004); and Pica glass from the Atacama Desert in Chile (Schultz et al., 2022a, 2022b). Alternative explanations for these observations may be combustion in plant-rich soils (Melson & Potts, 2002; Svensen et al., 2003), dry vegetation fires (Baker & Baker, 1964; Vélain, 1878), or past human activity, including metallurgy (Chirikure et al., 2010; Thy et al., 1995), as reviewed by Cicconi et al. (2022).

The case of Pica glass has been used as a reference for our experiments (i.e., caliche soil from the Atacama Desert was used as a reagent). As for other cases, the identification of dissociated zircon was used as evidence of a very high-temperature process ($\sim 1700^\circ\text{C}$), only reachable on a large surface by the kinetic energy dissipation of a high-velocity extraterrestrial body or by a lightning strike. The lack of an impact crater and glass transport as ejecta was explained by an atmospheric airburst (e.g., Boslough & Crawford, 2008). However, we propose that lower-temperature thermal events affecting the Atacama Desert surface, where caliche and salt-rich soils are ubiquitous (Voigt et al., 2020), could produce dissociated zircon at temperatures as low as $\sim 900^\circ\text{C}$, that do not necessarily imply events like meteoritic impacts and airbursts. The baddeleyite (ZrO_2) formed at 1000°C in our experiments is texturally and spectroscopically similar to rims formed around zircon dissociated by impact events (Figure 6b,d). Our experiments, however, differ from dissociated zircon reported in the literature by the presence of an interstitial Ca-rich olivine between baddeleyite crystals and the finer grain size of baddeleyite (coarser grains would be likely produced with longer duration or higher temperature). One experiment showed a Zr-rich rim composed not of baddeleyite but of a cubic ZrO_2 with 10% CaO, which could have been easily mistaken for baddeleyite due to its small grain size if diffraction analysis had not been performed.

For this reason, we suggest that a more careful approach is needed in the use of dissociated zircon and the presence of baddeleyite to establish the origin of unknown glasses (when other diagnostic shock features are not present). Moreover, a detailed characterization of rims for naturally dissociated zircon is not always done, and the diversity between natural and experimental cases

could be due to the lack of in-depth investigation of the variety of natural samples documented.

Finally, it is necessary to recognize that this experimental study is an oversimplified first attempt to explore the question of zircon dissociation in the presence of salts, focusing on very specific, extremely alkaline conditions where zircon crystals are not embedded in the host rock but are in direct contact with the sediments or soil. In the future, further investigations should explore more heterogeneous and common compositional conditions to assess the behavior of zircon crystals under varying circumstances.

CONCLUSIONS

The detection of dissociated zircon in glasses, alone, cannot be used as an unequivocal geothermometer for the identification of impact or airburst glasses. Experiments conducted at atmospheric pressure have shown that the dissociation of zircon, forming symplectitic ZrO_2 rims, can occur at a much lower temperature ($T \geq 900^\circ\text{C}$) than the ones previously assumed ($\sim 1670^\circ\text{C}$) if zircon reacts in a more complex chemical system, e.g., in the presence of evaporite crusts rich in Ca-sulfates and NaCl acting as flux. Since the occurrence, abundance, thickness, and composition of these rims might be related to different variables (e.g., temperature, heating duration, matrix composition, presence of impurities, etc.), the minimal P–T conditions required for the dissociation of zircon should be used carefully to assess the origin of glasses. At the same time, since concentrations of Na and Ca can be very variable at a small scale in a heterogeneous sample, glass samples formed during the same geological event can show dissociated zircon or not.

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Data Availability Statement—The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Fig S1. XRD results for caliche soils. Gypsum (light green) and anhydrite (dark green) are the minerals present. The plot shows a semi-quantitative composition of 96% gypsum and 4% anhydrite based on the XRD spectrum. The reference peaks used for the identification are 96-901-3166 for gypsum and 01-072-0503 for anhydrite (intensities are not to scale). Peaks identifying anhydrite are marked with a capital 'A'.

Fig S2. Pb/U Concordia diagram of the 27 single zircon grains screened as concordant, with their 2 s uncertainty (circles). The calculated Concordia age and its 2 s uncertainty are also displayed. The two outliers that are not included in the Concordia age calculation are

shown with empty circles. The plot and calculations were generated with IsoPlotR.

Fig S3. FMHM values of the $\nu_3(\text{SiO}_4)$ band in a random set of zircon crystals versus their global α -dose radiation damage. The calibration curve for unannealed zircon is derived from Equation 4 in Palenik et al. (2003). The red squares indicate the global dose age of zircon crystals ($3.84 \times 10^{18} \alpha/\text{g}$) whose FWHM has been measured (Table S2). The global α -dose age of the zircon grains used in the present study deviates from the expected trend for unannealed zircon, indicating that they were subjected to annealing.

Table S1. Summary of U–Pb dating results of the zircon crystals used in the experiments.

Table S2. FWHM values of the $\nu_3(\text{SiO}_4)$ band and the corresponding frequencies in a random set of zircon crystals.