Natural blue zircon from Vesuvius

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Abstract
Zircon from syenitic ejecta of Vesuvius (Campania, Italy) is unusually blue, a property shared with gem zircon from Ratanakiri province (Cambodia), which turns from natural red dish-brown to blue when heated under reducing conditions. Here, the origins of these unusual crystals were traced through geochronology, trace elements, and O-Hf isotopic compositions. The causes of its colour were investigated through optical and electron microscopy, optical absorption spectroscopy, and Raman microspectroscopy. Colour stability upon heating and ultraviolet light (UV) exposure was tested using Ratanakiri zircon as a control. Vesuvius zircon contains vesiculated zones with abundant inclusions ~2.5 μm to <100 nm in diameter (mostly U-rich thorianite and pyrochlore-group minerals), while homogeneous zircon domains are high in Th and U (up to 5.9 and 1.8 wt%, respectively). Its blue colouration is stable under UV radiation, as well as heat-treatment under reducing conditions (1000 °C; >15 h). Turbid domains rich in large inclusions change to yellow-brown after heating under oxidizing conditions, while transparent domains remain pale blue or colourless. Optical absorption spectra display sharp absorption lines attributed to U⁴⁺, and slightly elevated absorption towards shorter wavelengths. The ~1007 cm⁻¹ ν₃(SiO₄) Raman band is broadened due to lattice distortion by non-stoichiometric elements in high-Th/-U zircon, whereas narrow bands in inclusion-rich domains indicate a decrease in lattice strain due to inclusion precipitation. Blue colouration in Vesuvius zircon is explained by the effect of light scattering (Rayleigh and/or Mie scattering) on highly refractive actinide-rich inclusions ranging in size from <1/10 to few multiples of the wavelengths of visible light. Inclusions likely formed during fluid-mediated coupled dissolution-reprecipitation that locally transformed lattice-strained actinide-rich zircon within several hundreds of years prior to eruption.

Keywords Blue zircon · Vesuvius · Rayleigh/Mie scattering · Optical absorption · Raman microspectroscopy · Mineral inclusions · Syenite

Introduction
Zircon (ZrSiO₄) is a common accessory mineral in crustal igneous and metamorphic rocks, which primarily originates in evolved felsic melts (e.g., granite, syenite); owing to its resistance against chemical and physical weathering, it is also widespread as a detrital phase in sedimentary settings (e.g., Deer et al. 1982; Faulkner and Shigley 1989). More rarely, zircon megacrysts occur in pegmatites or as xenocrysts in alkaline basalts and are used as gemstones due to their outstanding dispersion, reflective index and relative hardness (e.g., Faulkner and Shigley 1989; Zeug et al. 2018). While chemically pure zirconium orthosilicate is colourless, natural zircon typically shows structural imperfections such as incorporation of trace elements or radiation damage, resulting in varied colourations ranging from red, yellow, brown, green, purple and blue to black (Rossman 1981; Kempe et al. 2016; Zeug et al. 2018).
Commercially marketed blue coloured gem zircon is generally artificially produced by heat-treatment of reddish-brown natural zircon crystals (Fig. 1 a) at temperatures of ~1000 °C under reducing conditions for several hours (e.g., Satitkune et al. 2013; Wittwer et al. 2013; Zeug et al. 2018). Dark red-brown zircon crystals from the Bei Srok area (Ratanakiri province, Cambodia) are specifically susceptible to this colour change (Piilonen et al. 2018), although less intense blue colouration can also be achieved using raw material from other mines in Ratanakiri province (Piilonen et al. 2018) as well as from Chanthaburi and Kanchanaburi (Thailand; Satitkune et al. 2013; Zeug et al. 2018); Shan State (Myanmar; Zeug et al. 2018) or the Central Highlands (Vietnam; Huong et al. 2016). Also, the colour of dark green metamict zircon from Ratnapura (Sri Lanka) can be thermally enhanced to light blue by heat treatment under similar conditions (Rupasinghe and Senaratne 1986).

At present, there is no theory which can fully explain both (1) the colour change to blue induced by heating under reduced conditions and (2) the special susceptibility of Ratanakiri brown zircon for this phenomenon (Zeug et al. 2018). While the presence of a broad absorption band centred at ~640 nm was shown to be responsible for the blue colour of heated Ratanakiri zircon by optical spectroscopy, its attribution to a specific chromophore (e.g., U⁴⁺, Tb³⁺) is still problematic and controversially discussed (Zeug et al. 2018).

Understanding the causes of blue colouration in zircon is of importance for optimization of the heat-treatment technique used and can help to improve the qualitative output of these heat-treated gemstones.

Blue zircon of unambiguously natural origin has only been reported for one occurrence: volcanic ejecta from the western flank of Vesuvius volcano (Campania, Italy; Russo and Punzo 2004; Kempe et al. 2016; Zeug et al. 2018). Kempe et al. (2016) suggested that reheating of early-formed zircon crystals by ascending magma during eruption might be responsible for the blue colour; thus Vesuvius blue zircon (Fig. 1 b; Fig. S1-S2 in the electronic supplementary material (ESM)) might represent a natural analogue for heat-treated Ratanakiri-type gem zircon. Insufficient sample dimensions, however, prevented the acquisition of optical spectra (Kempe et al. 2016), and no further mineralogical characterization of Vesuvius blue zircon has been published yet. Here, we present the first comprehensive characterization of Vesuvius blue zircon (including quantitative chemical analysis of trace elements and O-Hf isotopes, geochronology, optical and electron microscopy, as well as optical absorption spectroscopy and Raman microspectroscopy) to determine the origin of these unusual crystals, while also proposing a previously undocumented mechanism for the blue colour of Vesuvius zircon that differs from that of heat-treated Ratanakiri zircon.

**Geological setting**

The Bronze Age Avellino pumice eruption (3945 ± 10 cal BP; Sevink et al. 2011) represents one of the four major Plinian eruptions of Monte Somma-Vesuvius (Campania, Italy) during the last 22 ka BP (e.g., Di Renzo et al. 2007; Santacroce et al. 2008). The vent area of the Avellino pumice eruption was located at the Piano della Gianestre, and proximal pyroclastic fall deposits were deposited at the western flank of Somma-Vesuvius (Cioni et al. 1999; Linde et al. 2017). The syenitic ejecta originated from the crystalline carapace of the magma reservoir where they crystallized from highly fractionated melts or fluids in the uppermost, most evolved sections of the magma chamber (e.g., Fulignati et al. 2004). Magmatic temperatures are estimated as ~1200 °C for the
tephritic source magma, and ~800 °C for the highly evolved, phonolitic melts erupted during the Avellino eruption (Barberi et al. 1981; Balcone-Boissard et al. 2012). Extremely high zircon saturation levels (~12,000 ppm) are expected for the mafic, tephritic source melts of Vesuvius considering the conditions in the magma chamber (T = 1200 °C; P = 0.2 GPa; Balcone-Boissard et al. 2012) and equations by Shao et al. (2019), reinforcing a propensity for zircon to crystallize from their more felsic differentiates. Slightly oxidized magma conditions with oxygen fugacity (fO2) of +1.24 above the Ni-NiO buffer (NNO) were calculated for Avellino phonolite using stable sulphur isotope ratios (Marini et al. 1998).

Materials and methods

Sample material and thin-section petrography

Two zircon-bearing syenite clasts were collected from the San Vito Quarry, Ercolano (40°49′50.91″N – 14°22′54.84″E). The medium to coarse-grained syenite is porous (pore volume ~10–30%) with a granular isotropic texture and contains as a major constituent lath-shaped and idiomorphic sanidine crystals (Fig. 2 a) up to 2 mm length, often with Carlsbad twinning. Sodalite occurs as poikilitic crystals along with opaque Fe-Ti oxides and biotite forming subhedral crystals up to 2 mm in size (Fig. 2 a). Accessoryapatite, fluorite, and members of the pyrochlore group are present as minute (<500 μm), late-formed grains in interstitial volumes between the early-formed sanidine.

Zircon crystals are euhedral to subhedral, translucent, and mostly 1–3 mm in diameter. They show a bipyramidal habit with dominating {101} faces, which is typical for U- and Th-enriched zircons (Kostov 1973). In reflected light, the zircon grains show weak pleochroism and are greyish blue to purplish blue with minor colourless, transparent domains. In transmitted light, they appear nearly colourless to light brown (Fig. 2 a). Tens of similar looking crystals were extracted from a single specimen (~7 cm in diameter) of syenite; other Vesuvius syenite clasts contain zircon with identical appearance (Fig. S1–S2 in the ESM).

Brown alluvial zircon crystals from the Ratanakiri province (Cambodia) were included for comparative purposes during heating and irradiation experiments. In total, 13 waterworn crystals 5–10 mm in diameter were studied.

Sample preparation

Vesuvius zircon crystals were separated from the syenite groundmass by gentle grinding in an agate mortar and hand-picking under a stereo microscope. Twenty selected crystals (200–800 μm in diameter) were mounted in epoxy with grains of reference zircon samples AS3 and 91,500. This mount (Erc-z1) was ground and polished with SiC grinding paper (5 μm) and diamond polishing paste (0.25 μm). In addition, multiple grains of both untreated and heat-treated Vesuvius and Ratanakiri zircon were selected for optical investigation.
and spectroscopy. These crystals were mounted in epoxy, ground to a uniform thickness between ~200 μm and 400 μm (depending on crystal size), and polished on both sides. Samples were then removed from the epoxy resin; for easier handling, zircon chips were attached to 2.5 mm copper rings using a thermoplastic adhesive. After obtaining optical absorption spectra, the adhesive was dissolved in ethanol and the zircon chips were mounted in epoxy (Erc-z2) for further characterization.

**Heating and UV irradiation experiments**

Vesuvius and Ratanakiri zircon grains were heat-treated to compare their colour changes during thermal annealing at varying $f_{O_2}$. The colour stability of the zircon grains under ultraviolet (UV) irradiation was then tested on both heat-treated and natural zircon grains. A vertical CO$_2$/CO gas mixing furnace by Gero Hochtemperaturöfen GmbH was used for experiments under reduced conditions. The furnace was held at a constant temperature of 1000 °C during the course of the experiments, considering 900–1000 °C as the typical temperature range for commercial heat-treatment of gem zircon as reported in the literature (e.g., Wittwer et al. 2013; Zeug et al. 2018). Zircon grains were placed on a platinum mesh and introduced into the pre-heated furnace. As the exact method for thermal colour enhancement remains secret and further information about the $f_{O_2}$ conditions used were unavailable (e.g., Zeug et al. 2018), experiments were run at varying $f_{O_2}$ levels maintained by adjusting the CO$_2$:CO mixing ratio (Air Liquide carbon dioxide 4.5; UN 1013, Air Liquide carbon monoxide 3.7; UN 1016) in the furnace. The following mixing ratios were used during the experiments: (1) CO$_2$:CO = 60:40 vol%; (2) CO$_2$:CO = 80:20 vol%, corresponding to $f_{O_2}$ near the IW (iron-wüstite) buffer; (3) pure CO$_2$, representing the lowest $f_{O_2}$ achievable using CO-based gas mixing furnaces. Prior to sample removal, the furnace was flooded with pure CO for about one minute to prevent the emission of CO. As quenching in cold water could potentially destroy the zircon crystals, samples were directly released from the 1000 °C hot furnace onto a ceramic plate and immediately transferred into a porcelain crucible for cooling. After a series of initial experiments, single crystals of Vesuvius blue zircon and brown Ratanakiri zircon were heated together in a pure CO atmosphere at 1000 °C for 18 h. Heat-treating under oxidizing conditions was carried out in a box furnace, where zircon grains were placed in a platinum crucible and heated for 24 h at 1000 °C in ambient atmosphere.

The stability of blue zircon colouration under UV light was experimentally tested for both Vesuvius and Ratanakiri samples, as colour changes of blue gem zircons to light brown under the influence of long-wave UV light have been described before (Renfro 2016). For this purpose, heat-treated Ratanakiri samples and untreated Vesuvius blue zircon were irradiated under both short-wave (254 nm) and long-wave (365 nm) UV light for ca. 1 h each using a Vilber Lourmat VL-4.LC with 4 W lamps.

**Optical microscopy**

A Zeiss Stemi 508 stereo microscope with an attached AxiosCam ICc1 camera was used to image doubly-polished zircon chips immersed in mineral oil using transmitted and darkfield illumination. Comparison of the colour appearance in both illuminations is a test for scattering, as long-wavelength light is scattered less than short-wavelength light, leading to a brownish-reddish tint in transmitted light, and a blueish colour in darkfield illumination (e.g., Pelto 1956). This was verified by imaging a fragment of commercially available synthetic cryolite glass (aka opal glass) under the same conditions, where the variable colour appearance is attributed to light scattering by sub-μm Ca- and Na-fluoride particles (Ryde and Cooper 1931). A similar test was performed on a piece of blue chalcedony (Fig. S3 in the ESM), another material where blue colouration has been suspected as being due to scattering (Pelto 1956).

**Scanning electron microscopy (SEM) and microtomography (micro-CT)**

Epoxy mounts were conductively coated with 3 nm gold and imaged with a Zeiss EVO MA15 scanning electron microscope equipped with a Gatan ChromaCL2 detector for cathodoluminescence (CL) imaging. Back-scattered electron (BSE) and CL images were obtained from zircon to reveal its internal structure, including growth zones and inclusions. For semi-quantitative elemental analysis using energy dispersive X-ray spectroscopy (EDS) the epoxy mounts were recoated with carbon and analyzed with an Oxford Instruments X-MaxN 150 mm$^2$ EDS detector on the same instrument. Additional imaging and elemental analysis of heat-treated Vesuvius zircon crystals were performed using a Zeiss Leo 440 instrument equipped with an Oxford Instruments X-Max 80 mm$^2$ EDS detector.

The textural arrangement of inclusions in Vesuvius blue zircon was also visualized using computed microtomography (micro-CT) X-ray analysis using a Carl Zeiss Xradia Versa-410 3D X-ray microscope. The instrument was operated with a polychromatic microfocus X-ray source (150 kV, 10 W), a 2000 × 2000 pixel noise-suppressed charge-coupled detector, and a 10× objective lens to achieve a resolution of 1.88 μm/voxel. 3201 projections over 360° were generated for the measurement. Attenuation data were reconstructed through a filtered back-projection algorithm using the XRMRe constructor software, producing a stack of 967 cross-sectional, grey-scale digital images that are displayed in animation style (see Animation S1 in the ESM).
Secondary ionization mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis

Prior to SIMS analysis, the sample was cleaned in an ultrasonic bath following a three-stage cleaning process (ammoniacal EDTA solution, deionized water, and methanol) and a conductive gold layer of 50 nm thickness was applied to the sample surface. Uranium-Th disequilibrium dating and quantification of selected trace elements (including rare earth elements, REE; Table S1 in the ESM) were carried out by SIMS using a large-geometry CAMECA 1280-HR ion microprobe. A mass-filtered \( ^{16}\text{O}^- \) primary ion beam was accelerated at \(-13\) kV to deliver a probe current of \(~60\) nA at the sample surface. The diameter of the primary beam was \(30–40\) μm, and secondary ions were extracted at \(+10\) kV with an energy bandpass of \(50\) eV. The oxygen-flooding technique (sample chamber pressure \(~1.5 \times 10^{-5}\) Pa) was used to increase the production rates of secondary ThO\(^+\) and UO\(^+\) ions (Schuhmacher et al. 1994). Secondary ions were detected by Faraday cup (FC; for species with measured intensities >\(10^6\) counts/s) and axial electron multiplier (EM; for intensities <\(10^6\) counts/s). Counting times range from 0.5 to 10 s, and intensities for \(^{230}\text{ThO}^+\) were corrected for both background masses \(244.026\) and \(246.3\). Background contributions to the measured \(^{230}\text{ThO}^+\) peak range from 1.50 to 2.18%, making the analyses insensitive to background corrections despite the young age of the Vesuvius zircon. All measurements were performed at high mass resolution (M/ΔM) of \(~7000\). A U/Th relative sensitivity factor (RSF) was calibrated on the concordant zircon reference materials AS3 (Paces and Miller 1993; Schmitz et al. 2003) and 91500 (Wiedenbeck et al. 1995, 2004) using common-lead corrected \(^{208}\text{Pb}/^{206}\text{Pb}\) ratios and the known \(^{238}\text{U}/^{206}\text{Pb}\) ages of the reference zircon samples. Three replicate long-duration measurements gave a mean RSF value of \(1.08 \pm 0.02\).

For trace element analysis, an \(~4–5\) nA beam of \(^{16}\text{O}^-\) primary ions accelerated at \(-13\) kV resulted in a lateral resolution of \(~20\) μm. Energy filtering to suppress molecular interferences was applied using a \(-100\) V offset to the nominal acceleration potential of \(+13\) kV with an energy bandpass of \(50\) eV. Mass resolution was set at \(~1800\). The following ions were detected using a single axial EM (major oxide interferences stated in parentheses; single positive ionic charge unless stated otherwise): \(26\text{Mg}, 30\text{Si}, 31\text{P}, 48\text{Ca}, 55\text{Mn}, 57\text{Fe}, 177\text{Hf}^{2+}, 89\text{Y}, 96\text{Zr}, 139\text{La}, 140\text{Ce}, 141\text{Pr}, 143\text{Nd}, 149\text{Sm}, 151\text{Eu}, 158\text{Gd}, 142\text{CeO}, 142\text{NdO}, 159\text{Tb} (143\text{NdO}), 161\text{Dy} (142\text{NdO}), 165\text{Ho} (149\text{SmO}), 168\text{Er} (152\text{SmO}), 169\text{Tm} (153\text{EuO}), 172\text{Yb} (156\text{GdO}), 175\text{Lu} (159\text{TbO}), 178\text{Hf} (162\text{DyO}), 232\text{Th}, 238\text{U}.\) Contributions of light or middle REE (LREE and MREE, respectively) to the measured intensities of the heavier REE species were corrected by peak-stripping using LREE and MREE oxide production rates determined on interference-free, doped reference glasses prepared after Drake and Weil (1972). NIST SRM 610 (Pearce et al., 1997) was used as the primary reference, and RSF accuracies were tested by analysing 91500 (Wiedenbeck et al. 1995, 2004; Yuan et al. 2007) as a secondary reference; good agreement with published data was found (Fig. 3).

Fig. 3 Chondrite-normalized REE-Y patterns of 91,500 reference zircon and Vesuvius blue zircon. Recommended abundances for CI chondrite by McDonough and Sun (1995) were used for normalization. Note low abundances of heavy REE; variations at <10-times chondrite are due to counting errors and not geochemically significant.
Quantification of Sc, Nb, and Ta required separate analytical protocols with very high mass resolution \((M/\Delta M = \sim 20,000)\) because the sole or predominant stable isotopes of these elements show isobaric interferences by hydrides and mono- or polyatomic ions: \(^{45}\text{Sc} \ (90\text{Zr}^{2+}), \ ^{91}\text{Nb} \ (92\text{ZrH}), \ ^{181}\text{Ta} \ (90\text{Zr}^{91}\text{Zr}).\) Niobium was counted in static multi-collection using an axial EM with \(^{90}\text{Zr}^{2+}\) as a reference mass source and a UHTS300S spectrometer with a 1200 grooves/mm grating, and a WITec Yvon LabRAM HR800 Raman spectrometer with a 633 nm laser source to remove all conductive coatings. A Horiba Jobin zircon and inclusions were obtained after cleaning the mount. Comparative Raman microspectroscopy spectra of Vesuvius Raman microspectroscopy were corrected for cosmic ray interference and background; band fitting used a Voigt algorithm to display FWHM values. Wavenumber calibration was performed using a built-in Ar-Hg lamp which was also used to determine spectral resolution. Gaussian fitting of the 577 nm emission line yielded a full width at half maximum (FWHM) value of 2.4 cm\(^{-1}\). A value of 2.6 cm\(^{-1}\) was used as the instrument profile function (IPF) to correct bands for spectral broadening using eq. 5b from Váčzi (2014). The ~1007 cm\(^{-1}\) \(\nu_3(\text{SiO}_4)\) Raman band of high-purity synthetic zircon (Guillon et al. 2015) yielded a FWHM of 1.9 cm\(^{-1}\) on the Jobin Yvon LabRAM HR800 (IPF = 0.8 cm\(^{-1}\)) at 633 nm and an identical value for the WITec Alpha 300R in agreement with published data (Nasdala et al. 2008a, 2008b). Effective alpha self-radiation doses were calculated for Vesuvian zircon using measured U and Th concentrations, the crystallization age obtained by U/Th isochron dating and the equation by Holland and Gottfried (1955).

**Optical absorption spectroscopy**

Optical absorption spectroscopy in the ultraviolet-visible to near-infrared (UV-VIS-NIR) wavelength range was carried out using a J&M TIDAS UV-VIS-NIR spectrometer equipped with CCD/InGaAs detectors and 10× UV-transparent objective lenses. Light sources include a Hg vapor lamp and a xenon lamp, which generated minor spectral artefacts at 656 nm, 904–1247 nm, and 1384 nm in the optical absorption spectra. Each randomly sectioned sample was measured with polarized light at its two extinction positions in cross polarized light. Light intensity without sample was tuned to 70–85% of detector saturation by adjusting the counting time (145 ms for the UV and visible ranges, 190 ms for the NIR range), and 100 cycles were measured at each position to improve the signal-to-noise ratio.

**Results**

**Microtexture, chemical and isotopic composition, and age**

Vesuvian zircon shows oscillatory zoning in all studied grains, with additional sector zoning present in a few crystals, that is
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visible both in BSE and CL images (Fig. 2 b–c; 4 a–c). Micro-
inclusions of mineral phases occur concentrated in vesicle-rich
domains where the zircon host is low in BSE intensity. These
zones are characterized by low trace element abundances
(based on SEM-EDS analysis) and are aligned along crystallo-
graphically oriented growth zones or primary cracks (Fig. 2 b–
c), which were also imaged in three-dimensions for a selected
zircon (Animation S1 in the ESM). The inclusions are of either
isometric or irregular, elongated shape and exhibit a large var-
iation in grain sizes (Fig. 2 b–d). While a few larger inclusions
up to ~60 μm in diameter are present, most inclusion dimen-
sions are in the micro- to nanometer range (~2.5 μm –
<<100 nm; Fig. 2 d). Based on combined SEM-EDS and
Raman microspectroscopy, the solid inclusions were identified as
U-, Th- and REE-rich minerals among which U-bearing
thorianite and thorite inclusions are the most abundant. In addi-
tion, inclusions of pyrochlore group members are common.
Britholite-(Ce) and steacyte (ThNa3K7-xΣ2SiO14; with x ≈ 0.5; Uvarova et al. 2004) were only identified as rare and com-
paratively large inclusions. Although SEM-EDS and Raman
microscopy methods only permitted identification of in-
clusions that were at least a few μm in diameter, similar BSE
brightness between large and small inclusions suggests that
the same phases are also present as small inclusions down to
the <<100 nm size range (Fig. 2 b–d).

Where homogeneous and with high BSE brightness, the
Vesuvius blue zircon crystals contain 59.1–66.3 wt% ZrO2 and
30.2–34.0 wt% SiO2. Minor non-stoichiometric compo-
nents include Th (0.7–5.9 wt%), U (0.3–1.8 wt%), Hf (3380–
5760 ppm), Nb (287–3150 ppm), and REE, particularly Ce
(1131–7610 ppm) and Nd (287–3150 ppm). Phosphorus
(25.1–49.1 ppm), Ti (1.68–8.10 ppm), and Ta (0.44–
4.51 ppm) are present at ppm levels; Sc (0.06–0.16 ppm)
and Mg (up to 0.42 ppm) were detected in traces. Vesuvius
zircon is characterized by unusually flat chondrite normalized
REE patterns with a negative slope and high (Ce/Yb)n values
of 13.3–196 (Fig. 3). While abundances of LREEs are highly
enriched relative to CI chondrite by a factor of up to ~105,
enrichments for MREE and HREE are only between ~20 and
700 times CI chondrite. Vesuvius blue zircon shows positive
Ce anomalies with Ce/Ce* of 3.85–17.6, with La being sig-
nificantly depleted relative to Pr and Nd. Characteristic nega-
tive Eu anomalies of Eu/Eu* = 0.22–0.58 exist. Vesuvius zir-
cron shows super-chondritic ratios of Nb/Ta (>37.0) and
(Y/Ho)n = 1.40–6.97.

Zircon δ18O averages for individual crystals (n = 20) range
between +6.5 and +8.6‰. The overall variability is about
twice that of the reference zircon, suggesting that there is
minor heterogeneity. Hafnium isotopic compositions are ho-

geneous with an average εHf value of ~0.4 ± 0.5 (1 stan-
dard deviation, n = 19). Vesuvius whole-rock compositions
from the literature have values of δ18O = +9.8 (two nearly
identical compositions for Avellino pumice data; Ayuso
et al. 1998) and εHf = +0.5 (two nearly identical
compositions for Vesuvius mafic lava; Gasperini et al.
2002). The similarity of εHf between Vesuvius zircon and
lava is a strong indication for consanguinity, because zircon
faithfully records the Hf-isotopic composition of its parent
melt. By contrast, zircon δ18O values are at least 1.2‰ lower
than whole-rock compositions (assumed to be representative
of the melt). Model zircon crystallization temperatures
<540 °C are obtained from Δ18Omelt-zircon as calculated for
fractionation factors from Qin et al. (2016) and a melt com-
position equivalent to Avellino pumice (Ayuso et al. 1998).
Such low temperatures are indicative of subsolidus re-
crystallization rather than equilibrium crystallization at mag-
matic temperatures.

Vesuvius blue zircon (238U)/(232Th) ratios (parentheses
indicate activity ratios) range from 0.75 to 1.60 (Table S3 in the
ESM). With (230Th)/(232Th) below unity (values ranging from
0.901 to 0.930), most analyses plot to the right of the equiline
which is defined by a slope of unity and therefore with activity
ratios indicating secular equilibrium (Fig. 5). The deviation
of the data from the equiline indicates strong (230Th)/(238U)
dis-equilibrium in Vesuvius zircon and hence a young age. Linear
fitting of all zircon analyses yielded an isochron age of 3.41 ±
0.59 ka (1σ; MSWD = 0.81; n = 20; Fig. 5), which agrees with
the published eruption age for Avellino pumice (3.95 ±
0.01 ka; 14C dating of organic matter within distal fall out
units; Sevink et al. 2011) within uncertainties, further
underscoring that syenitic ejecta are co-genetic with the
erupted phonolite magma.

Colour in optical microscopy

Cryolite glass imaged as a reference for scattering displays
blue streaks in darkfield illumination. These streaks appear
orange-brown colour in transmitted light (Fig. 6 a–b), whereas
transparent domains are black in darkfield. Similarly, some
parts of Vesuvius zircon appear blueish-purplish in darkfield
illumination (Fig. 6 c–d). In contrast to the cryolite glass, some
zircon domains are nearly opaque in transmitted light due to
abundant inclusions which are larger than those in the glass;
where inclusions are absent and light is transmitted, however,
the transparent light colour is mostly greyish-brown with
weak hints of purple (Fig. 6 c–d). Heated blue Ratanakiri
zircon sectioned and polished to the same thickness as the
Vesuvius zircon chips is colourless in both transmitted light
and darkfield illumination (Fig. 6 e–f).

Colour change under heating and irradiation

In our heating experiments, the original, dark-brown colour of
Ratanakiri zircon vanished after thermal annealing at 950 °C
for 1 h; it could not be restored by subsequent heating, neither
under oxidizing nor reducing conditions. Intensities of blue
colouration in heat-treated Ratanakiri zircon are highly dependent on the individual composition of the grains, as samples from the same experimental runs attained different shades of blue. Regardless, the intensity of the blue colouration generally increased with lower $f_{O_2}$ and increasing heating duration. The most intense blue colour in Ratanakiri zircon was achieved by heating at 1000 °C in 100% CO atmosphere for >15 h. Under oxidizing conditions, untreated dark-brown and previously blue Ratanakiri zircon faded to light brown or orange after being heated to 1000 °C for 24 h in ambient air, consistent with observations in Zeug et al. (2018).

After heating under oxidizing conditions Vesuvius zircon crystals developed a muddy yellow-brown colour (Fig. 7 a). Heat-treatment under reducing conditions did not induce significantly changes of colouration in Vesuvius blue zircon (Fig. 7 b–c). The yellow-brown colouration generated by heating under oxidizing conditions is most prominent in inclusion-rich zircon domains (Fig. 7 d–h), whereas transparent zircon zones devoid of microscopically visible inclusions still retain a pale blue colouration (Fig. 7 a).

UV radiation had no visible effect (neither short-wave nor long-wave) on the colouration of Vesuvius zircon. By contrast, the blue colour of heat-treated Ratanakiri zircon turned into a slightly brownish hue when irradiated by long-wave UV light (365 nm).

**Optical absorption spectroscopy**

Optical absorption spectra obtained from Ratanakiri zircon (a heat-treated blue gem crystal) show a strongly polarized absorption band at ~640 nm that is typical for blue zircon from Ratanakiri (Zeug et al. 2018) and elsewhere (Fig. 8 a–b). The optical absorption spectra of untreated and heat-treated (both oxidizing and reducing conditions) Vesuvius zircon, however, are characterized by the presence of multiple sharp lines that are typical for zircon rich in actinides and lanthanides (e.g., U, Th, Ce) (Nasdala et al. 2003) and a gentle increase in absorbance towards shorter wavelengths (Fig. 8 c–d; Table S4–5 in the ESM). All major sharp bands can be attributed with U$^{4+}$-bands (e.g., at 654.0 nm, 691.2 nm, and 1115.5 nm) detected in U-rich zircon, e.g. Mogok green zircon (Fig. 8 c; http://minerals.gps.caltech.edu/FILES/Visible/zircon/Index.html; last accessed 10.03.2020). Heated and natural Vesuvius zircon samples share the same spectral characteristics and show minor differences in total intensities, with higher intensities observed for the sample heated under oxidizing conditions and decreased absorption for the sample treated under reduced conditions.

**Raman microspectroscopy**

Vesuvius blue zircon shows a FWHM for the $\nu_3$(SiO$_4$) Raman band at ~1007 cm$^{-1}$ ranging from ~3 to ~9 cm$^{-1}$ (Fig. 4 and

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**Fig. 4** Overview BSE (a) and CL (b) images of natural Vesuvius zircon (grain 19) showing oscillatory zonation cross-cut by intergrowth of low BSE intensity zircon domains dotted with abundant inclusions showing high BSE intensities. Raman microspectroscopy map (c) generated with a 532 nm laser using lateral step widths of 1 µm. Colour scale shows the full width at half maximum (FWHM) of the ~1007 cm$^{-1}$ $\nu_3$(SiO$_4$) band after correction for spectral broadening. Note the reduction in FWHM in irregular, inclusion-rich zones (especially in the left part of the exposed crystal), as well as in growth domains with high BSE intensities. Crosses are fiduciary marks.
Fig. S4–6 in the ESM). A broad photoluminescence signal causing elevated backgrounds at ~1007 cm$^{-1}$ is present in some spectra generated with 633 nm excitation (Figs. S4 and 5 in the ESM at points 1 and 4), but not in the spectra obtained with 532 nm excitation. Raman microspectroscopy mapping reveals that homogeneous zircon domains high in BSE intensity generally have broader (and possibly split) bands compared to domains low in BSE intensity (Fig. 4 c). Mapping also reveals that the original oscillatory zonation is overprinted by irregular and often cross-cutting zones where the FWHM of the ~1007 cm$^{-1}$ band is reduced relative to the original domain; these zones are typically inclusion-rich where zircon shows low and inclusions high BSE intensities (Fig. 4). Variations in FWHM for the ~1007 cm$^{-1}$ band also correlate with a minor shift to lower Raman-shift values e.g. from 1008 cm$^{-1}$ (low BSE intensity) to 1004 cm$^{-1}$ (high BSE intensity; Fig. S4–S6 in ESM). Bands are narrowest (~3 cm$^{-1}$) in domains with large inclusions where zircon has low BSE intensity (point 1 in Fig. 4) and in those with low BSE intensities and no inclusions (point 2). High-brightness BSE domains without inclusions have intermediate FWHM values (point 3), whereas the widest bands (~9 cm$^{-1}$) were detected in zones where zircon has high BSE brightness, and inclusions are scarce or absent (point 4; see also example spectra for these domains in Fig. S5 in the ESM).

Using Th and U abundances of homogeneous zircon showing high BSE intensities and the U-Th isochron age, an effective self-radiation dose of $2.20 \times 10^{11} \alpha$/mg was calculated for Vesuvius zircon. Because of the wt% level Th and U abundances of Vesuvius zircon, these low effective $\alpha$-doses are owed primarily to minor exposure times to self-radiation due to their very young crystallization age. This calculated dose value is well below the minimum self-radiation dose of $0.1 \times 10^{18} \alpha$/g (Zhang et al. 2000, Nasdala et al. 2004) required to induce minute, spectrscopically detectable structural damage in zircon. Therefore band broadening in Vesuvius zircon is not due to accumulated radiation damage (e.g., Nasdala et al. 1998).

**Discussion**

As the only naturally occurring blue zircon known, syenite-hosted zircon from the Avellino eruption of Vesuvius is a very unusual material whose origins and causes of colour deserve attention. Geochronology and O-Hf isotopic data are consistent with crystallization of zircon from magmas that were consanguineous to the host phonolite. Textural evidence of interstitial zircon growth along with the unusual enrichment in LREE imply late-stage crystallization in highly evolved residual melts in a largely solidified part of the pre-eruptive magma reservoir. Oxygen isotopes are consistent with subsolidus crystallization at conditions significantly below phonolite eruption temperatures of ~800 °C (Barberi et al. 1981; Balcone-Boissard et al. 2012). In this regard, Vesuvius blue zircon is genetically similar to syenite-hosted...
zircon from other alkaline magma systems (e.g., Eifel; Schmitt et al. 2017).

Disparate behaviour under long-wave UV, strongly divergent trace element compositions, and prominent differences in optical absorption spectra, suggest that the colouring mechanism for natural Vesuvius zircon must be different from that of heat-treated Ratanakiri zircon. Because the blue colouration of natural Vesuvius zircon remained stable after UV irradiation and heating, electron or hole defects can be ruled out as causes for its colour (e.g., Kempe et al. 2016). Trace elements do not seem to significantly contribute to the colouration of Vesuvius blue zircon either. Vanadium, which is responsible for the

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**Fig. 6** Darkfield (DF) and plane-polarised transmitted light (PPL) photomicrographs of synthetic cryolite glass (a–b), natural Vesuvius blue zircon (c–d), and blue Ratanakiri zircon, which was heat-treated under reducing conditions (e–f)

**Fig. 7** Vesuvius zircon crystals after heating under (a) oxidizing and (b) reducing conditions. Areas which have remained bluish after heat-treatment under oxidizing conditions are marked by dashed lines in (a). Polished thick sections of natural (c) and (d) Vesuvius zircon heat-treated under oxidizing conditions in reflected light (RL) on white background; e–f the same crystals in PPL on a dark background and g–h as BSE images. Arrows are drawn as fiduciary markers indicating the orientation of the crystals
Natural blue zircon from Vesuvius
colour of synthetic blue zircon pigment (e.g., Demiray et al. 1970; Waal et al. 1996), is present in concentrations below SIMS limits of detection (<<1 ppm), and absorption bands attributed to V were not observed in the optical absorption spectra of Vesuvius zircon (Fig. 8 d). Other chromophores typically responsible for blue colouration in minerals (e.g., Fe$^{2+}$, Cu) are also insignificant in zircon. Synthetic zircon doped with tetravalent U is known to show a purplish-blue colour (Zeug et al. 2018). While U$^{4+}$ is present in Vesuvius blue zircon at highly elevated concentrations as indicated by optical absorption spectroscopy and chemical analysis, its contribution to the blue colour of Vesuvius zircon is deemed negligible because the most U-rich domains (which lack inclusions) appear nearly colourless in transmitted light (Fig. 6 d).

Instead, we attribute the blue colour in Vesuvius zircon to Rayleigh- and/or Mie-type scattering of incident light by submicrometre-sized inclusions, where long (red) wavelengths are less efficiently scattered compared to short (blue) wavelengths (see review of this effect in minerals by Rossman 2014). Rayleigh scattering occurs for particle sizes considerably smaller (by <1/10) than the wavelength of the incident light, and it is strongly wavelength-dependent; Mie scattering in contrast refers to scattering from particles similar to or larger than the wavelength of the incident light, and it shows a weaker dependence on wavelength than Rayleigh scattering (e.g., Lockwood 2016). Scattering has been cited as the origin of colour in blue quartz, where submicrometric crystallites of rutile, mica or ilmenite are present (Zolensky et al. 1988; Seifert et al. 2011). In corundum, light scattering is caused by rutile micro-inclusions (Wehrmeister and Häger 2006; Krzemnicki et al. 2019).

Other geomaterials where blue colouration has been attributed to scattering include blue chalcedony (Pelto 1956) and moonstone (alkali feldspar; Fritsch and Rossman 1988). In blue zhamanshinite impact glass (Zolensky and Koeberl 1991) and blue-coloured fulgurite (Feng et al. 2019), microspherules of glass formed by liquid-state exsolution are responsible for light scattering and ultimately for the blue colouration (Feng et al. 2019). Previous studies on blue

![Fig. 8](http://minerals.gps.caltech.edu/FILES/Visible/zircon/Index.html) Optical absorption spectra in the UV-VIS-NIR wavelength range for a) heat-treated “Burma” blue zircon; b) natural and heat-treated Ratanakiri gem zircon; c) natural green metamict zircon from Mogok; d) natural blue Vesuvius zircon. Spectra of Ratanakiri and Vesuvius zircons are in random orientation; spectra were generated in two positions, rotating the specimens by 90°. The marked absorption lines in c and d are attributed to U$^{4+}$. Spectra for “Burma” blue and Mogok green zircon from: http://minerals.gps.caltech.edu/FILES/Visible/zircon/Index.html (last accessed 10.03.2020)
quartz indicate that a relatively small inclusion density (0.5–1.7 particles <55 nm in diameter per μm³ for Llano blue quartz) is sufficient to induce blue colouration in a mineral (Seifert et al. 2011).

Rayleigh and/or Mie scattering is consistent with the blue appearance of Vesuvius zircon because of the following observations: (1) Vesuvius zircon is colourless in transmitted light, and blue only when obliquely illuminated; this is also the case for synthetic cryolite glass whose changing colour appearance is caused by light scattering (Figs. 1 and 6); (2) the blue colouration in darkfield illumination is strongest in domains where nano-inclusions dominate with dimensions smaller than the wavelength of visible light (Figs. 2 and 6); and (3) absorbance generally increases towards shorter wavelengths (Fig. 8). Hence, the ultimate cause for scattering in Vesuvius zircon is the presence of abundant actinide-rich nano-inclusions (e.g., U-rich thorianite), which have a higher index of refraction (n) than the zircon host (e.g., n = 2.11 for cubic ThO₂ and 1.93–1.99 for zircon at λ = 589.3 nm; Medenbach and Shannon 1997). These inclusions are heterogeneously distributed throughout the crystals (Figs. 2 and 4); in domains where they are most abundant, inclusion density is estimated to be >5 particles of <100 nm size per μm³ based on high-resolution BSE images (Fig. 2), which is consistent with the inclusion density in blue quartz (Seifert et al. 2011). Because the size of these inclusions continuously extends across the relevant particle sizes for Rayleigh and Mie scattering (Figs. 2 and 6), both processes are expected to contribute to the blue colour appearance of Vesuvius zircon.

Inclusions of Th- and U-rich phases in Vesuvius zircon are always associated with abundant pore space and low BSE intensity zircon domains. This suggests a cogenetic formation by exsolution from primary Th- and U-rich zircon along with a reduction in volume. Similar textures, albeit with a different mineralogy of the inclusion assemblage, have been described for zircon from Island Park-Mount Jackson Rhyolite (Yellowstone, USA) and are interpreted as the result of a coupled dissolution-reprecipitation processes in the presence of hydrothermal fluids (Troch et al. 2018). In this scenario, primary magmatic zircon rich in Th and U becomes metastable upon cooling, causing dissolution along fluid pathways (e.g., fractures) when it resides in a crystalline and fluid-rich part of a magma reservoir. The resulting re-equilibrated assemblage involves secondary zircon with low trace element abundances, as well as Th- and U-rich phases and pore space, effectively minimizing lattice strain in the zircon crystal (Geisler et al. 2007; Troch et al. 2018). This dissolution-reprecipitation process is also supported by the results of Raman microspectroscopy, which shows narrower ν₃(SiO₄) bands for the often irregular and vein-like recrystallized domains compared to primary and undisturbed zircon zones (Fig. 4). Narrowing of the Raman band reflects a reduction in lattice strain during recrystallization and formation of more stoichiometrically composed zircon compared to the high actinide abundances in primary zircon. Notably, inclusion formation is less prominent in zircon domains, where primary Th

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**Fig. 9** Schematic summary of the main conclusions: a) formation of Th-U-rich mineral inclusions and secondary low-Th-U zircon by dissolution-reprecipitation of primary high-Th-U zircon along fluid pathways; b) Rayleigh/Mie scattering, preferentially of shorter wavelengths, on numerous tiny inclusions in Vesuvius blue zircon causes blue colouration when viewed in reflected light. In contrast, the zircon appears reddish brown in transmitted light due to the less intense scattering of long (red) wavelengths.
und U abundances are low as indicated by homogeneously low BSE intensities and comparatively narrow Raman bands (e.g., point 2, Fig. 4. Our preferred model for the formation of Vesuvius blue zircon (Fig. 9) also explains why it is rare in nature: it requires high abundances of Th and/or U to exsolve tiny inclusions, but at the same time these actinide-rich zircon crystals are highly vulnerable to internal radiation damage which produces electron traps and the corresponding brownish red to nearly black (“malachon”) colour of zircon (Rossman 1981).

The emergence of a yellowish-brown colouration in inclusion-rich, re-equilibrated zones of Vesuvius zircon after heat treatment under oxidizing conditions remains ambiguous. Scanning electron microscopy and Raman microspectroscopy failed to detect chemical or structural changes in either host zircon or inclusion phases, and inclusions appeared unchanged in frequency, size, and shape after heating. Optical spectroscopy of the brown-coloured domains was not successful due to their poor transparency, resulting in insufficient transmission rates. The most reasonable redox-sensitive chromophore would be $U^{4+}/U^{5+}$, as a contribution of $Fe^{2+}/Fe^{3+}$ is unlikely based on the low Fe abundances in zircon and most inclusion phases (e.g., thorianite, thorite) as indicated by SIMS analysis and optical absorption spectroscopy (see spectrum obtained on transparent domains in heated Vesuvius zircon; Table S6 of the ESM). Oxidation of Fe-bearing pyrochlore group minerals, however, is possible as they contain up to 0.5 wt% Fe as detected by standardless EDS analyses. Oxidation of $Fe^{3+}$ and possibly $U^{4+}$ in inclusion phases is thus tentatively invoked as the cause for the brown colouration of heat-treated Vesuvius zircon.

### Conclusion

Vesuvius blue zircon is an unusual mineral which combines highly elevated concentrations of Th (up to 5.9 wt%) and U (up to 1.8 wt%) with low radiation damage due to its very young ($3.41 \pm 0.59$ ka) crystallization age. Partial dissolution-reprecipitation of originally high-Th and high-U zircon occurred along fractures or internal growth zones prior to eruption, causing exsolution of abundant micro- to nanometre scale mineral inclusions. Rayleigh and/or Mie scattering of light on the smallest of these inclusions is a feasible mechanism to explain the blue colour of Vesuvius zircon. Vesuvius zircon is thus not a natural occurring analogue for heat-treated blue zircon gemstones, which are low in actinides and lack corresponding mineral inclusions that could cause scattering (Zeug et al. 2018).

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