

Research Paper

Periodic SiO₂ mineralization dated by LA–ICP–MS and ID–TIMS, an example from Golobradovo agate, Rhodopes, BulgariaArmin Zeh^{a,*}, Jens Götze^b, Marion Tichomirowa^b, Alexandra Käbner^b, Maximilian Mrozik^c^a KIT - Karlsruhe Institute of Technology, Institute for Applied Geosciences, Mineralogy and Petrology, Adenauerring 20b, Geb. 50.4, D-76131 Karlsruhe, Germany^b TU Bergakademie Freiberg, Institute of Mineralogy, Brennhaugasse 14, D-09596 Freiberg, Germany^c TU Bergakademie Freiberg, Geoscientific collection, Brennhaugasse 14, D-09596 Freiberg, Germany

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ABSTRACT

Agates from Oligocene acidic volcanic rocks in the Eastern Rhodopes (Bulgaria) were investigated by combined mineralogical and radiometric methods. Petrographic–CL–spectroscopic observations reveal distinct SiO₂-rich zones made up by cristobalite, celadonite, zeolite, opal-CT, chalcedony, and quartzine with U contents up to 67 µg/g. Results of laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) of nine agate zones (Z1 to Z9), mostly <250 µm across, provide evidence for four, successively younger stages of SiO₂ mineralization at 19.3 ± 0.3 Ma (Z1–Z3), 13.2 ± 0.7 Ma (Z4–Z6), 10.3 ± 0.3 Ma (Z7), and 6.8 ± 0.2 Ma (Z8). The age of the biggest zone Z7, up to 5000 µm across, is independently confirmed by isotope dilution–thermal ionization mass spectrometry (ID–TIMS) of six fragments, which yielded within uncertainties an identical weighted mean ²⁰⁶Pb/²³⁸U* age of 10.02 ± 0.05 Ma. The results show that agate formation can occur periodically by multiple fluid–rock interaction over ca. 12 million years, significantly later than formation of surrounding volcanic host rocks. In addition, they demonstrate that the U–Pb system of respectively older agate zones, made up of different SiO₂ mineralizations remain stable during formation of younger agate generations, and that agate dating by LA–ICP–MS and ID–TIMS yield identical ages within uncertainties.

1. Introduction

Agates belong to the most fascinating mineral objects in nature and there are ongoing debates about their origin and formation (Götze et al., 2020a and references therein). In many cases, agate formation is closely related to periods of intense volcanic activities, resulting in basaltic and acidic lava flows and related tuffs. However, agate growth also can occur completely unrelated to volcanic activities, as is indicated by hydrothermal vein agates or sedimentary agates in the subsurface region of certain sedimentary and volcano-sedimentary rock units (Götze et al., 2020a). The oldest known occurrence of agate, the Warrawoona agate in Western Australia, was found in 3.48 Ga old metamorphosed rhyolitic tuffs (Moxon et al., 2008).

Agates commonly result from the multiple precipitation of silica from aqueous solutions, causing the formation of spectacular zoning patterns. However, the timing and duration of precipitation is mostly unknown, preventing detailed interpretation of fluid–rock interaction processes. In many cases, it is assumed that agate formation is temporally related to volcanic activities, implying that the SiO₂ mineralization

of agate precipitated immediately after host rock formation. However, there is growing evidence that agate formation can also occur much later than the surrounding volcanic host rocks, as has been recently demonstrated for agates from the Paraná Continental Flood Basalt Province in Brazil, and the Deccan Trap Province in India (Gilg et al., 2014; Ottens et al., 2019; Götze et al., 2020b; Arduine-Rode et al., 2024).

Direct dating of agate is commonly difficult, in particular as elements used for geochronology (Rb, Sr, K, Ar, U and Pb) do not substitute into quartz structures in sufficient amounts. Furthermore, there can be problems related to post-agate growth alteration, which potentially can cause serious perturbation of certain isotope systems, and significant age reset (see the detailed discussion in Neymark et al., 2002). Quartz from magmatic and metamorphic rocks as well as pegmatite quartz commonly exhibit very low U contents at sub-µg/g levels, whereas chalcedony and macrocrystalline quartz within geodes can show several tens or even up to hundreds of µg/g, as has been revealed by a systematic investigation of agates from different occurrences in Europe, Northern and Southern America (Götze et al., 2015, 2021). Spatially resolved trace-element analyses by laser ablation – inductively coupled plasma –

* Corresponding author.

E-mail address: armin.zeh@kit.edu (A. Zeh).<https://doi.org/10.1016/j.chemgeo.2026.123681>

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mass spectrometry (LA-ICP-MS) further show that the distribution of U within zoned agate samples is heterogeneous and commonly coincides with the structural banding (e.g., Möckel et al., 2009; Götze et al., 2009, 2015; this study). Detailed spectroscopic investigations additionally revealed that U is commonly incorporated into agate as uranyl-silicate complex (Pan et al., 2021).

First attempts to date chalcedony by means of ID-TIMS technique, applying the U–Pb isotope system, have been made by Neymark et al. (2002), Romer et al. (2003), and Pfaff et al. (2009). The results of these studies show that precise ages can be obtained from opal and chalcedony mineralization with variable U contents ranging from about 0.8 to 780 µg/g. While some ID-TIMS studies suggest SiO₂ mineralization during single, relatively short-lived hydrothermal events, e.g., at 115.7 ± 2.7 Ma (Pfaff et al., 2009) or 263.7 ± 2.2 Ma (Romer et al., 2003), point others to a prolonged period of more or less continuous SiO₂ mineralization over several million years, e.g., from 9.8 ± 0.2 to 0.59 ± 0.03 Ma, much outside of analytical uncertainties (Neymark et al., 2002). However, dating of zoned agate by ID-TIMS is cumbersome, and for agates with a complex zoning limited by preparation techniques, necessary to select appropriate sample material of a few milligram weight from a single zone. This on the other hand can be achieved easily by LA-ICP-MS technique, where individual zones can be selectively ablated with spot sizes <100 µm, resulting in less than 1 µg sample weight per spot. However, application of LA-ICP-MS for U–Pb dating of SiO₂ mineralization is still in its infancy, and several effects untested. The most important problem results from the non-existence of matrix-matched reference material for chalcedony and/or opal, as well as the lack of knowledge about the effects of laser ablation on different SiO₂ mineralization, and with variable U, Th, and Pb contents (also see discussion in Franz et al., 2026).

In the following, we present results of a study combining petrographic-spectroscopic methods with U–Pb dating of agate from Golobradovo in the Rhodope Mountains (Bulgaria). Individual agate zones are characterized for their mineralogy and microstructures, and dated by LA-ICP-MS. Furthermore, the accuracy of the LA-ICP-MS ages is tested by isotope dilution – thermal ionization mass spectrometry (ID-TIMS). Finally, the combined results are discussed with respect to the usability of the LA-ICP-MS technique for detailed agate dating, as well as for deciphering the hydrothermal processes, which led to the formation of the complex SiO₂ mineralization at Golobradovo.

2. Materials and methods

2.1. Geological background and sample material

The investigated sample material represents agates from acidic volcanic rocks of the eastern Rhodopes in southeastern Bulgaria. The study area was affected by bimodal volcanism during the Early Oligocene at ca. 32 Ma (Lilov et al., 1987) accompanied by the effusion of mainly intermediate and acidic lavas (Yanev, 2003). The lava compositions vary from trachydacites to trachyrhyolites, and from dacites (very rare) to rhyolites with high silica content up to 75 wt.-% (Yanev, 2022). In the volcanoes, endogenous domes with short flows and sills were formed, many with glassy rims. The agates, locally termed as thundereggs (Fig. 1) are spatially related to lithophysae, i.e., high-temperature crystallization domains (Breitkreuz, 2013) within the volcanic units. The agate samples were taken from the location Golobradovo, which occurs several kilometers East of the Studen Kladenets dam.

Several agate-bearing lithophysae were cut and polished to investigate the agate zoning patterns and their mineralogy in detail. Polished thin sections (30 µm thick) of host rocks, lithophysae and agates were made for polarizing microscopy, cathodoluminescence (CL) imaging and spectroscopy, as well as for scanning electron microscopy (SEM) – (Figs. 2, 3). A polished thick section (200 µm thick) of one representative sample with typical zoning was prepared for LA-ICP-MS dating (Fig. 4a). From the same sample, but a different slice, fragments of up to

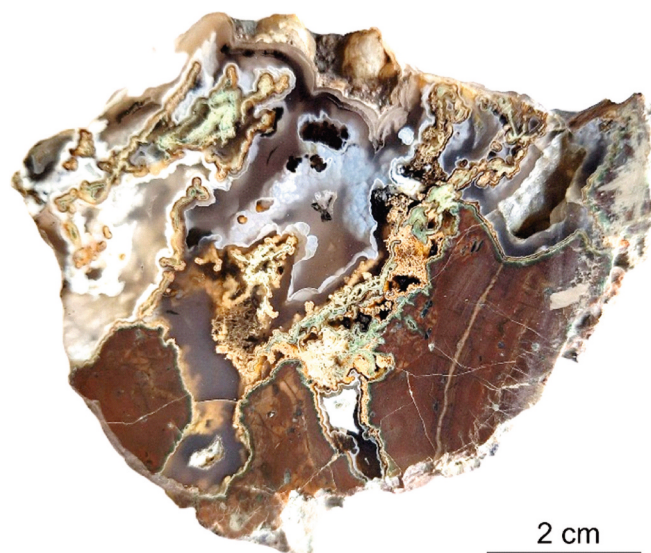


Fig. 1. Lithophysa from the Golobradovo location with zoned silica mineralization in altered volcanic rock.

10 mg were separated from the innermost part of the agate by micro-drilling for ID-TIMS measurements.

3. Analytical methods

3.1. Microscopy, spectroscopy, and diffractometry

Petrographic characterization of the rock fabric and phase composition was carried out by conventional polarization microscopy using a Zeiss Axio Imager A1m microscope. The various SiO₂ phases of agate were identified using a combination of microscopic techniques, comprising polarizing microscopy, cathodoluminescence (CL), scanning electron microscopy (SEM), and X-ray diffraction analysis. The SEM analyses were carried out in SE (secondary electrons) and BSE (back scattered electrons) mode using a JEOL JSM-7001F (20 kV, 2.64 nA) with a BRUKER Quantax 800 EDX system at TU Bergakademie Freiberg, Germany. CL-imaging and spectroscopy were made on carbon coated, polished thin and thick sections using a hot cathode CL microscope HC1-LM (Neuser et al., 1995). The system was operated at 14 kV accelerating voltage and a current of 0.2 mA with a Peltier-cooled digital video camera (OLYMPUS DP72) and an Acton Research SP-2356 digital triple-grating spectrograph with a Princeton Spec-10 charge-coupled device (CCD) detector, respectively. CL spectra in the wavelength range 380 to 900 nm were measured under standardized conditions (wavelength calibration was realized by a Hg-halogen lamp), using an electron beam spot width of 30 µm, and 5 s measuring time per spot. Qualitative and quantitative phase analyses were carried out on rock powders of <20 µm size by means of a “Orion Comet P2” X-ray diffractometer from XRD Eigenmann GmbH using Co-K α radiation in the range 5–80° 2 θ (0.01 step, 10 s/step) with a Si drift detector. The quantitative evaluation using Rietveld refinement was carried out with the program package BGMN/Profex v 3.9.2 (Taut et al., 1998; Doebelin and Kleeberg, 2015).

3.2. LA-ICP-MS dating

Uranium–Pb dating of distinguishable agate zones (Fig. 4) was carried out in situ by laser ablation – inductively coupled plasma – sector field – mass spectrometry (LA-ICP-SF-MS) at Karlsruhe Institute of Technology, using an ELEMENT XR (Thermo-Scientific) coupled to a 193 nm Excimer laser (Teledyne Photon Machines, Analyte Excite+). Agate zones were analyzed in sequence with soda-lime glass NIST-SRM612 (Jochum et al., 2011), used as reference material for

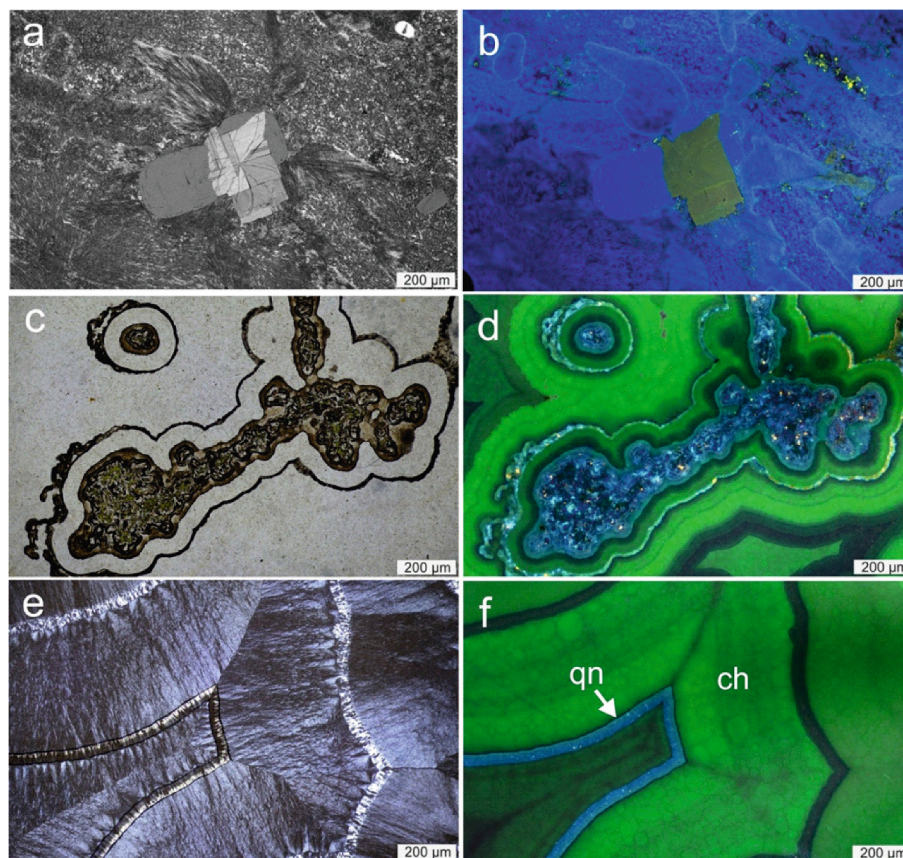


Fig. 2. Photomicrographs of the volcanic host rocks and the silica mineralization. (a, b) Polarized light and CL images showing the acidic volcanic host rock with fine-grained intergrowths of K-feldspar (bright blue CL) and cristobalite (dark blue CL) with yellow-greenish phenocrysts and dots of plagioclase. K-feldspar and plagioclase phenocrysts often occur as glomerophytic intergrowths. (c, d) Plain polarized light/CL photomicrograph pair from the oldest part of the mineralization with fine-grained Fe-oxides/-hydroxides, greenish celadonite and opal-CT (blue CL) surrounded by green luminescent chalcedony. (e, f) Crossed polars/CL image pair showing compact silica mineralization with fibrous chalcedony (ch) and thin bands of quartzine (qn – blue CL). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

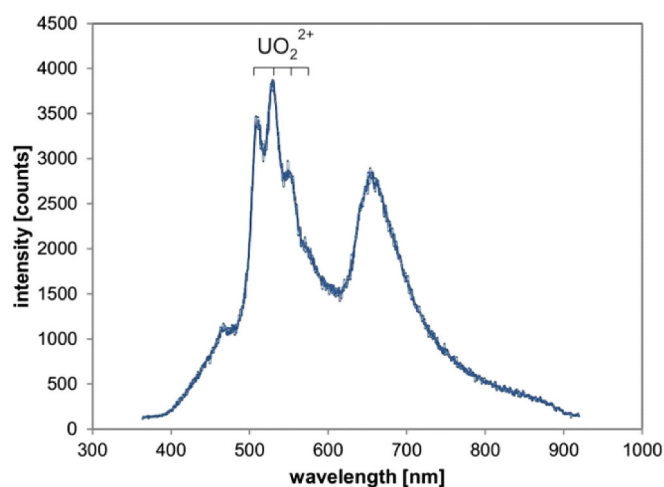


Fig. 3. CL spectrum of green luminescent chalcedony in the agate from Golobradovo with the typical emission lines of uranyl complexes (UO_2^{2+}), see Pan et al. (2021). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

calibration. Ablation of reference glass and agate was carried out during two sessions, using the following instrument parameters: laser spot diameter = 85 μm (session 1) and 135 μm (session 2), laser fluence = 7.5 Jcm^{-2} (session 1), 8.5 Jcm^{-2} (session 2), 10 Hz repetition rate, RF

power = 1245 W, and a mixed Ar-He- N_2 carrier gas consisting of Ar = 0.94 Lmin^{-1} , He = 0.3cell + 0.21cup (both Lmin^{-1}), and N_2 = 0.0095 Lmin^{-1} . Five pulses of pre-ablation were obtained prior to each analysis of 15 s duration following 15 s background measurement. All masses (^{202}Hg , $^{204}\text{Hg} + \text{Pb}$, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U) were analyzed in E-scan mode, without any magnet switch in between, using the following dwell times, all in milliseconds (^{202}Hg = 0.004, $^{204}\text{Hg} + \text{Pb}$ = 0.004, ^{206}Pb = 0.024, ^{207}Pb = 0.040, ^{208}Pb = 0.009, ^{232}Th = 0.006, ^{238}U = 0.006).

All raw data were corrected offline using an in-house MS Excel© spreadsheet program (AGeRap v.3.08; Gerdes and Zeh, 2006, 2009, updated by Richard Albert; FIERCE Frankfurt am Main). Corrections were done for background, outliers in the U, Pb and Th signals, commonly by applying 5 outlier iteration steps (for more details see discussion; and Figs. 5 and 6), as well as for daily drift of the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, based on repeated NIST glass measurements. Concentrations for U, Th and Pb were calculated relative to NIST-SRM612 glass, assuming a similar ablation and fractionation behavior. All ages were calculated using the software AGeRap v.3.08, resulting in regression line ages (isochrons) identical to the freeware ISOPLOT (Ludwig, 2001), by assuming a matrix offset factor of 1.0 between NIST-SRM612 glass and SiO_2 mineralization. Results of standard measurements and unknowns are presented in electronic supplementary materials (ESM-Table S1), and summarized in Table 1 and Fig. 7. All uncertainties are quoted at the 2 sigma level. The freeware AGeRap v.3.08 was also used to calculate ages biased by ^{230}Th and ^{234}U disequilibria (see section: Discussion).

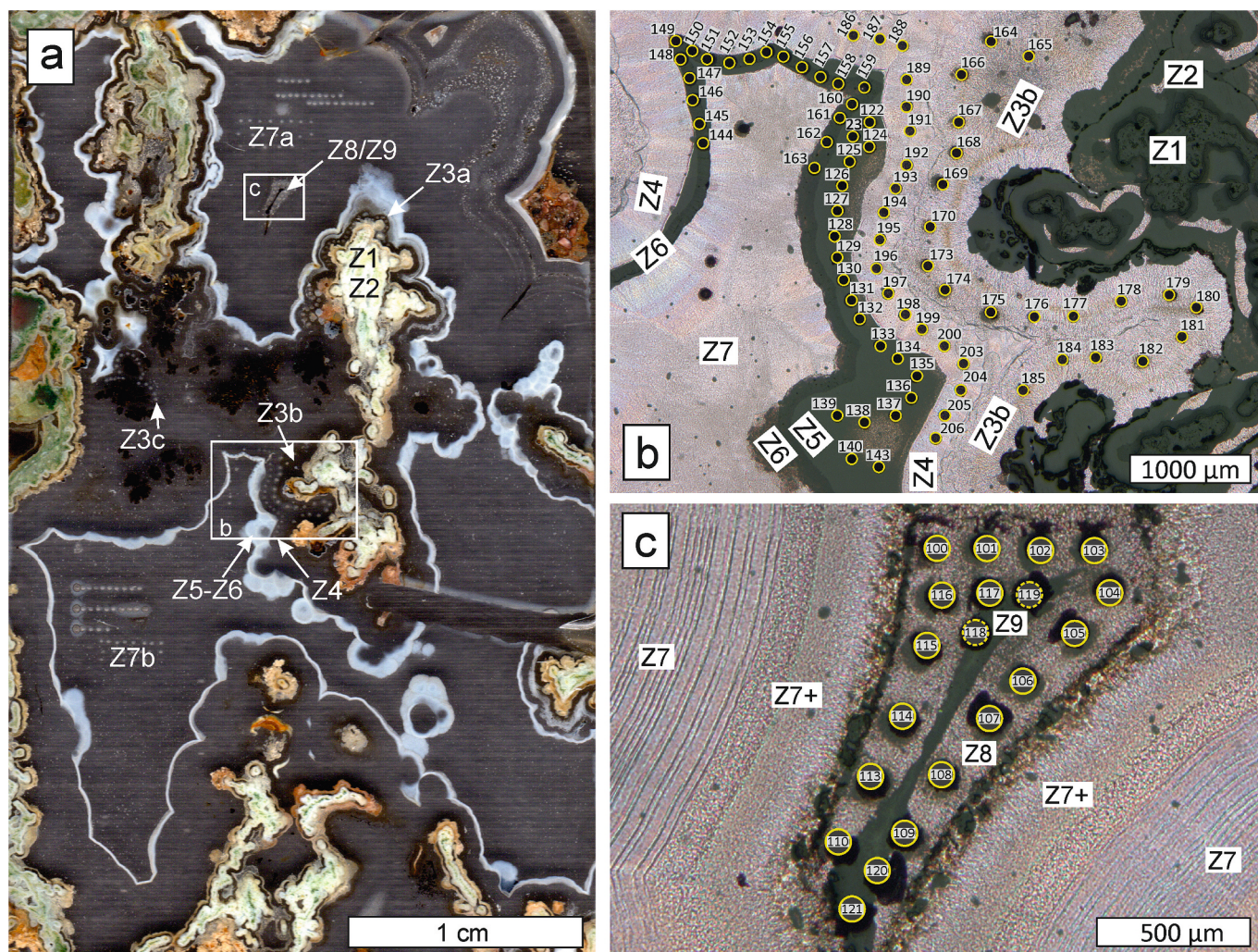


Fig. 4. Position of dated agate zones on a thick section of the Golobradovo agate. (a) Scan image showing all domains (Z1 to Z9) used for in situ LA-ICP-MS dating. Note that the subzones Z3a, Z3b, Z3c, and Z7a, Z7b (only fibrous-banded chalcedony) were analyzed in spatially distinct domains. (b, c) Details of two analyzed agate domains with laser spot positions and related numbers (mixed transmitted-reflected light images). Note that zone Z7 can be subdivided in an older inner zone of fibrous-banded chalcedony, and a younger outer zone dominated by spherulic chalcedony and quartzine (Z7+).

3.3. ID-TIMS dating

From the widest agate zone Z7 (Fig. 4) four fragments were separated from a weakly polished agate plate of approximately 200 μm thickness, sampled from the same lithophysae dated by LA-ICP-MS. From this plate, a strip of approximately 4 mm width and 6 mm length was cut out with a microdrill and subdivided into four large fragments (3, 5, 6, 7), which subsequently were carefully split with a mortar pestel into 13 subfractions (e.g., 3a, 3b; 7a, 7b; etc.; ESM_Table S2). The fragments 6 and 7 sample the fibrous-banded chalcedony in close vicinity to zone Z6, and the fragments 3 to 5 the transition zone towards zone Z8, dominated by spherulitic chalcedony with quartzine (zone Z7+ in Fig. 4c). Zone Z7+ is commonly small, but can have a width of up to 1.5 mm in some samples. The 13 subfractions with weights between 0.1 and 3.0 mg (ESM_Table S2) were transferred into cleaned 3 ml Teflon beakers. Surface Pb was removed by adding 3.5 N HNO₃ and subsequent heating at 80 °C on a hot plate for 30 min. Several cleaning cycles with ultrapure water, combined with repeated ultrasonic treatment, were conducted before the fragments were dried on a hotplate. All used agents had high purity and blank masses lower than 1 pg.

One ml HF was added to the cleaned and dried agate fragments, which were left to dissolve for more than 72 h. The samples were then spiked with two drops (10–20 mg) of a ²⁰⁵Pb-²³³U-²³⁵U-tracer solution

(FG535 at TU Bergakademie Freiberg, Condon et al., 2015, Schoene et al., 2006), dried at 90 °C, and then re-dissolved in 20 drops of 6 N HCl for 24 h at 90 °C to convert them into chlorides. After another drying step, the samples were dissolved in 10 drops of 3.1 N HCl and transferred into resin-filled micro-columns for column chemistry. Uranium and Pb were separated from the rest of the sample by anion exchange chromatography using the Bio-Rad AG 1-X8 resin (200–400 mesh) with HCl and H₂O, respectively. Each U–Pb containing fraction was loaded on pre-degassed rhenium filaments with a drop of silica gel (Gerstenberger and Haase, 1997) and measured with an IsotopX Phoenix Thermal Ionization Mass Spectrometer using a Daly detector for Pb measurements and ATONA Faraday amplifiers for U measurements. Data reduction was performed with freeware “Tripoli” and “ET Redux” (www.cirdles.org). The results are shown in ESM-Table S2 and Fig. 8. The accuracy of the ID-TIMS ages was constantly checked through analysis of the reference zircons 91,500 and Temora 2. For details see Tichomirowa et al. (2025).

4. Results

4.1. Mineralogy of host rocks and agates

The volcanic host rock close to the thunderegg was classified as

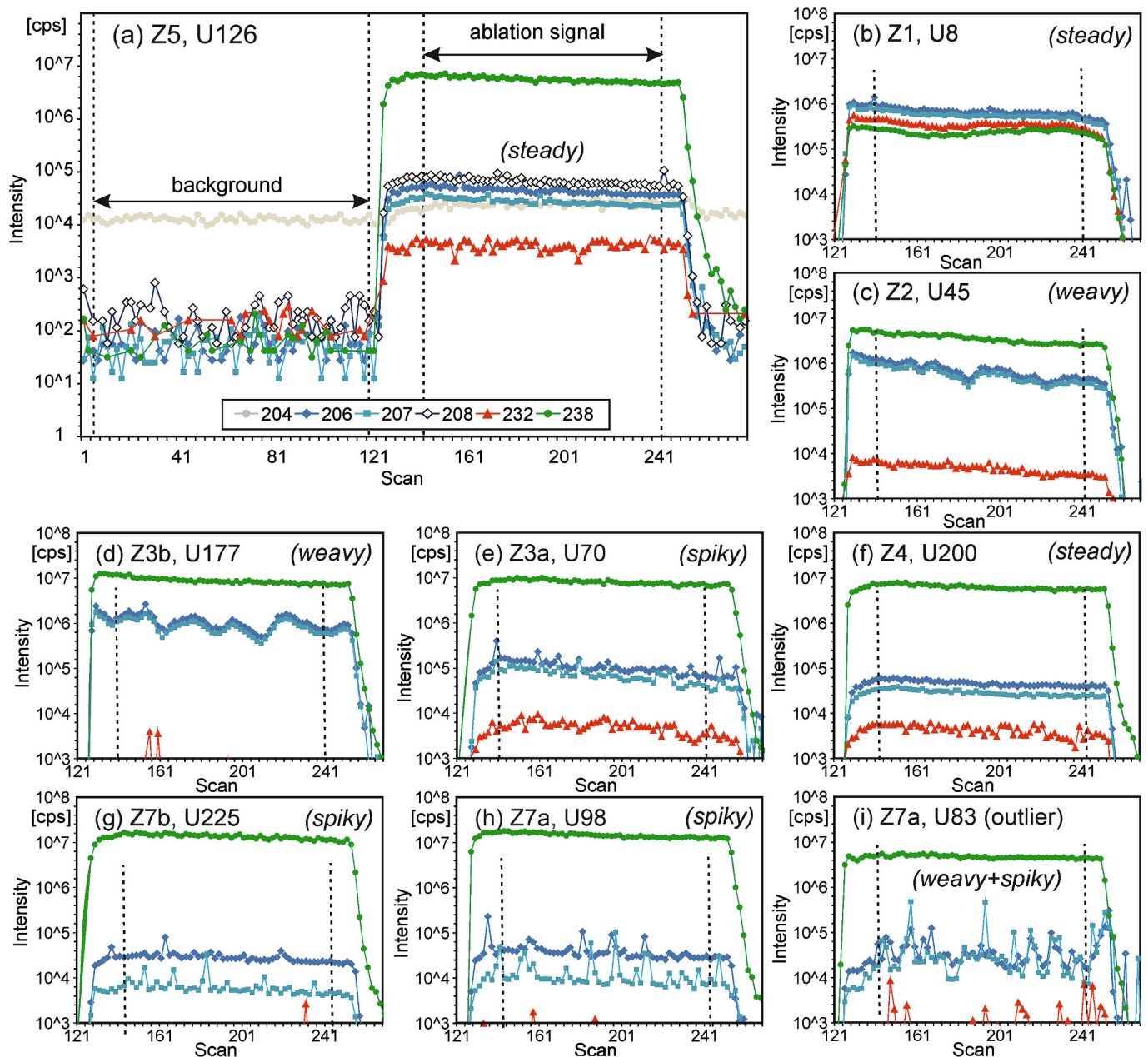


Fig. 5. Representative time-resolved isotope signals obtained by LA-ICP-MS during the analyses of agate zones with different SiO₂ mineralization and microstructures. (a) Typical steady signal of all isotopes obtained during 15 s background and 15 s ablation acquisition. (b-i) Signals of selected U (238), Th (232) and Pb (206, 207) isotopes obtained during laser ablation. Note that the U signal in all analyses is steady, whereas the Pb isotope signals can be quite different dependent on SiO₂ mineralization: (1) steady signal - mostly in zones with fine-grained SiO₂ mineralization (Z1, Z2, Z4, Z5), (2) wavy signal - in zones with fine-grained, fibrous chalcedony and granular quartz, and (3) spiky signal - only zones with fibrous chalcedony and granular quartz. Cts – counts per second. The dotted black vertical lines mark the limits used for data processing. U8, U177 – numbers of spot analyses. For more details see text.

ryholite with 75.8 wt.-% SiO₂, consisting of 52.0 wt.-% K-feldspar, 22.6 wt.-% plagioclase, 23.7 wt.-% cristobalite, and 1.7 wt.-% quartz, as determined by XRD. The high amount of cristobalite indicates high formation temperatures. Microscopic investigations reveal a groundmass consisting mainly of fine-grained intergrowths of K-feldspar and cristobalite, rarely with plagioclase (Fig. 2a-b). Phenocrysts of plagioclase and K-feldspar are common, locally forming glomerophytic intergrowths, whereas quartz phenocrysts are rare. In the groundmass spherulitic crystallization domains occur locally, mostly around large phenocrysts (Fig. 2a).

The agate mineralization within the lithophysae consists on average of 80.0 wt.-% alpha-quartz, mostly chalcedony/quartzine, 16.3 wt.-% opal-CT, 3.6 wt.-% cristobalite, and 3.6 wt.-% clinoptilolite-Ca (zeolite).

Cristobalite and clinoptilolite only occur as thin crusts of lath-shaped crystals along the outermost wall of the former cavities, defining the transition zone between host rock and silica mineralization. The agate silica mineralization (zone Z1) starts with a fine-grained mixture of Fe-oxides/-hydroxides, greenish celadonite and opal-CT, appearing blue in CL images (Fig. 2c-d). In the transition zone lath-shaped crystals of zeolite (clinoptilolite-Ca) were additionally detected. The next mineralization steps (Z2 to Z8) are dominated by spherulitic and fibrous-banded chalcedony locally interrupted by thin layers of quartzine (Z5, Z6), which also appear blue in CL images (Fig. 2e-f). Chalcedony always exhibits a bright green luminescence, which can be related to the incorporation of uranyl ions (UO₂²⁺) as uranyl-silicate complex (Götze et al., 2015; Pan et al., 2021), as indicated by CL spectroscopy (Fig. 3).

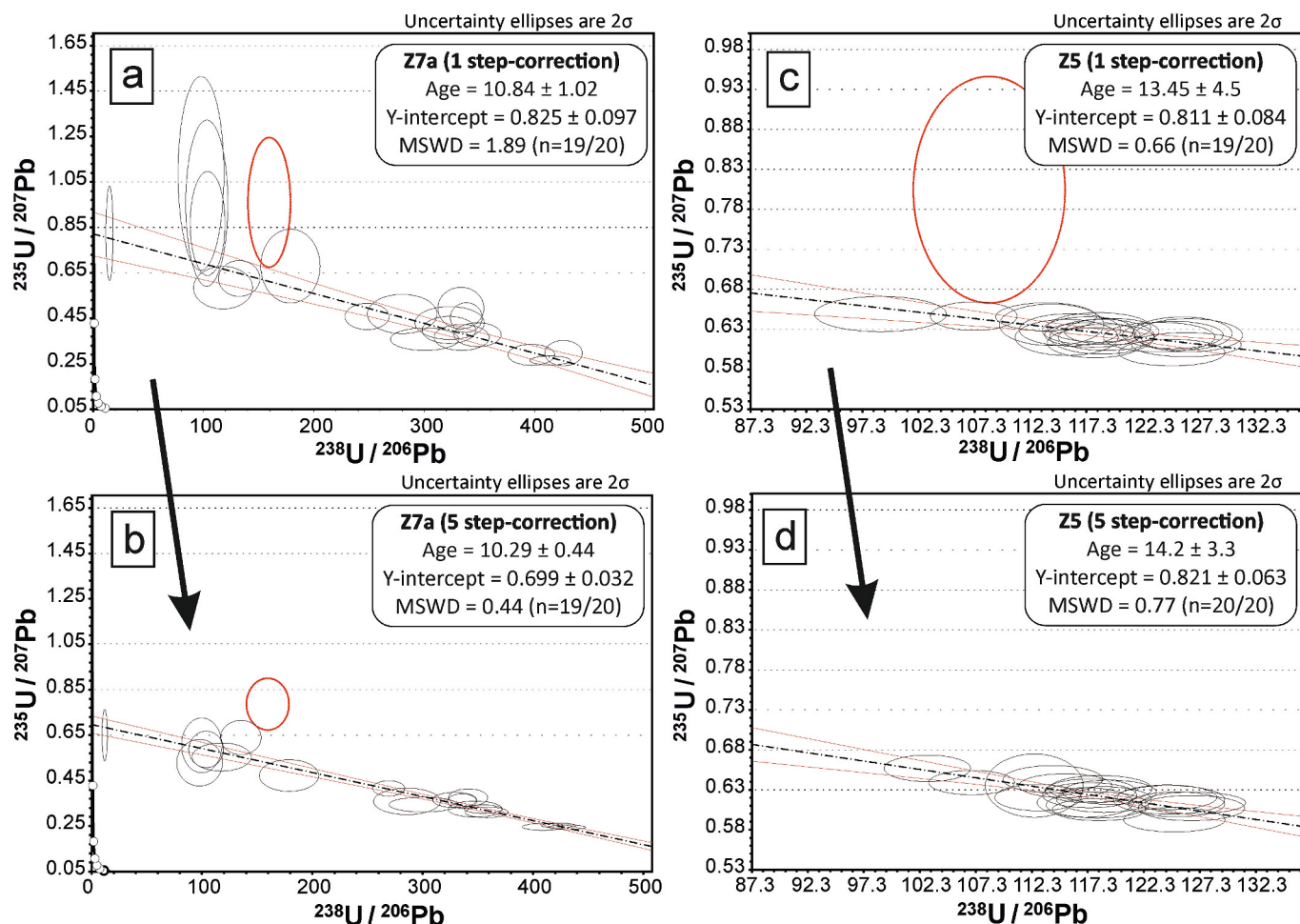


Fig. 6. Effect of time-resolved signal correction on regression line age and precision, demonstrated for 20 spot analyses of zone Z7a (a-b), dominated by fibrous-banded chalcedony, which mostly yielded spiky Pb signals during ablation, and zone Z5 (c-d), made up by fine-grained quartzine with mostly smooth, steady Pb signals. (a, c) Regression line resulting from a 1-step outlier correction, (b-d) base on 5-step outlier correction. For more details see text.

4.2. LA-ICP-MS dating

During session 1 (85 μm laser spot size, 7.5 Jcm^{-2}) LA-ICP-MS measurements were carried out on nine distinct agate zones (Z1 to Z9; Fig. 4a), which are commonly <250 μm across, except zone Z7 with up to 5000 μm extension (Fig. 4a-c). During session 2 (135 μm laser spot size, 8.5 Jcm^{-2}), only the zones Z1 + Z2, Z3, and Z7 were analyzed (for laser spot positions see ESM Fig. S1). We note that for both LA-ICP-MS sessions only the innermost part of zone Z7 was considered, consisting of fibrous-banded chalcedony, but not the outermost part dominated by spherulic chalcedony and quartzine (zone Z7+ in Fig. 4c). During session 1, 20 spot analyses were carried out from most zones, except for the oldest zone Z1 (30 analyses), and the two innermost (youngest) zones Z8 and Z9, with 18 and 2 spot analyses, respectively (Table 1). The zones Z3 and Z7 (fibrous-banded chalcedony) were measured on spatially distinct locations of the same thick section (domains Z3a-Z3c and Z7a-Z7b in Fig. 4a), to gain information about chronological-compositional variations. During session 2, 25 spot analyses were carried out on the zones Z1 + Z2 + Z3, and 50 analyses on two different domains of zone Z7 (Z7a and Z7b).

Agate zones made up by distinct SiO_2 varieties show a different ablation behavior, with consequences for data processing. A common feature of all zones is that the U signal remains steady during the 15 s of ablation, only showing a slight decrease in signal strength, whereas the Pb isotope signals can behave significantly differently. In general, three Pb patterns can be distinguished in time-resolved signals. (1) The ^{206}Pb ,

^{207}Pb , ^{208}Pb signals are all steady and follow the U signal subparallel (Fig. 5a, b, f), resulting in analyses with small uncertainties. This is the case for most analyses of the oldest zones Z1, Z2, made up of fine-crystalline lepispheres of opal-CT locally admixed with celadonite and zeolite, as well as for the zones Z5, Z6, Z8 consisting of fine-crystalline quartzine (Fig. 5b). (2) The Pb signals appear wavy compared to the time-resolved U signal, resulting in relatively large uncertainties of the $^{206}\text{Pb}/^{238}\text{U}$ ratios. Such signals have been observed during ablation of some spots of the zones Z2, Z3, and rarely also of the zones Z5, Z6, Z8 (Fig. 5c, d). (3) Ablation of the chalcedony-dominated zones (Z3, Z4, Z7) mostly yield “spiky” time-resolved Pb isotope signals (Fig. 5e, g-i). These spikes, if abundant, can have a significant influence on the calculated intercept ages and uncertainties (Fig. 6), and are the major reason for outliers above but also below the regression line (for more details see section: Discussion).

The uranium content of most agate zones is >20 $\mu\text{g/g}$, up to 56 $\mu\text{g/g}$ (median values), except the zones Z1 (1.1 $\mu\text{g/g}$) and Z6 (3.7 $\mu\text{g/g}$). The Th/U ratios are mostly very low (<0.008), except of the zone Z1 with 0.78 (Table 1). Results of U–Pb dating of individual agate zones during session 1 and 2 yielded variable ages ranging from 19.6 Ma to 6.8 Ma, albeit of variable precision, mainly due to variations in the spread of $^{238}\text{U}/^{206}\text{Pb}$ ratios (Fig. 7). This spread is least for the two oldest zones Z1 and Z2, with all analyses very close to the Y-intercept of the Tera-Wasserburg diagram, defining the initial common Pb composition, and much wider for the analyses of all other zones. We note that during session 1 spot analyses of the spatially separated subzones Z3a, Z3b, and

Table 1

Results of U–Th–Pb dating of agate by LA–ICP–MS.

event ¹	zone ²	U ³ μg/g	Pb ³ μg/g	Th ³ μg/g	Th/U ³	Age ⁴ Ma	±2σ	MSWD ⁵	n ⁶	²⁰⁷ Pb/ ²⁰⁶ Pb Y-intercept	±2σ	Min ⁷
Session 1												
E1	Z1	1.1	10.6	0.85	0.78	18	47	0.65	30/30	0.8249	0.0035	o,c,s,z
	Z2	23	18	0.13	0.0054	18	11	0.60	19/20	0.8262	0.0072	c, cl
	Z3a	37	1.6	0.0070	0.00022	19.2	2.1	0.26	13/20	0.808	0.026	cl
	Z3b	22	1.9	0.0068	0.00031	18.55	0.50	1.2	17/20	0.783	0.019	cl
	Z3c	36	0.54	0.0012	0.000033	19.6	1.3	0.93	19/20	0.8146	0.0058	cl
	Z1–Z3*					19.34	0.33	1.2	98/110	0.8233	0.0018	
E2	Z4	28	0.59	0.0098	0.00036	14.2	4.2	0.68	20/20	0.845	0.095	cl
	Z5	23	0.54	0.021	0.00094	14.2	3.3	0.77	20/20	0.821	0.063	q
	Z6	3.7	0.19	0.039	0.0077	12.5	5.0	1.0	20/20	0.810	0.040	q
	Z4–Z6*					13.22	0.66	1.5	60/60	0.813	0.011	
						13.26	(§1)					
						12.98	(§3)					
E3	Z7a	41	0.37	0.0045	0.00020	10.29	0.44	1.2	19/20	0.699	0.032	cl
	Z7b	56	0.28	0.00061	0.000014	10.30	0.49	1.3	19/20	0.690	0.059	cl
	Z7a–7b*					10.33	0.32	1.2	38/40	0.700	0.027	
						10.42	(§1)					
						10.05	(§2)					
						10.13	(§3)					
E4	Z8*	41	5.2	0.0070	0.00017	6.81	0.20	1.0	18/18	0.7611	0.0074	q
						6.88	(§1)					
						6.60	(§3)					
	Z9	42	53	0.006	0.0012	9.2	4.8		2/2	0.5548	0.0099	q
Session 2												
E1	Z1 + Z2	12	7.0	0.28	0.29	20.1	3.0	2.3	14/15	0.8249	0.0078	c, cl
	Z3	26	4.6	0.0037	0.00014	19.4	1.1	0.82	10/10	0.8349	0.0126	cl
	Z1–Z2–Z3*					19.3	1.3	1.8	24/25	0.8255	0.0058	
						19.4	(§1)					
E3	Z7a	45	0.38	0.0048	0.00012	10.14	0.58	1.8	24/25	0.762	0.057	cl
	Z7b	36	0.34	0.0014	0.000087	10.37	0.29	0.88	25/25	0.779	0.016	cl
	Z7a–7b*					10.30	0.23	1.3	49/50	0.776	0.015	
						10.38	(§1)					
						10.09	(§3)					

1 - fluid event resulting in the formation of agate zones.

2 - agate zones mentioned in text.

3 - median values based on all laser spot analyses per zone.

4 - intercept age of regression line with Concordia line.

5 - MSWD - mean standard weighted deviation of regression line.

6 - number of analyses used for regression line calculation / total number of analyses.

7 - mineralogical composition: s - celadonite, c - cristobalite, z - zeolite, cl - chalcedony, q - quartzine, o - opal-CT.

* - best result of age dating, including all analyses of several zones and/or subzones, without disequilibrium.

§1 - age calculated for ²³⁰Th disequilibrium, assuming an initial whole rock Th/U of 8.0, i.e., average for rhyolitic rocks with SiO₂ = 73 wt% (Kirkland et al., 2015).§2 - age calculated for assuming an initial ²³⁴U/²³⁸U of 1.75 (weighted average of data obtained from opal, silcretes and calcretes (Maher et al., 2007; Neymark, 2011; Oster et al., 2017).§3 - age resulting from ²³⁰Th and ²³⁴U disequilibrium.

Z3c (Fig. 4a) yielded all within uncertainties identical intercept ages of 19.2 ± 2.1 Ma, 18.6 ± 0.5 Ma and 19.6 ± 1.3 Ma, respectively, although with some outliers (Table 1, Fig. 7a). An overlapping age of 19.4 ± 1.1 Ma was also estimated for zone Z3 during session 2. Identical ages, within uncertainties, of 10.29 ± 0.44 and 10.30 ± 0.49 Ma were also obtained for the two subzones Z7a and Z7b, respectively during session 1, and of 10.14 ± 0.58 and 10.37 ± 0.29 Ma during session 2 (Table 1). Considering microstructural observations and uncertainties, the in situ dating results obtained from several zones during session 1 can be combined, resulting in four, successively younger isochrons with MSWD < 1.5 (Fig. 7; Table 1). These reflect ages of 19.3 ± 0.3 Ma (Z1–Z3), 13.2 ± 0.7 Ma (Z4–Z6), 10.33 ± 0.32 Ma (Z7) and 6.8 ± 0.2 Ma (Z8). The age of the youngest zone Z9 (9.2 ± 4.8 Ma) is very imprecise and only constrained by two analyses. These ages are identical, within uncertainties, to those obtained during session 2 (Z1–Z3 = 19.3 ± 1.3 Ma, Z7 = 10.30 ± 0.23 Ma: Table 1, Fig. 7e–f).

4.3. ID–TIMS measurements

The uranium contents estimated by ID–TIMS from the 13 fractions vary from 40 to 67 μg/g, and the ²⁰⁶Pb/²⁰⁴Pb ratios from 43 to 127, indicating ratios of about one between radiogenic and common Pb (ESM-Table S2). Smaller subfractions generally yielded better ionization, likely because they were better matched to the capacity of the ion-exchange columns.

Measured U–Pb and Pb–Pb ratios were corrected for tracer contribution and laboratory blank. Based on zircon analyses conducted during the course of this study, the laboratory blank was assumed to be 1 pg for all agate samples and corrected using the common Pb model of Stacey and Kramers (1975). No correction for initial Pb was applied for Tera–Wasserburg and inverse isochron diagrams, allowing the initial Pb composition to be constrained from correlation lines. Six out of the 13 fractions (comprising the five fractions of the fibrous-banded chalcedony fragment 7) define a regression line, which reflects an age of 9.9 ± 0.4 Ma (MSWD = 3.5) when plotted in the Tera–Wasserburg diagram

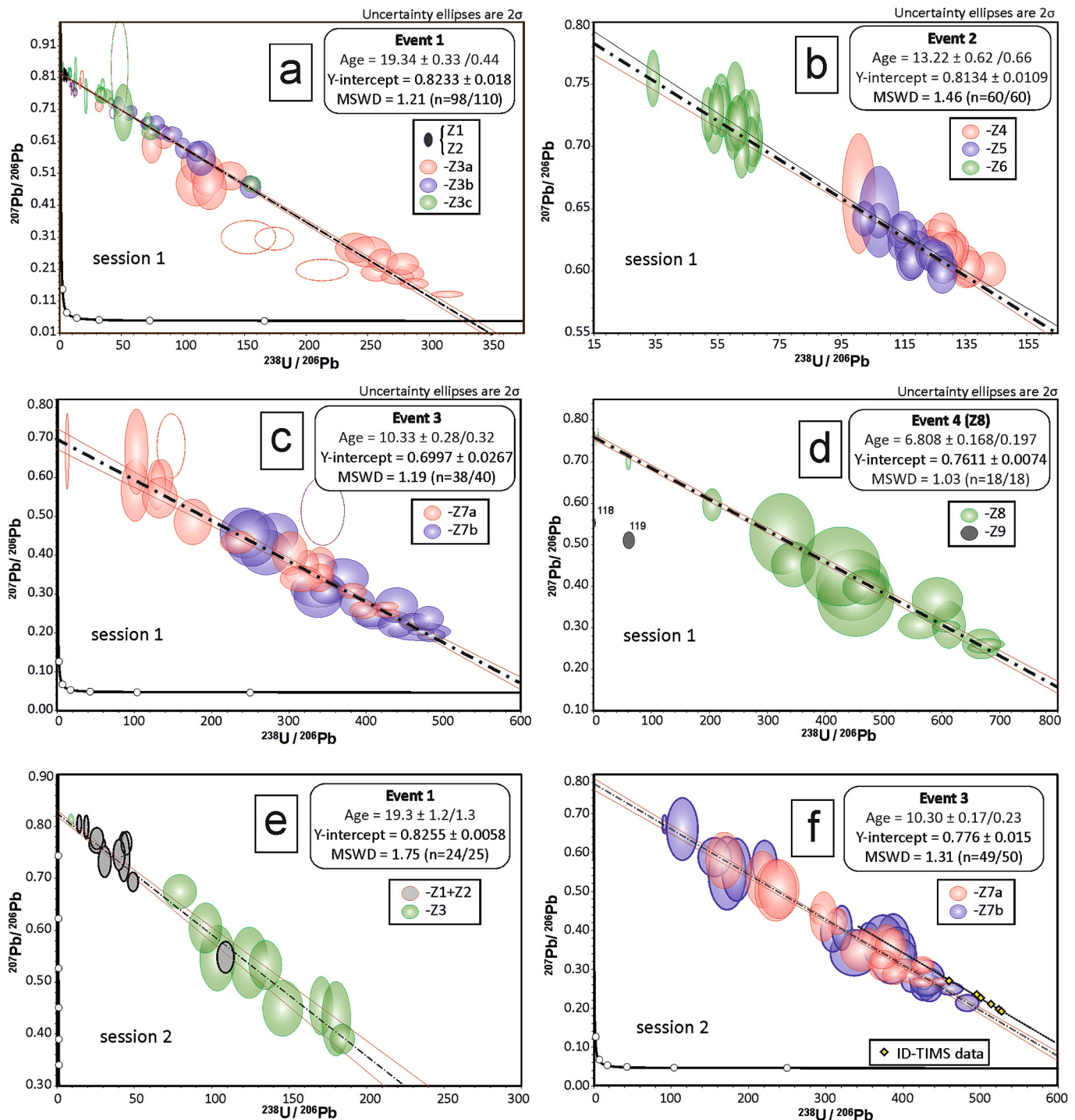


Fig. 7. Tera-Wasserburg diagrams showing the results of U–Pb dating by LA–ICP–MS during session 1 (a–d), and session 2 (e–f). Note that in most diagrams the results of several zones and/or subzones are combined (event 1 to event 4), and that the ages become successively younger from the structurally oldest zones (Z1–Z3) to the youngest, most innermost zone (Z8). Results of zone 9 are only shown for comparison. In Fig. 7f the results of ID-TIMS dating are shown for comparison.

(Fig. 8a, b), and 9.9 ± 0.2 Ma (MSWD = 1.6) in the $^{238}\text{U}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 8c). Five other analyses (all from the fragments 3 and 5 of zone Z7+) plot significantly above the Tera-Wasserburg regression line, pointing to younger ages, and the two fragments 6 and 7 slightly below it (for reasons see section: Discussion).

Common Pb corrected $^{206}\text{Pb}^*/^{238}\text{U}$ and $^{207}\text{Pb}^*/^{235}\text{U}$ dates were calculated for each analysis by applying the standard procedure commonly used for zircon ID-TIMS analyses, including the Stacey and Kramers (1975) model. The resulting $^{206}\text{Pb}^*/^{238}\text{U}$ ages vary between

11.0 ± 0.4 and 5.0 ± 0.1 Ma (ESM-Table S2, Fig. 8d). The six analyses, defining the regression lines mentioned above, are within uncertainties identical, and result in a weighted mean age of 10.04 ± 0.05 Ma with MSWD = 0.81 (Fig. 8d). Applying the initial Pb composition obtained from the regression lines, i.e. $^{207}\text{Pb}/^{206}\text{Pb} = 0.794$, instead of the Stacey and Kramers (1975) model, decreases the weighted mean age slightly to 10.02 Ma. An additional Th-correction increases it to 10.15 Ma. For the Th correction a Th/U whole rock value of 8.0 was used (Kirkland et al., 2015). All these ages are within error to that obtained by LA–ICP–MS for

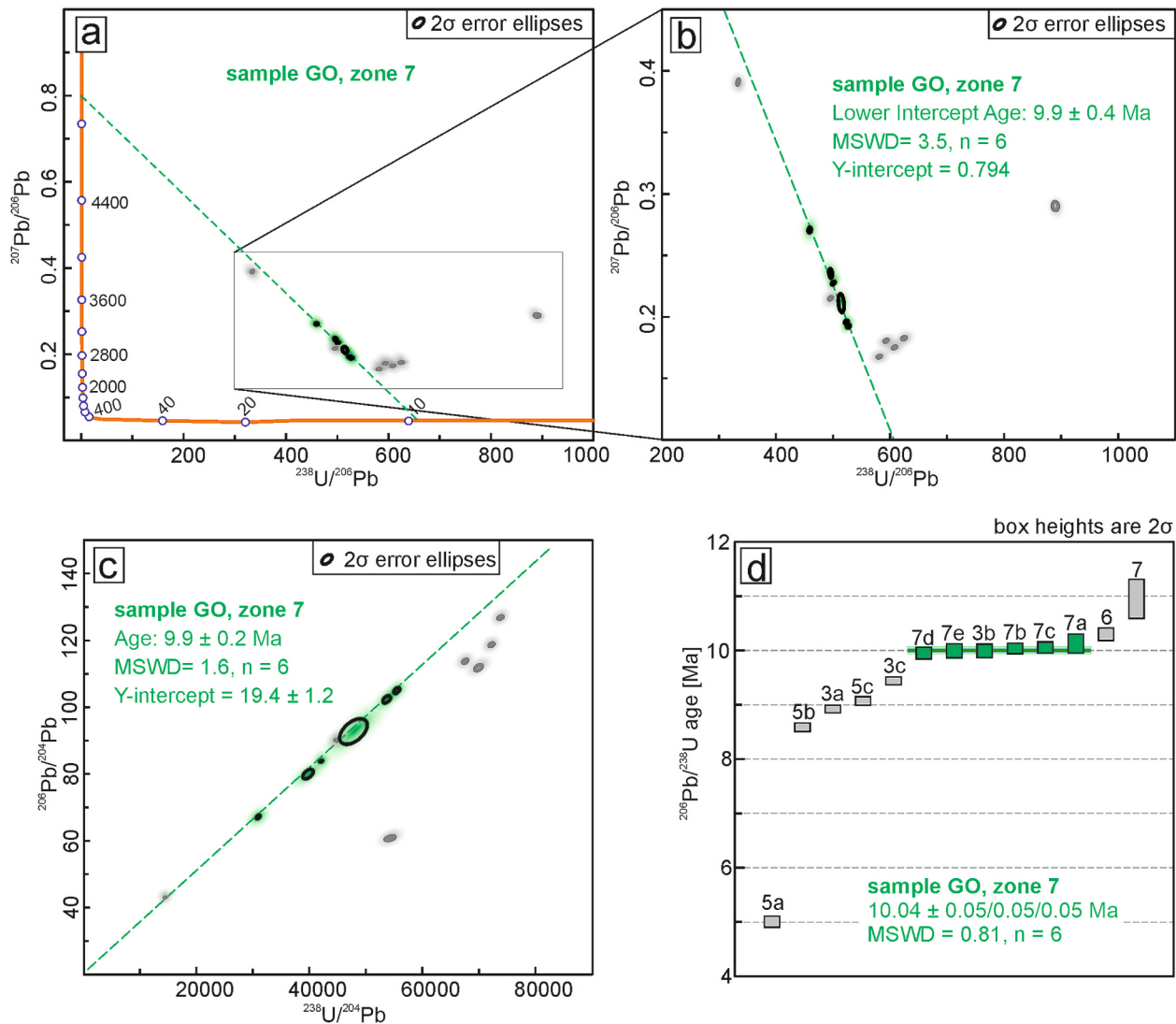


Fig. 8. Results of ID-TIMS dating of 13 aliquots from the innermost domains of the Golobradovo agate presented in (a-b) Tera-Wasserburg diagram, and (c) $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{238}\text{U}/^{204}\text{Pb}$ diagram. Individual data points are highlighted by grey or green halos due to their small size. Data with green halos were used for age calculation. (d) Common Pb corrected $^{206}\text{Pb}^*/^{238}\text{U}$ ages obtained from the investigated samples. Note that the six samples marked with green reflect the age of agate zone Z7. All uncertainties are quoted at the 2 sigma level. The uncertainty of the weighted mean age is reported as $\pm x/y/z$, with $x - 2\sigma$ internal, $y - 2\sigma$ external uncertainty including tracer calibration and $z - 2\sigma$ external uncertainty including ^{238}U decay constant uncertainty (Schoene et al., 2006). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

zone Z7.

5. Discussion

5.1. Silica dating by LA-ICP-MS

The results of this study show that precise intercept ages with low MSWD <1.5 (in Tera-Wasserburg diagrams) can be obtained by in situ LA-ICP-MS analyses of agate zones of <250 μm width, made up by different types of SiO_2 mineralization. For most zones, 20–30 spot analyses result in regression lines with uncertainties ranging from ± 0.44 Ma to ± 4.2 Ma (Table 1), mainly dependent on the spread in $^{238}\text{U}/^{206}\text{Pb}$ ratios, and the precision of individual LA-ICP-MS analyses. The spread is least for the zones Z1 and Z2, dominated by common Pb, and highly variable for all other zones (Fig. 7). The precision of individual spots is closely related to the intensity and smoothness of the time-resolved laser signals.

Signals for ^{238}U are $>4 \times 10^6$ cts (counts per second) for most agate zones and NIST-SRM612 glass (during the sessions 1 and 2), and

therefore measured in analogue detector mode, except most analyses of the zones Z1 and Z6 (only measured during session 1). These mostly have signals for ^{238}U between 1×10^5 and 2×10^6 cts and were measured in counting mode. The ^{207}Pb signals (commonly parallel to the higher ^{206}Pb signals) vary between 2.5×10^3 and 4.5×10^6 cts (ESM-TableS1). Time-resolved signals of ^{238}U are mostly smooth (steady), whereas signals of Pb isotopes are either (1) steady, (2) wavy, or (3) spiky, dependent on the type of SiO_2 mineralization (Fig. 5). Zones dominated by fine-grained SiO_2 varieties (opal-CT, quartzine; zones Z2, Z5, Z6, Z8, Z9) or with mixed mineral content (cristobalite $\pm$ opal-CT $\pm$ celadonite $\pm$ zeolite; zones Z1, Z2), commonly show a smooth ablation and parallel alignment of all isotope signals (Fig. 5a, b, f), except a few analyses with wavy Pb-signals (Fig. 5c, d).

In contrast, zones dominated by fibrous-banded calcedony (Z3, Z4, Z7) often show spiky signals of variable intensity (compare Fig. 5g and h). These spikes can influence the precision and accuracy of the regression line ages significantly. This is illustrated in Fig. 6, showing the results of different outlier corrections applied to one and the same dataset, comprising 20 spot analyses of the domains Z7a and Z5 (only

session 1), respectively. Applying only 1 step of 2sigma outlier correction with the software AGERAp (Fig. 6a) eliminates only the most extreme spikes and results in a regression line with an intercept age of 10.84 ± 1.02 Ma (MSWD = 1.89; excluding 1 outlier), whereas 5 successive steps of outlier correction eliminate all important Pb spikes and result in a significantly younger, more precise intercept age of 10.29 ± 0.44 Ma (MSWD = 0.44). The only outlier remaining, above the regression line in Fig. 6b, results from analysis U83, characterized by very noisy ^{206}Pb , ^{207}Pb isotope signals (see Fig. 5i).

For samples with steady and wavy Pb signals, the 5-step outlier correction causes elimination of extreme outliers, and commonly yield within uncertainties identical ages when compared with the 1-step outlier correction (for example see Fig. 6c-d). In this context, we note that ^{206}Pb and ^{207}Pb spikes are in most cases non-synchronous in the time-resolved signals (for examples see Figs. 5g, h), due to the sequential analyses of all isotopes by single-collector ICP-MS. This temporal offset can under some circumstances cause an over- or underestimation of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio, and result in outliers significantly above or below the regression line. This, in particular, can be the case for analyses characterized by a large number of outlier spikes, either prevailed by ^{207}Pb or ^{206}Pb . We presume, that the Pb spikes result from a “pulsed release of Pb” during the ablation of fibrous-banded chalcedony, a process not really understood so far.

The LA-ICP-MS dating results reveal that the intercept ages become successively younger from agate zone Z1 to Z9, from about 19 to 7 Ma. Although ages estimated from the structurally oldest and youngest zones (Z1-Z2, Z9) show large uncertainties, mainly due to low spread in $^{206}\text{Pb}/^{238}\text{U}$ (Table 1; Fig. 7a, d). The results further show that analyses obtained from spatially separated domains of the zones Z3 and Z7 during session 1 yield within uncertainties identical ages (Z3a-b-c: 19.2 ± 2.1 , 18.55 ± 0.5 , 19.6 ± 1.3 Ma; Z7a-b: 10.29 ± 0.44 , 10.30 ± 0.49 Ma; Table 1, Fig. 7), and that these ages could be reproduced during session 2 (Z3: 19.4 ± 1.1 Ma; Z7a-b: 10.14 ± 0.58 , 10.37 ± 0.29 Ma) by applying slightly different analytical conditions (session 1: 85 μm laser spot size, 7.5 J cm^{-2} ; session 2: 135 μm laser spot size, 8.5 J cm^{-2}). This suggest that (1) the U–Pb system was closed in different domains of the same agate zone at the same time (within uncertainties), (2) that structurally younger zones were formed significantly later, and (3) that variable instrument conditions yield identical results within uncertainties. Taken the agate zoning and dating uncertainties into account, the analyses of certain agate zones and domains can be combined, resulting in 4 regression lines, all with MSWD < 1.5. These yield successively younger intercept $^{206}\text{Pb}/^{238}\text{U}$ ages of 19.3 ± 0.3 Ma (Z1–Z3), 13.2 ± 0.7 Ma (Z4–Z6), 10.3 ± 0.3 Ma (Z7) and 6.8 ± 0.2 Ma (Z8; Figs. 7), in agreement with the observed agate zoning (Fig. 4). Nevertheless, the precision and meaning of these ages in a geological context needs to be discussed. This in particular concerns the accuracy of the ages obtained by LA-ICP-MS, the problem of closure of the U–Pb system for different types of SiO_2 mineralization, and potential excess ^{206}Pb , due to the incorporation of additional radioisotopes (e.g., ^{230}Th or ^{234}U) during SiO_2 mineralization.

5.2. Accuracy of LA-ICP-MS dating

All LA-ICP-MS ages presented above rely on the assumption that the U–Pb fractionation during laser ablation of the different agate zones is identical to that of NIST-SRM612 glass used as reference material. This hypothesis is tested here by independent ID-TIMS analyses of fragments separated from the innermost part of the Golobradovo agate, dominated by zone Z7. Six analyses from fibrous-banded chalcedony, yielded a common Pb corrected, weighted mean $^{206}\text{Pb}/^{238}\text{U}^*$ age of 10.02 ± 0.05 Ma (applying $^{207}\text{Pb}/^{206}\text{Pb} = 0.794$), which is identical within uncertainties to intercept ages of 9.9 ± 0.4 Ma ($^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{238}\text{U}/^{206}\text{Pb}$) and 9.9 ± 0.2 Ma ($^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{238}\text{U}/^{204}\text{Pb}$), respectively (Fig. 8). All these ID-TIMS ages are within uncertainties identical with the LA-ICP-MS age obtained from the fibrous-banded chalcedony of

zone Z7 during session 1 (10.33 ± 0.32 Ma) and session 2 (10.30 ± 0.23 Ma), and suggests that NIST-SRM612 glass can be used as a reference material for the dating of chalcedony, despite a different matrix. The maximum difference of the mean values is ca. 3% (2 sigma). This difference, however, might be different by applying other LA-ICP-MS equipment and analytical conditions, which has not been tested systematically during this study. In addition, we note that the regression lines obtained by LA-ICP-MS and ID-TIMS for zone 7 show a slight off set (see Fig. 7f), i.e., the laser data start at lower initial $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (session 1: 0.700 ± 0.023 ; session 2: 0.776 ± 0.015) compared to the ID-TIMS data (0.794).

Younger ID-TIMS ages were obtained from the fragments 3 and 5, sampling the outer part of zone Z7 dominated by spherulic chalcedony and quartzine (i.e. zone 7+ in Figs. 4c, 7). Either subzone Z7+ was formed significantly later than the fibrous-banded chalcedony, or it was partially reset during the formation of zone Z8, dated at 6.8 ± 0.2 Ma by LA-ICP-MS (Fig. 7d). Partial age reset during Z8 growth could account for the variable $^{206}\text{Pb}/^{238}\text{U}^*$ ages, ranging from 10.00 ± 0.12 Ma (fraction 3b) to 8.6 ± 0.1 Ma (fraction 5b). The youngest age of fraction 5a (5.0 ± 0.1 Ma) would require additional Pb loss after zone Z8 formation, and/or additional radioisotopes like ^{234}U (see next section). The older $^{206}\text{Pb}/^{238}\text{U}^*$ ages obtained from the two fractions 6 (10.3 ± 0.1 Ma) and 7 (11.0 ± 0.4 Ma) might be explained by sample preparation. Considering the complexity of the agate structure, these fragments could result from minor admixing of material from the older zone Z6.

Taking all information into account, we suggest that the weighted mean $^{206}\text{Pb}/^{238}\text{U}^*$ age of 10.02 ± 0.05 Ma obtained from the fibrous-banded chalcedony of zone Z7 by ID-TIMS most likely represents the integral time of chalcedony formation, providing that this age is not biased by additional radioisotopes like ^{131}Pa , ^{227}Ac , ^{230}Th , ^{226}Ra and ^{234}U , which potentially can contribute to excess ^{206}Pb (Wendt and Carl, 1985). Except for ^{234}U , all other radioisotopes are highly immobile in oxidized fluids, from which SiO_2 mineralization is commonly precipitated (for detailed discussion see Neymark et al., 2002).

Assuming a Th/U ratio of 8.0, which is a typical value for rhyolitic rocks with $\text{SiO}_2 = 73 \text{ wt\%}$ (see Kirkland et al., 2015), increases the isochron ages of the four events E1 to E4 only slightly between 0.04 and 0.09 Ma (see Table 1). Considering ^{234}U disequilibrium causes an age decrease, those magnitude is strongly depends on the initial $^{234}\text{U}/^{238}\text{U}$ activity ($^{234}\text{U}/^{238}\text{U}_i$) at the time of agate growth. Initial ratios for $^{234}\text{U}/^{238}\text{U}$ are always > 1, but can be highly variable (e.g. between 1.1 and 8.2), as has been shown during previous studies on opal, silcrets and calcrets (e.g., Maher et al., 2007; Neymark, 2011; Oster et al., 2017). As ^{234}U has not been measured during this study, we simulate this affect by assuming a weighted average $^{234}\text{U}/^{238}\text{U}_i$ of 1.75 ± 0.32 (2 sigma), which results from the three studies mentioned above (also see Ritter et al., 2023). Applying this mean ratio will drop all isochron and TIMS ages by about 0.3 Ma (~2.8%), e.g., from 10.33 to 10.05 Ma for zone Z7 (LA-ICP-MS data; see Table 1), or from 10.02 Ma to 9.78 Ma (ID-TIMS data). Combining the effects of initial ^{230}Th and ^{234}U would result in a decrease of the uncorrected (equilibrium) ages by about 0.2 Ma (~2.0%; Table 1), still within the uncertainties of the LA-ICP-MS data. The ID-TIMS data would decrease from 10.02 Ma to 9.88 Ma.

However, it cannot be excluded that subsurface waters in the Rhodopes, which was controlled by a semi-arid climate during the Miocene (e.g., Scheiner et al., 2023), had significantly higher $^{234}\text{U}/^{238}\text{U}_i$ ratios than 1.75. For example, Neymark and Paces (2000) reported $^{234}\text{U}/^{238}\text{U}_i$ ratios of up to 8.2 for Quarternary opal from the Yucca Mountains in Nevada, and related these to slow opal growth rates (also see the discussions in Neymark et al., 2002). Assuming such an extreme $^{234}\text{U}/^{238}\text{U}_i$ ratio of 8.2 would decrease the age of zone Z7 from 10.33 to 7.68 Ma, close to the “uncorrected” isochron age obtained from zone Z8 (6.81 Ma). Thus, in theory, the zones Z7 and Z8 could have been formed at nearly the same time, but from fluids with extremely different $^{234}\text{U}/^{238}\text{U}_i$ ratios, of ca. 8.8 for zone Z7 and close to 1.0 for zone Z8.

Nevertheless, formation of all four zones of the Golobradovo agate

during a single short-lived hydrothermal event seems to be highly unlikely. In such a case, even more extreme $^{234}\text{U}/^{238}\text{U}_i$ ratios of 17.5, 25.2, and 34.5 would be needed, to decrease the age of zone Z1–Z3 (19.34 Ma), to that of zone Z4–Z6 (13.22 Ma), Z7 (10.33 Ma), and Z8 (6.8 Ma), respectively. A significant age bias due to ^{234}U disequilibrium also appears less likely, if we consider that the $^{206}\text{Pb}/^{238}\text{U}^*$ and $^{207}\text{Pb}/^{235}\text{U}^*$ ages (not affected by ^{234}U disequilibrium) obtained by ID-TIMS are within uncertainties identical for all aliquots (ESM-Table 2).

5.3. Geological meaning of U–Pb ages

The petrographic-spectroscopic results of this study show that the agates from Golobradovo exhibit a heterogeneous structure pointing to a complex formation history. The earliest stage along the transition zone between the rock matrix and agate, i.e., zone Z1, is defined by a complex mineralization made up by iron-rich sheet silicates (celadonite) and zeolites (clinoptilolite-Ca) enclosed by opal-CT (Fig. 2c–d). This mineralization suggests extensive alteration of the volcanic country rock by interaction with oxidized SiO_2 -rich fluids, resulting in the mobilization and re-precipitation of Si, Al, Ca, and Fe-bearing minerals. This alteration is well visible in the field by a successively more brownish colour and increasing rock hardness towards the thundereggs.

Zone Z1 was subsequently overgrown by SiO_2 -dominated zones (Z2 – Z9), made up by varying contents of opal-CT, fibrous-banded chalcedony, quartzine and a small amount of macrocrystalline quartz. These zones can clearly be distinguished from each other by different structures and/or mineral contents (Fig. 2c–f). The contacts between these zones are mostly knife sharp but in some cases grade continuously into each other (Figs. 2, 4, 9). Such a gradual transition is observed in particular between the zones Z7 and Z8, where an innermost zone, made up by fibrous-banded chalcedony grades into a zone dominated by spherulic chalcedony with quartzine (zone Z7+; Fig. 9).

Based on microscopic-spectroscopic observations, there is no evidence for any post-growth alteration of the zoning patterns. Neither dissolution or reaction fronts, nor cross-cutting veins have been observed. Nonetheless, it cannot be excluded that the primary SiO_2 mineralization of some zones was affected by alteration, accompanied by a partial reset of the U–Pb system. This, in particular, might be expected for all fine-grained zones, predominately made up by spherical aggregates of opal-CT (zones Z1, Z2), or quartzine $\pm$ spherical chalcedony (Z5, Z6, Z7+, Z8, Z9). Such zones are prone to aging, whereby losing H_2O , and undergo structural and mineralogical transformations, e.g. from opal into microcrystalline quartz (e.g., Kano, 1983; Thiry and Millot, 1987; Herdianita et al., 2000). On the other hand, the fibrous chalcedony of the zones Z3 and Z7 might have been precipitated directly from the aqueous solutions without any significant change afterwards (for example see Heaney, 1993). Aging processes can occur in less than

0.8 Ma, as is reflected by the U–Pb ages presented by Neymark et al. (2002) from zoned silica aggregates of the Yucca Mountains, Nevada (e.g., their sample 2019A1a). This timing is in good agreement with the results of this study, showing that individual zones, but also packages of zones with different SiO_2 mineralization, reached closure of their respective U–Pb systems in mostly less than 0.7 Ma (Table 1), significantly before the formation of younger zones. This is best demonstrated by the ID-TIMS $^{206}\text{Pb}^*/^{238}\text{U}$ mean age of 10.02 ± 0.05 Ma of the inner, fibrous-banded chalcedony part of zone Z7, and the LA-ICP-MS age of 6.81 ± 0.20 Ma of zone Z8. However, the results of ID-TIMS dating suggest, that the outer, quartzine-bearing part of zone Z7 (Z7+) was affected by a prolonged period of Pb loss, ranging from ca. 10 to 5 Ma, albeit extreme ^{234}U disequilibrium cannot completely be excluded.

Taking all information into account, the results of this study show that the Golobradovo agate zones of variable mineralogy and structures were periodically formed over ca. 12 million years, during 4 distinct fluid events at 19.3 ± 0.3 Ma (E1), 13.2 ± 0.7 Ma (E2), 10.3 ± 0.3 Ma (E3), and 6.8 ± 0.2 Ma (E4) – (Figs. 7, 9). The four mean ages would be ca. 0.2 Ma younger, if both the ^{230}Th and ^{234}U disequilibrium, with the parameters presented above, are taken into account. The data further indicate that the U–Pb system of stratigraphically older zones was, at least in some cases not significantly reset during subsequent fluid-rock interaction processes, except for the zone Z7+ as discussed above. This implies that after the process of silica aging has ceased, diffusion of U and Pb was insignificant in most zones of different SiO_2 mineralization (commonly <250 μm across), and that coupled dissolution-reprecipitation processes (Putnis and Putnis, 2007) did not occur. Furthermore, this suggests that the agate zones were precipitated from low-T, neutral to basic aqueous solutions, preventing selective Pb leaching and SiO_2 dissolution. Both processes were observed in experiments of Ohtake et al. (1982), investigating the interaction of glass with acidic solutions. Another important finding of this study is that the formation of agate (19–7 Ma) occurred significantly later than the volcanic host rock (ca. 32 Ma). Such an age gap between volcanic activity and agate genesis has already been noted for agate deposits in basic volcanic rocks (e.g., Gilg et al., 2014; Ottens et al., 2019; Götze et al., 2020b; Arduine-Rode et al., 2024). Here it is now also evidenced for the thunderegg agates in the acidic volcanic rocks of the Eastern Rhodopes.

6. Conclusions

1. Combined results of petrography, spectroscopy and U–Pb dating indicate that agates from acidic volcanic rocks at the Golobradovo site in the Eastern Rhodopes (Bulgaria) formed over a period of 12 Ma, between ca. 19 and 7 Ma, much later than volcanic host rock formation during the Oligocene.

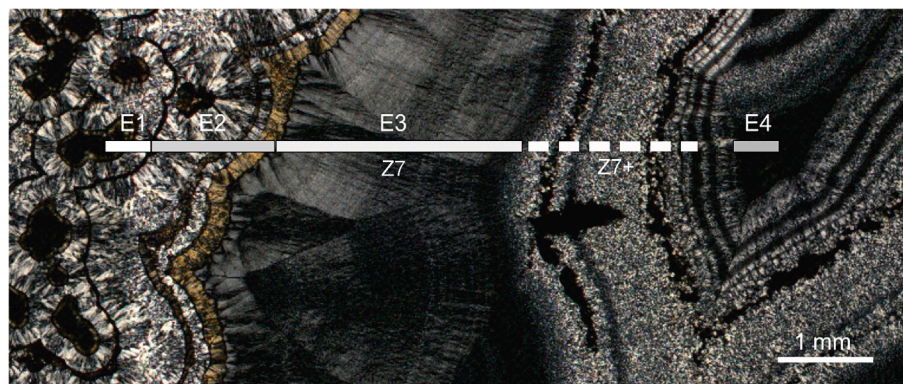


Fig. 9. Photomicrograph (crossed pols) showing the investigated Golobradovo agate with zones of different SiO_2 mineralization. The domains E1 to E4 mark agate zones of different age (see Table 1). Z7 and Z7+ mark different subdomains of zone Z7 dated by ID-TIMS (Z7 – fibrous-banded chalcedony, Z7+ – spherulic chalcedony with quartzine).

- Variations in SiO₂ phases and microstructure, combined with results of U–Pb dating indicate periodic precipitation of agate zones with different SiO₂ phases (opal-CT, quartzine, fibrous-banded chalcedony, macrocrystalline quartz) during 4 major stages of hydrothermalism at 19.3 ± 0.3 Ma, 13.2 ± 0.7 Ma, 10.3 ± 0.3 Ma, and 6.8 ± 0.2 Ma.
- The results further indicate that zones with variable SiO₂-rich mineralization and < 250 µm across, can be dated with high precision by LA-ICP-MS, and that these ages are identical within uncertainties to such obtained by ID-TIMS.
- Comparable results can be obtained by applying NIST-SRM612 glass as reference material for LA-ICP-MS, and by applying appropriate outlier corrections for time-resolved Pb-signals.
- The combined results further suggest that the U–Pb system of older agate zones, made up by different SiO₂ mineralization, mostly remains stable during subsequent fluid overprint, and is barely affected by U–Pb diffusion and/or coupled dissolution-reprecipitation processes.

CRedit authorship contribution statement

Armin Zeh: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Jens Götz:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Marion Tichomirowa:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alexandra Käßner:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Maximilian Mroczek:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2026.123681>.

Data availability

Data will be made available on request.

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