U–Pb geochronology of epidote by LA–ICP–MS as a tool for dating hydrothermal-vein formation

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Abstract. ~~Monoclinic e~~Epidote – here defined as minerals belonging to the epidote–clinozoisite solid solution – is a low-μ (μ = ~~238~~3$U/^{204}Pb$) mineral occurring in a variety of geological environments, participating in many metamorphic reactions and stable throughout a wide range of pressure–temperature conditions. Despite containing fair amounts of U, its use as a U–Pb geochronometer has been hindered by the commonly high contents of initial Pb with isotopic compositions that cannot be assumed a priori. We present U–Pb geochronology of hydrothermal-vein epidote spanning a wide range of Pb (3.9–190 μg g⁻¹), Th (0.0~~109~~1–38 μg g⁻¹) and U (2.6–530 μg g⁻¹) contents and with μ values between 7–510 from the Albula area (eastern Swiss Alps), from the Grimsel area (central Swiss Alps) and from the Heyuan fault (Guangdong province, China). The investigated epidote samples show appreciable fractions of initial Pb contents (f_{206} = 0.7–1.0) – i.e. relative to radiogenic Pb – that vary to different extents. A protocol has been developed for in situ U–Pb dating of epidote by spot-analysis laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) with a magmatic allanite as primary reference material. The suitability of the protocol and the reliability of the measured isotopic ratios have been ascertained by independent measurements of $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios respectively by quadrupole and multicollector ICP–MS applied to epidote micro-separates digested and diluted in acids. For age calculation, we used the Tera–Wasserburg ($^{207}Pb/^{206}Pb$ versus $^{238}U/^{206}Pb$) diagram, which does not require corrections for initial Pb and provides the initial $^{207}Pb/^{206}Pb$ ratio ~~if all intra-sample analyses are co-genetic~~. Petrographic and microstructural data indicate that the calculated ages date the crystallization of vein epidote from a hydrothermal fluid and that the U–Pb system was not reset to younger ages by later events. Vein epidote from the Albula area formed in the Paleocene (62.7 ± 3.0 Ma) and is related to Alpine greenschist-facies metamorphism. The Miocene (19.2~~1~~ ± 4.3~~0~~ Ma and 16.9 ± 3.7 Ma) epidote veins from the Grimsel area formed during the Handegg deformation phase (22–17 Ma) of the Alpine evolution of the Aar Massif. Identical initial $^{207}Pb/^{206}Pb$ ratios reveal homogeneity in Pb isotopic compositions of the fluid across ca. ~~2~~100 m. Vein epidote from the Heyuan fault is Cretaceous in age (10~~7.2~~~~8.1~~ ± 8.~~9~~4 Ma) and formed during the early movements of the fault. In situ U–Pb analyses of epidote returned reliable ages of otherwise undatable epidote-quartz veins. The Tera–Wasserburg approach has proven pivotal for in situ U–Pb dating of epidote and the decisive aspect for low age uncertainties is the variability in intra-sample initial Pb fractions.

1 Introduction

Linking petrological and structural information to the timing of geological events is crucial to better constrain the sequence of geodynamic processes. In this context, the role of fluids in the continental crust is particularly relevant because they
35 mediate and influence deformation and metamorphism (e.g. Wyllie, 1977; Etheridge et al., 1983; Johannes, 1984; Pennacchioni and Cesare, 1997; Malaspina et al., 2011; Wehrens et al., 2016). The formation of a hydrothermal vein represents a specific deformation and hydration event in the geological history of the host rock, during which the vein-filling minerals record the geochemical signature of the mineralizing fluid (e.g. Elburg et al., 2002; Barker et al., 2009; Bons et al., 2012; Parrish et al., 2018; Ricchi et al., 2019; 2020). By combining different geochemical and geochronological techniques
40 to suitable vein-filling minerals it is therefore possible to determine when the vein formed and the isotopic signature of the fluids for insight into their origin (e.g. Pettke et al., 2000; Barker et al., 2006; Elburg et al., 2002).

~~Monoclinic~~The epidote~~–~~clinozoisite solid solution [Ca$_2$Al$_3$Si$_3$O$_{12}$(OH)–Ca$_2$Al$_2$Fe^{3+}Si$_3$O$_{12}$(OH)], hereafter referred to as epidote, produces ~~is a~~ common rock-forming and vein-filling mineral_s_ (e.g. Bird and Spieler, 2004; Franz and Liebscher, 2004; Guo et al., 2014; Zanoni et al., 2016). ~~It~~Epidote is stable over a wide range of pressure–temperature conditions and in
45 a multitude of magmatic, metamorphic and hydrothermal mineral assemblages (Bird and Spieler, 2004; Enami et al., 2004; Grapes and Hoskin, 2004; Schmidt and Poli, 2004). Its complex crystal structure incorporates ~~of~~ a large variety of elements, enabling the measurements of trace element (e.g. Frei et al., 2004) and isotopic (e.g. Guo et al., 2014) signatures. Uranium and thorium are readily accepted into the epidote structure, with contents that are highly variable but generally in trace element levels (Frei et al., 2004). Hence, attempts have been made at using it as a geochronometer by step-wise leaching Pb–
50 Pb dating (e.g. Buick et al., 1999) and thermal ionization mass spectrometry (TIMS) U–Pb dating (e.g. Oberli et al., 2004). Buick et al. (1999) constrained the timing of vein formation and that of subsequent fluid pulses in garnet-epidote-quartz veins in the Reynolds Range (central Australia). Oberli et al. (2004; their Sect. 5.3 and their Fig. 5) obtained a U–Pb age of magmatic epidote from the Bergell pluton (eastern Central Alps) and identified epidote formation as a late-stage process during the solidification of the pluton. However, these techniques allow microstructural control only if sampling by micro-
55 drilling is viable.~~none of these techniques are in situ, and they cannot target different microstructural and textural domains.~~ ~~Monoclinic e~~Epidote could provide valuable geochronological and isotopic information where no other datable minerals are available. Good examples are epidote-quartz veins that are widespread in the Alps (e.g. Aar Massif and Albula area). Syn-kinematic epidote in breccias associated with rift-related faults in the Campos basin (southeastern Brazil) may highlight successive phases of fault movement (Savastano et al., 2017). In the Zermatt-Saas Zone (Western Alps), epidote is a peak-
60 pressure rock-forming mineral in epidote-bearing rodingites (Zanoni et al., 2016) and it may help to better constrain the P–T–d–t paths related to pressure-peak metamorphism.

This contribution discusses the applicability of in situ U–Pb dating to minerals compositionally within the epidote–clinozoisite solid solution ~~monoclinic epidote~~. To our knowledge, no analytical protocols have been proposed in this respect. To fill this gap, we present U–Pb ages measured in hydrothermal-vein epidote by LA–ICP–MS using a magmatic allanite for

65 standardization, following a protocol similar to that applied to apatite U–Pb dating (e.g. Odlum and Stockli, 2019; 2020). The main issues related to the proposed geochronometer and addressed in this contribution are 1) the suitability of magmatic allanite as the most closely matrix-matched reference material for LA–ICP–MS U–Pb dating of ~~monoclinic~~ epidote in spot-analysis mode, 2) the applicability of the protocol with respect to the different contents of initial Pb fractions (i.e. relative to radiogenic Pb in total Pb) and U in the studied samples and 3) the effects on age precision of the interplay between analyzed

70 volumes and preservation of chemical variability. The Tera–Wasserburg diagram proves to be the key tool for successful epidote U–Pb geochronology, allowing to add minerals of the epidote–clinozoisite solid solution ~~monoclinic epidote~~ to the list of low-μ U–Pb geochronometers. Notably, by investigating epidote on its own, it is possible to combine U–Pb ages and isotopic systematics with data from trace element analyses and other isotopic systems; this may permit to reconstruct fluid flow and its origin with information that is all provided by a single mineral.

75 **1.1 The challenges of investigating ~~monoclinic~~ epidote as a geochronometer**

Along with relevant amounts of U^{4+} and Th^{4+} as Ca substitution in the A site and of U^{6+} as Al or Fe substitution in the M site (Frei et al., 2004), high contents of initial Pb are incorporated by epidote during crystallization. This causes the dilution of ingrown radiogenic Pb, whose precise measurements are imperative for U–Pb geochronology, and makes epidote a low parent-to-daughter or low-μ phase (i.e. μ < ca. 2000; Romer, 2001; Romer and Xiao, 2005). U–Pb dating of initial Pb-rich

80 minerals can proceed in two ways depending on whether or not the isotopic composition of the initial Pb is known or can be reasonably assumed. Assumptions can be based on the modeled evolution of global Pb isotopic compositions such as those proposed by Cumming and Richards (1975) and Stacey and Kramers (1975). In the first case, a correction for initial Pb can be applied, and an initial Pb-corrected U–Pb age can be calculated from the measured U($\pm$Th)–Pb isotopic ratios of each analysis (Williams, 1998). However, age inaccuracies due to wrong assumptions regarding initial Pb isotopic compositions

85 ~~are remarkable~~can be significant (see Romer, 2001; Romer and Xiao, 2005). An initial Pb-correction can be applied ~~without any assumptions~~ if the contents of ^{204}Pb – the only non-radiogenic lead isotope – can be measured precisely, which is not always the case ~~.~~(e.g. because of the analytical technique employed). Hence, if no other dating method is viable (e.g. too low Th contents hampering Th–Pb dating), the best solution for dating of low-μ phases is to use a regression through the analyses uncorrected for initial Pb on the Tera–Wasserburg diagram (Tera and Wasserburg, 1972), which plots measured $^{207}Pb/^{206}Pb$

90 versus $^{238}U/^{206}Pb$ ratios. ~~If the isotopic composition of initial Pb is unknown, ^{204}Pb contents cannot be precisely determined (e.g. because of the analytical technique employed) and no other dating method is viable (e.g. too low Th contents hampering Th Pb dating), a valuable tool for U Pb dating of low μ phases is the Tera Wasserburg diagram (Tera and Wasserburg, 1972) that plots measured $^{207}Pb/^{206}Pb$ versus $^{238}U/^{206}Pb$ ratios.~~ Its advantages are that 1) it does not require corrections for initial Pb isotopic compositions, 2) it provides the initial $^{207}Pb/^{206}Pb$ ratio itself in addition to an initial ^{207}Pb-

95 corrected U–Pb age, and 3) it gives an estimate of the fractions of initial lead relative to those of radiogenic Pb in each analysis (Tera and Wasserburg, 1972; Ludwig, 1998). This approach is based on the hypotheses that multiple analyses are performed on material of the same age ~~and~~ sharing the same initial Pb isotopic composition. If these criteria are met, one

regression is defined by the alignment of the measurements of $^{207}Pb/^{206}Pb$ vs. $^{238}U/^{206}Pb$ ratios, whose lower intercept with the concordia yields the age of the sample. If the hypotheses prove to be wrong (e.g. multiple mineral generations or co-genetic minerals with different initial Pb isotopic compositions; e.g. Romer and Siegesmund, 2003), this is highlighted by the statistical parameters of the regression. The fraction of initial Pb in each analysis can be estimated from the proximity of individual data points to the upper $^{207}Pb/^{206}Pb$ intercept of the regression (Tera and Wasserburg, 1972; Ludwig, 1998) which gives the initial $^{207}Pb/^{206}Pb$ ratio of the sample. The regression in the Tera–Wasserburg diagram is better constrained and yields more precise ages if the variability in initial Pb and U contents is high enough to produce spread-out data points. The Tera Wasserburg approach, however, is not suitable for all initial Pb rich mineral. In fact, key to a successful use of this diagram is a reasonable spread in plotted data points, which depends on the variability in initial Pb fractions and U contents. If the analyzed mineral has poorly variable fractions of initial Pb and U concentrations, the regression cannot be well constrained and age precision is low. Epidote minerals are commonly characterized by chemical zoning (Franz and Liebscher, 2004), which may also reflect result in variability in initial Pb fractions and U contents and may promote spread of the data points along the Tera–Wasserburg regression.

A suitable technique for in situ U–Th–Pb dating is LA–ICP–MS in spot-analysis mode, provided that U/Pb and Th/Pb elemental fractionation at the ablation site (downhole fractionation, DF) is appropriately corrected for over ablation time by relying on an external reference material (e.g. Sylvester, 2005; Košler, 2007; McFarlane et al., 2016). Since DF is matrix dependent (e.g. Sylvester, 2005; Košler, 2007; Sylvester, 2008; El Korh, 2014), a matrix-matched reference material is most commonly used. To date, no reference epidote exists, posing the problem of correction for DF of $^{238}U/^{206}Pb$ ratios measured in epidote, crucial for accurate age determinations by LA–ICP–MS (Horstwood et al., 2016). One way to date epidote by LA–ICP–MS would be by dynamic (raster) ablation with a non-matrix-matched reference material (e.g. Darling et al., 2012). However, large-enough areas within epidote grains are frequently not available for dynamic ablation. However, in recent years, magmatic allaniteA mineral with a matrix that closely matches that of epidote is allanite. After early work by ID–TIMS (e.g. Barth et al., 1994), magmatic allanite has been dated by SIMS (e.g. Catlos et al., 2000) and in recent years it has been successfully characterized and dated by U–Th–Pb LA–ICP–MS (e.g. Gregory et al., 2007; 2012; El Korh, 2014; Smye et al., 2014)., and sSeveral allanite samples have been proposed as suitable primary reference materials for LA–ICP–MS dating (e.g. Gregory et al., 2007; Smye et al., 2014). Allanite [(Ca, REE, Th)$_2$(Fe^{3+}, Al)$_3$Si$_3$O$_{12}$(OH)] is the REE-rich member of the epidote mineral group with ThO$_2$ contents of 2–3 wt% and U concentrations often below 1000 ppm (Gieré and Sorensen, 2004; and references therein), and it is a promising candidate as a closely matrix-matched reference material for monoclinic epidote minerals of the epidote–clinozoisite solid solution. The possible issues in the use of allanite as reference material for accurate U–Th–Pb geochronology are mostly related to local isotopic heterogeneity, excess ^{206}Pb due to incorporation of ^{230}Th during crystallization, variable contents of initial Pb and disturbance of the geochronometer by secondary processes (e.g. hydrothermal alteration; Gregory et al., 2007; Darling et al., 2012; Smye et al., 2014; Burn et al., 2017). Nevertheless, these issues can be largely avoided by careful selection of spot analyses referring to backscattered electron (BSE) images, and by identifying and excluding problematic analyses from calculations.

A disadvantage of U–Pb analyses by LA–ICP–MS is the large isobaric interference on mass 204 by ^{204}Hg of the carrier gas. A correction for such an interference in order to apply a ^{204}Pb-correction – whether based on measurements of the initial Pb isotopic composition in the same mineral or in coexisting ones (e.g. Cenki-Tok et al., 2014) – is complex (e.g. Storey et al., 2006)., and therefore leaves one with the only option of the application of the Tera–Wasserburg approach. For this reason, and considering that epidote-bearing veins may not include other minerals suitable to determine the initial Pb isotopic composition, the application of the Tera–Wasserburg approach is preferable. In this study, epidote ages and initial ^{207}Pb/^{206}Pb ratios are assessed from the Tera–Wasserburg diagram. If initial ^{207}Pb/^{206}Pb ratios are consistent with modeled values of initial Pb isotopic compositions (e.g. Stacey and Kramers, 1975), then an accurate ^{238}U/^{206}Pb age can be obtained by averaging single-spot ages, which are calculated from each analysis corrected for initial Pb by applying a ^{207}Pb-correction (i.e. weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb age; see Williams, 1998).

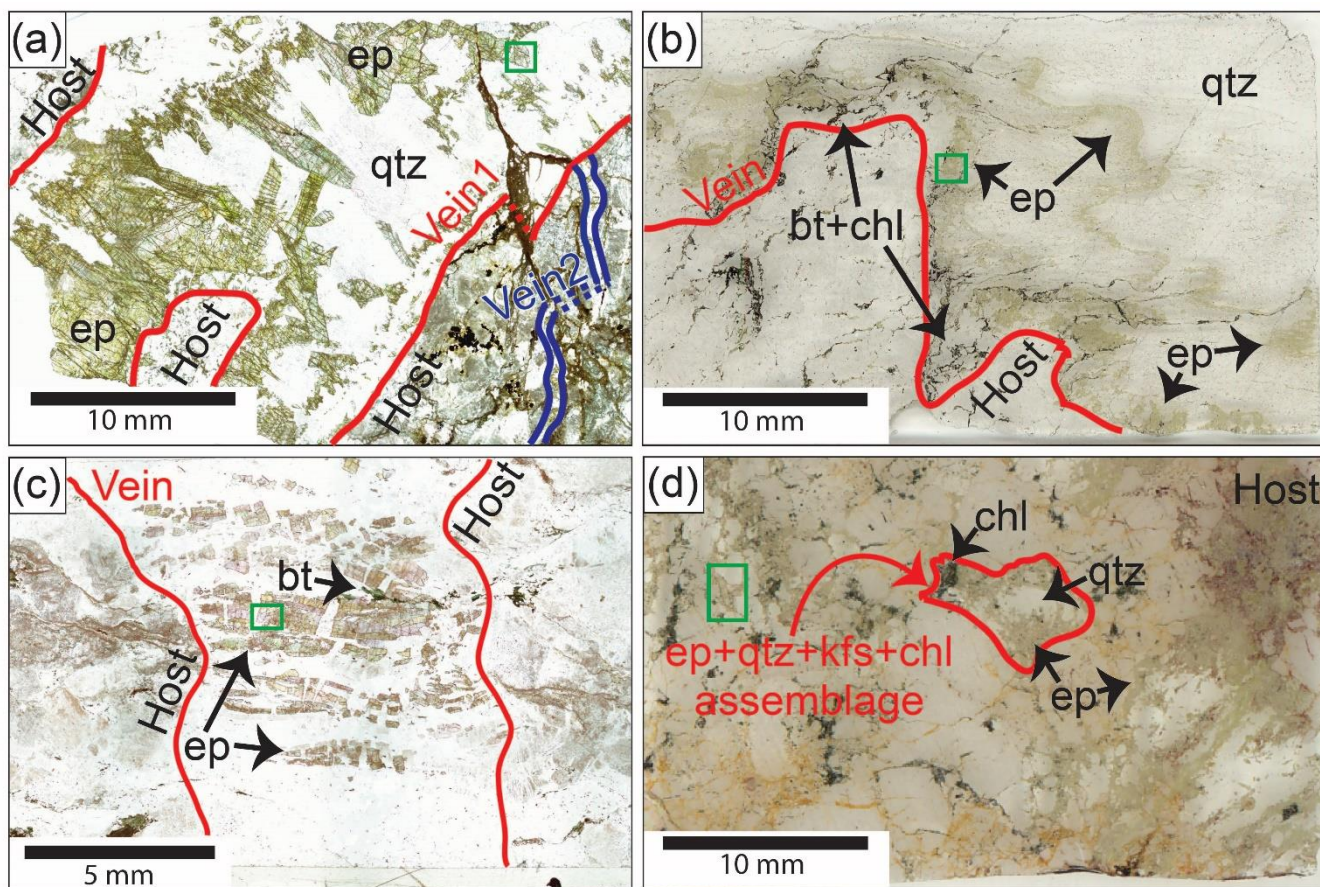## 2 Geological context and field relations
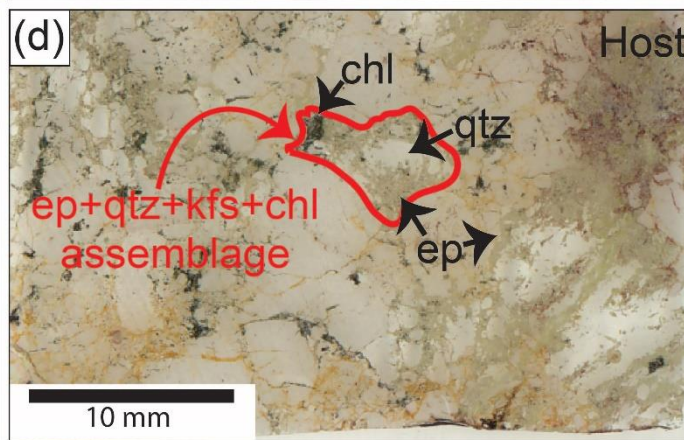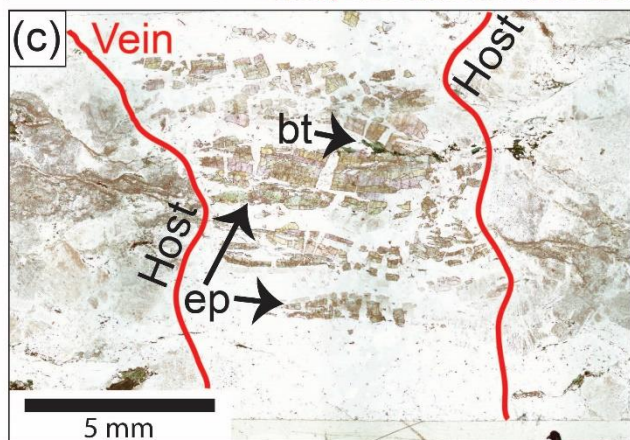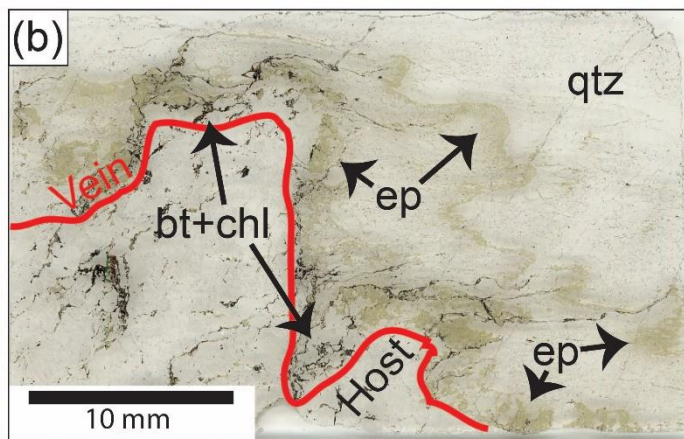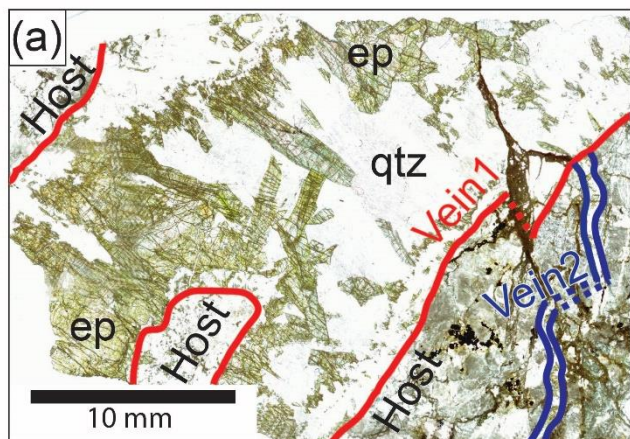
Figure 1: Scans of thin sections of (a) Albula-1, (b) Grimsel-1, (c) Grimsel-2 and (d) Heyuan-1 samples. (a) and (b): plane polarized light on petrographic microscope; (c) and (d): plane light. Green rectangles indicate the location of the BSE images shown in Fig. 2. bt = biotite; chl = chlorite; ep = epidote; kfs = K-feldspar; plg = plagioclase; qtz = quartz.

Hydrothermal epidote veins (Fig. 1) were sampled at Albula Pass (eastern Swiss Alps), at Grimsel Pass (central Swiss Alps) and at the Heyuan Fault (Guangdong Province, China). Although there are no precise anticipated ages for the selected epidote samples, the well-constrained tectonic histories of the sampling areas and of the lithologies hosting the studied epidote-bearing veins allow to verify whether or not the obtained ages are geologically reasonable. Sampling locations are respectively shown in Fig. 1 of Şengör (2016), in Fig. 1 of Wehrens et al. (2017), and in Figs. 1 and 2 of Tannock et al. (2020a). The Albula area was chosen because the weak Alpine overprint allows for the hypothesis that epidote veins were not geochemically and isotopically altered after their formation. The Grimsel area is advantageous because of the vast knowledge about the tectono-metamorphic events that affected the region. The Heyuan Fault was selected because structural constraints allow to assess if the calculated U–Pb age is reasonable for epidote crystallization.

The Albula area is located in the upper Err nappe, close to the tectonic contact with the Ela nappe. It belongs to the Austroalpine domain, the basement of the former Adriatic continental margin (e.g. Froitzheim and Eberli, 1990; Froitzheim

8

et al., 1994). The most common lithology in the Err basement is the Albula Granite, a granodiorite of Variscan to post-Variscan age (e.g. Manatschal and Nievergelt, 1997; Incerpi et al., 2017) and in which epidote ± quartz veins are widespread. In the late Carboniferous and early Permian, the Albula Granite intruded into the metamorphic basement of the Err nappe at < 3 km depth (Mohn et al., 2011; and references therein). Subsequently, the Lower Austroalpine was involved in the Jurassic rifting that led to the break-up of Pangea (e.g. Manatschal et al., 2000). During the Alpine orogeny, the Err nappe mainly recorded the deformation resulting from the W- to NW-directed vergence of the Austroalpine domain from Cretaceous until early Cenozoic times ~~with maximum metamorphic conditions reaching lower greenschist facies,~~ and was only weakly affected by the Cenozoic tectonics, when temperatures reached ca. 300 °C (i.e. lower-greenschist facies conditions; e.g. Froitzheim and Manatschal, 1996; Mohn et al., 2011; Epin et al., 2017). Sample Albula-1 was collected at coordinates 46°34'36"N/9°48'06"E and has not been described in previous studies.

The Grimsel area is in the Aar Massif, one of the External Crystalline Massifs of the Alps (Rolland et al., 2009; Wehrens et al., 2017; Herwegh et al., 2020). Here, epidote-quartz veins are common in the Central Aar granite and in the Grimsel granodiorite, which during the earliest Permian intruded into a polycyclic basement bearing evidence of Ordovician metamorphism and Variscan overprint (Schaltegger and Corfu, 1992; Berger et al., 2017). After being affected by the Jurassic rifting, the Aar Massif was involved in the continent–continent collision during the Alpine orogeny, as demonstrated by the presence of anastomosing high-strain shear zones of Alpine age (e.g. Goncalves et al., 2012; Wehrens et al., 2017). Metamorphism at greenschist facies conditions reached 450 ± 30 °C at 0.6 ± 0.1 kbar in this area (Challandes et al., 2008; Goncalves et al., 2012). The Alpine history of the Aar Massif is subdivided into three phases: 1) the Handegg phase (22–17 Ma; Challandes et al., 2008), with stable green biotite in the shear zones (Challandes et al., 2008; Rolland et al., 2009; Herwegh et al., 2017; Wehrens et al., 2017); 2) the Oberaar phase in the southern Aar Massif (14–3.4 Ma; Hofmann et al., 2004; Rolland et al., 2009), with white mica and chlorite stable in the shear zones, and metastable biotite (Herwegh et al., 2017; Wehrens et al., 2017); 3) the Pfaffenchopf phase in the northern Aar Massif (< 12 Ma; Herwegh et al., 2020). The epidote-quartz veins analyzed in this study were sampled ~~at a distance of ca. 200 m~~ in the Nagra Felslabor tunnel at Grimsel Pass. As these veins are only visible within the tunnel, their relationships with Alpine structures and between each other are not ~~understood~~known. Samples Grimsel-1 and Grimsel-2 have not been previously described and they were sampled at a distance of ca. 100 m, respectively close to "F100" and in the BK cavern in Fig. 1.2 of Schneeberger et al. (2019).

The Heyuan Fault is a crustal-scale fault that formed in Mesozoic times as a low-angle normal fault, but is currently active under a transpressive regime (Tannock et al., 2020a; 2020b). The footwall of this fault mainly consists of the Xinfengjiang pluton (the eastern portion of the Fogang batholith), a late Jurassic biotite granite that intruded into the basement of Proterozoic to Silurian age during the Yanshanian orogeny (Li et al., 2007; Tannock et al., 2020a; 2020b). Epidote veins are located in the mylonites at the transition between undeformed granite and fault zone (Tannock et al., 2020a). The hanging wall is composed of a quartz-sericite ultracataclasite/phyllonite in contact with a quartz reef and finally abutted by the sedimentary "Red Beds" of Cretaceous age (Tannock et al., 2020a). Since the epidote veins are either pre- or syn-kinematic with respect to the mylonites (Tannock et al., 2020b), we infer that the epidote veins cannot be older than the pluton itself,

but they are also among the earliest structures related to the early movements of the Heyuan Fault (Tannock et al., 2020a; 2020b). Epidote veins are absent in the footwall cataclasite and in the quartz reef, which formed after the mylonite. Syn-

195 kinematic epidote veins formed at a temperature of ca. 330 °C as indicated by the white mica composition in the mylonites (Tannock et al., 2020a). Sample Heyuan-1 is discussed in Tannock et al. (2020a; 2020b) and its sampling location is shown in Fig. 1 of Tannock et al. (2020a; their sample HY17-5).

3 Methods

Except where stated, sample preparation and measurements were carried out in the laboratory facilities of the Institute of
200 Geological Sciences, University of Bern, Switzerland.

3.1 Imaging and screening methods for sample selection

Thin (30 μm) and thick (50–60 μm) sections were inspected by petrographic and electron microscopy, respectively on a ZEISS Axioplan microscope and on a ZEISS EVO50 SEM using BSE imaging (ca. 1 nA beam current, 20 kV accelerating voltage, working distance 8.5–10.0 mm). BSE images were used to plan analysis spots – all of the same size – within epidote
205 grains so as to avoid mixing of different zonings in each single measurement, as well as mineral and fluid inclusions. Major element contents were acquired by electron probe micro-analyses (EPMA), and REE, U, Th and Pb contents were measured by LA–ICP–MS upon screening many samples, employing methods presented elsewhere (Pettke et al., 2012). The details of the EPMA and LA–ICP–MS setups are reported in Appendix A.

3.2 U–Pb geochronology by LA–ICP–MS

210 Isotopic measurements of U, Th and Pb were performed on thin/thick sections for epidote and on acryl grain mounts for allanite. To minimize surface contamination, the thin/thick sections were cleaned with ethanol, and the grain mounts with ethanol and 5 % HNO_3. Measurements of U, Th and Pb isotopic ratios were performed with a Resonetics RESOlutionSE 193 nm excimer laser system (Applied Spectra, USA) equipped with a S-155 large-volume constant-geometry chamber (Laurin Technic, Australia) coupled with an Agilent 7900 ICP–QMS. The suitability of analytical conditions (Table 1) was checked
215 in each session by performing preliminary analyses on secondary reference materials of known ages – namely CAP[b] allanite (CAP[b] allanite; for details see Burn et al., 2017); and CAP and AVC allanites; (for details see Barth et al., 1994; Gregory et al., 2007) – and comparing them to their published U–Pb ages reference values(see Table 2). Low fluence of 3 J s^{-2}, low repetition rate of 5 Hz and large spot size of 50 μm were combined to ensure a slow increase in depth/diameter ratio of the laser crater during a 40 sec ablation time, hence to minimize elemental (U/Th/Pb) DF.

220

Table 1: Measurement conditions on Agilent 7900 for U–Th–Pb isotopic data by LA–ICP–MS.

RF power

14 June 2019	23 July 2019	16 January 2020
1280 W	1320 W	1380 W

Fluence (all sessions)

3 J cm^{-2}

Repetition rate (all sessions)

5 Hz

Cell gas flow

14 June and 23 July 2019	16 January 2020
3.0 ml min^{-1} N$_2$ and 350 ml min^{-1} He	3.0 ml min^{-1} N$_2$ and 400 ml min^{-1} He

Sensitivity on mass 232 measured on NIST SRM612 by dynamic ablation (beam size, fluence, repetition rate, scan rate)

14 June 2019	23 July 2019	16 January 2020
4150 cps/ppm~~ea. 1'500'000 cps~~ (50 µm, 2.5 J cm^{-2}, 5 Hz, 5 µm sec^{-1})	~~ca. 1'600'500 cps~~4410 cps/ppm~~-~~ (50 µm, 2.5 J cm^{-2}, 5 Hz, 5 µm sec^{-1})	~~ca. 1'300'400 cps~~3590 cps/ppm (50 µm, 2.5 J cm^{-2}, 5 Hz, 5 µm sec^{-1})

232/238 ratio (all sessions)

> 0.97

248/232 ratio (all sessions)

< 0.002

Background (all sessions)

30 sec

Pre-cleaning (beam size in µm)

14 June and 23 July 2019	16 January 2020
10 pulses (64); followed by wait time of 10 s before ablation	10 pulses (30); followed by wait time of 10 s before ablation

Ablation time (beam size in µm)

14 June and 23 July 2019	16 January 2020
40 sec (50)	4~~3~~0 sec (30)

An additional session was carried out with a laser spot of 30 μm and the same laser conditions. The aim was to assess the effects of using a smaller spot size on the correction for DF (see Chew et al., 2014) and to explore whether the use of allanite

225 as primary reference material can still provide accurate data at these conditions. If so, this would extend the applicability of the present protocol to smaller epidote grains. For this test, we selected two samples: the one also used for solution ICP–MS measurements (sample Abula-1; see Sect. 3.3), and the one with the smallest averaged analytical errors on ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios (sample Grimsel-1). The 30 μm analyses were done in the same areas and crystals analyzed in the previous sessions after polishing the thin/thick sections to remove the condensation blankets around the ablation craters. In all

230 sessions, Tara allanite (see Gregory et al., 2007; Smye et al., 2014) is chosen as primary reference material because it is the most homogenous allanite in terms of U–Th–Pb isotopes (Gregory et al., 2007; Burn et al., 2017) and the most promising reference material for U–Pb geochronology (Gregory et al., 2007; Smye et al., 2014; Burn et al., 2017; Liao et al., 2020). Tara allanite reference isotopic ratios and their uncertainties (Table 2) were calculated by averaging five of the six ID–TIMS measurements reported by Smye et al. (2014), excluding the measurement that yielded the youngest U–Pb age outside

235 uncertainty (Smye et al., 2014). The analytical sequence involved measurements of the reference Tara allanite interspersed between 3–9 sample measurements including allanite secondary reference materials for quality control. Analysis spots in allanite were planned based on BSE images to avoid chemical and isotopic heterogeneity (i.e. mixing of zoning) within each single analysis, and inclusions (e.g. rare < 1 μm sized thorite; Smye et al., 2014). A few analyses were however intentionally planned on fluid inclusions and across zoning in sample Albula-1 to ascertain that these features would not compromise the

240 use of this sample for solutions ICP–MS (see Sects. 3.3 and 4.3).

Table 2: Reference data of Tara allanite for normalization of U–Th–Pb isotopic data by LA–ICP–MS, and published U–Pb Tera–Wasserburg ages of CAP[b], CAP and AVC allanite secondary reference materials. The ratios for Tara allanite are averages calculated from the measurements by Smye et al. (2014) by ID–TIMS; one measurement was excluded (see text). Uncertainties are

245 **given in brackets and are calculated as 2 standard errors. Subscript r = radiogenic ratio; subscript i = initial; superscript a = U–Pb**

age used as reference in this contribution (see Sect. 5.1 for details). (a) = calculated from five ID–TIMS data of Smye et al. (2014), unanchored regression; (b) = from Burn et al. (2017); (c) = from Gregory et al. (2007). c = common.

Isotopic ratio	Tara allanite			
$(^{206}Pb/^{238}U)_r$	0.0678 (0.0008)			
$(^{207}Pb/^{235}U)_r$	0.5020 (0.0173)			
$(^{208}Pb/^{232}Th)_r$	0.0195 (0.0021)			
$(^{207}Pb/^{206}Pb)_r$	0.0537 (0.0016)			
$(^{207}Pb/^{206}Pb)_{ci}$	0.866 (0.079)			
Reference age[a]	Tara allanite	CAP[b] allanite	CAP allanite	AVC allanite
U–Pb age	420 ± 16 Ma (a)	284.9 ± 2.8 Ma (b)	275.0 ± 4.7 Ma (c)	289.6 ± 5.6 Ma (c)

Raw data were treated in the software Iolite (version 7.08) by the VisualAge_UcomPbine Data Reduction Scheme (Chew et al., 2014), and the correction for DF was carried out by selecting an exponential function. Iolite fits this function to model the measured DF on the analyses of the primary reference material, and then applies it to all unknown analyses to correct them for DF. The quality of signals and that of the correction for DF were considered to determine the validity of each measurement. Assessing the quality of signals implies inspection of the laser signal of each isotope across each measurement to discard – partially or entirely – those that are contaminated by impurities such as mineral or fluid inclusions, or that show isotopic heterogeneity during ablation. Assessing the correction for The accuracy of DF correction depends is based on the fact that if the ablation behavior is being the same between primary reference material and sample, the correction for DF of the isotopic ratios measured in the latter is accurately carried out, as and is assessed by the unknowns giving flat their DF-corrected $^{206}Pb/^{238}U$ ratios being flat during across the ablation once corrected for DF. Although we do not apply an initial Pb correction for age calculation, correcting the time-resolved DF-corrected $^{206}Pb/^{238}U$ ratios for initial Pb ensures that no sloping results from zoning in initial Pb contents, which can be prominent in minerals with high initial Pb contents. A ^{208}Pb-correction is therefore applied to each analysis of the epidote unknowns using initial $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios obtained from preliminary Tera–Wasserburg diagrams. This and the subsequent normalization of the measured ratios based on the reference values of the primary reference material ensure that the $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios used in the Tera–Wasserburg diagrams are true values, and that the U–Pb age calculated with these ratios is accurate. Since the isotopic fractionation between ^{207}Pb and ^{206}Pb is negligible (e.g. Burn et al., 2017), we address the suitability of the DF correction based on Tara allanite as primary reference material only on $^{206}Pb/^{238}U$ ratios. A ^{207}Pb-correction was applied to the primary reference material (i.e. Tara allanite) by the VisualAge_UcomPbine Data Reduction Scheme (DRS) before it was used for normalization (Chew et al., 2014) using an initial $^{207}Pb/^{206}Pb$ value of 0.866 ± 0.079 obtained from a Tera–Wasserburg diagram plotting five ID–TIMS analyses by Smye et al. (2014), since it has been shown that initial $^{207}Pb/^{206}Pb$ ratios of allanite can deviate from model values (e.g. Cenki-Tok et al., 2014). 4 ± 0.015 (420 Ma) following Stacey and Kramers (1975). The need to correct measurements of Tara allanite as primary reference material for initial Pb using such a value was

proposed by Gregory et al. (2007) and confirmed by Smye et al. (2014). The uncertainties on the ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios obtained from the VisualAge_UcomPbine DRS (Chew et al., 2014) include an overall propagated uncertainty coming from the reproducibility of the primary reference material. Isoplot 3.7.5 (Ludwig, 2012) was used for age calculations. Age

275 determination of epidote samples and allanite secondary reference materials relies on the Tera–Wasserburg approach (Tera and Wasserburg, 1972; Ludwig, 1998). Since the initial Pb isotopic composition of CAP, CAP^b and AVC allanite is known and consistent with a modeled two-stage evolution of initial Pb isotopic compositions (Barth et al., 1994; Gregory et al., 2007; Burn et al., 2017), we ensured better age precision by anchoring their Tera–Wasserburg regressions of these allanite samples to an initial ^{207}Pb/^{206}Pb ratio of 0.854 ± 0.015 (275 Ma; Stacey & Kramers, 1975) and calculated their weighted

280 average ^{207}Pb-corrected ^{238}U/^{206}Pb ages using the same value. Regression and weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb ages of allanite secondary reference materials are summarized in Table 3, and their Tera–Wasserburg diagrams are presented in Fig. B1 (Appendix B). Allanite secondary standard age uncertainties are 95 % confidence.

Table 3: U–Pb LA–ICP–MS ages of allanite secondary standards reference materials measured in three analytical sessions in this
285 **study. Age uncertainties are 95 % confidence. (a) = regression anchored to a ^{207}Pb/^{206}Pb value of 0.854 ± 0.015 (275 Ma; Stacey and Kramers, 1975); (b) = unanchored regression.**

Sample	14 June 2019		23 July 2019		16 January 2020	
	Isochron Regression U–Pb age [Ma]	Weighted average U–Pb age [Ma]	Isochron Regression U–Pb age [Ma]	Weighted average U–Pb age [Ma]	Isochron Regression U–Pb age [Ma]	Weighted average U–Pb age [Ma]
CAP^b	284.2 ± 2.6 (a) MSWD = 0.34 274 ± 29 (b) MSWD = 0.33	284.2 ± 2.0 MSWD = 0.34	-	-	-	-
CAP	-	-	288.5 ± 2.9 (a) MSWD = 1.04 286.9 ± 5.2 (b) MSWD = 1.11	288.6 ± 2.3 MSWD = 1.03	283.0 ± 3.4 (a) MSWD = 1.2 299 ± 20 (b) MSWD = 1.14	282.5 ± 3.2 MSWD = 1.2
AVC	-	-	292.4 ± 3.7 (a) MSWD = 0.49 293.2 ± 7.4 (b) MSWD = 0.53	292.2 ± 2.3 MSWD = 0.48	285.2 ± 4.5 (a) MSWD = 0.70 283 ± 16 (b) MSWD = 0.78	285.1 ± 3.5 MSWD = 0.69

3.3 Solution ICP–MS

Independent measurements of ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios were performed on two epidote micro-separates to check their consistency with U–Pb isotopic data measured by LA–ICP–MS and hence the reliability of the latter data. The material was

290 separated from the epidote-quartz vein of the sample from the Albula-1 area, which is the one with the lowest degree of deformation and largest epidote crystals (see Sect. 4.1). Clean and pure epidote grains were handpicked under a binocular

microscope. The epidote separates were pre-cleaned with MilliQ[TM] water. Based on LA–ICP–MS U and Pb concentration data, four sample aliquots – two from each epidote micro-separate and each corresponding to ca. 300 ng of total Pb – were weighed in acid-cleaned Teflon beakers and dissolved following the procedure of Nägler and Kamber (1996). Samples were

295 leached with aqua regia at 120 °C for two days. The leachate was transferred into a second pre-cleaned Teflon beaker. To ensure complete dissolution a concentrated $HF:HNO_3$ (3:1 by volume) was added to the supernatant, and the beakers were placed on a heating~~ot~~ plate at 90 °C for two days. After drying, 2 ml of 6.4 M HCl were added, and the beakers were placed on a heating plate at 150 °C for two days. The same procedure was applied to standard AGV-2 (Weis et al., 2006) as well as to two blanks, and complete dissolution was achieved for all samples and standards. Finally, the samples were dissolved in 1

300 ml 0.5 M HNO_3.

To determine $^{238}U/^{206}Pb$ ratios, a 10 % aliquot of digested samples and standards was further diluted with 0.5 M HNO_3 up to a final volume of 10 ml. Two solutions with two different dilution factors were prepared from each sample aliquot and were analyzed on a 7700x Agilent[TM] quadrupole ICP–MS at the Department of Geography, University of Bern, Switzerland. Standard AGV-2 (Weis et al., 2006) was used to correct for instrumental fractionation and to check accuracy of

305 measurements. Final sample concentrations of ^{206}Pb, ^{207}Pb and ^{238}U ~~—~~(for both dilution factors of each sample aliquot)~~—~~ and their corresponding analytical uncertainties as relative standard deviations – solely based on counting statistics – were calculated by referring to a calibration curve based on three dilution factors of AGV-2 standard. The $^{238}U/^{206}Pb$ ratio and uncertainty as 2 SE of each sample aliquot were calculated with Isoplot 3.7.5 (Ludwig, 2012) as weighted average values between the $^{238}U/^{206}Pb$ ratios calculated from the measurements of both dilution factors, which were the same within

310 uncertainty for all sample aliquots. The remaining sample material was dried and re-dissolved in 0.5 ml 1 M HNO_3 for Sr–Pb column chemistry using a pre-cleaned Sr-spec[TM] resin (Horwitz et al., 1992). After loading, the sample matrix was eluted from the column with 1.5 ml 1 M HNO_3 while Sr and Pb were retained on the column. The Sr and Pb fractions were eluted with 1 ml of 0.01 M HNO_3 and 8 ml of 0.01 M HCl respectively, following Villa (2009) and Quistini et al. (2017). After drying, the Pb fraction was dissolved and further diluted in 0.5 M HNO_3 for measurement of Pb isotopes on a Thermo Fisher

315 Neptune Plus MC–ICP–MS. Measurements were carried out in dry plasma mode using a CETAC Aridus 2 desolvating system. Thallium was added to samples and standards to correct for instrumental mass fractionation with repeated measurements of NIST SRM 981 to quantify the external reproducibility of the measurements (Villa, 2009); the measured Pb isotopic composition was indistinguishable from those reported by Rehkämper and Mezger (2000). The four pairs of isotopic ratios measured by solution ICP–MS are only compared to the Tera–Wasserburg diagram based on LA–ICP–MS

320 data (50 μm spot size) and are not used to calculate an age because the statistical robustness of a regression based on only four data points is limited ~~for an unanchored regression to be statistically robust a minimum of 15 analyses is necessary~~.

4 Results

4.1 Petrography and U–Th–Pb contents of samples selected for U–Pb geochronology

Four samples were selected for this contribution mainly based on 1) size of epidote grains in order to use the largest laser beam possible for LA–ICP–MS and 2) U contents that are both as high ~~as possible~~ and as variable as possible within the sample. Larger laser beams maximize the precision of U–Pb geochronology measurements. High U contents ~~are related to~~ensure higher contents of uranogenic Pb isotopes and therefore improve the precision of U and Pb isotopic measurements; their variability contributes to a larger spread of the analyses in Tera–Wasserburg diagrams for well-constrained regressions. The studied samples have epidote components (X_{Epi}) between 0.52–0.98 (calculated as $Fe^{3+}/(Al + Fe^{3+} – 2)$; Cr < limit of detection) and ΣREE between 3.3–210 µg g^{-1}.

One sample from the Albula area, sample Albula-1, was selected for U–Pb geochronology. Two veins can be recognized (Fig. 1a), both crosscutting the host rock with sharp boundaries:

1) 2–3 cm wide epidote-quartz-plagioclase vein (Vein1). Epidote grains are elongated, with lengths between ca. 0.5 mm along the vein boundaries to ca. 1 cm towards the center of the vein, with an aspect ratio up to ca. 7:1. Fractures are common and grains are euhedral to subhedral. Quartz is fractured and plagioclase is limited to a ca. 2 mm wide portion along the vein boundaries, associated with the smallest epidote grains. U contents of epidote range between 3.7–89 µg g^{-1} (Table 4). Th contents are 0.01~~09~~–0.05~~47~~ µg g^{-1} (19/25 measurements are below the limits of detection of 0.03–0.07 µg g^{-1} with a spot size of 24 µm and 0.003 µg g^{-1} with a 60 µm spot size). Pb contents are 3.9–62 µg g^{-1}, total Pb/U ratios 0.14–10 and µ values 7–510.

Table 4: Concentrations of Pb, Th and U, Th/U and Pb/U ratios, and µ values measured by laser ablation ICP–MS with the trace element protocol in Appendix A. The symbol < is followed by limits of detection (calculated for each element in each measurement individually following the formulation in Pettke et al., 2012) ~~for those analyses below it with spot size indicated in brackets (in µm)~~**. µ values are calculated from total Pb and total U contents by considering an isotopic abundance of 1.4 % for ^{204}Pb and 93 % for ^{238}U. N/A = non-applicable.**

Sample Albula-1 Vein1					
Pb	**Th**	**U**	**Th/U**	**Pb/U**	**µ = ^{238}U/^{204}Pb**
[µg g^{-1}]	**[µg g^{-1}]**	**[µg g^{-1}]**	**[-]**	**[-]**	**[-]**
17	0.02	89	0.0002	0.20	360
19	0.04	22	0.002	0.87	81
6.5	<0.03~~25~~	11	N/A	0.60	120
7.9	0.05	12	0.004	0.66	110
7.9	0.03	8.9	0.004	0.89	80
3.9	<0.01~~4~~	28	N/A	0.14	510
9.7	<0.005	28	N/A	0.35	210
18	<0.02~~2~~	7.1	N/A	2.5	28

16

Pb	Th	U	Th/U	Pb/U	μ
21	0.03	11	0.003	1.8	39
11	<0.004	16	N/A	0.70	100
8.2	<0.07~~2~~	11	N/A	0.74	96
8.5	<0.03~~0~~	3.7	N/A	2.3	31
7.5	<0.05<u>4</u>~~8~~	4.5	N/A	1.7	43
10	<0.05<u>4</u>~~9~~	5.9	N/A	1.7	42
16	<0.04<u>3</u>~~9~~	5.5	N/A	2.8	25
24	<0.06~~4~~	8.3	N/A	2.9	25
5.7	<0.03~~0~~	23	N/A	0.25	290
61	<0.01<u>0</u>~~7~~	6.0	N/A	10	6.9
46	<0.005~~4~~	7.5	N/A	6.1	12
9.0	<0.02<u>1</u>~~8~~	3.7	N/A	2.4	29
6.4	<0.06~~4~~	12	N/A	0.51	140
8.3	0.01	26	0.0003	0.32	220
7.6	<0.01<u>0</u>~~7~~	27	N/A	0.28	260
6.9	<0.01<u>0</u>~~8~~	9.6	N/A	0.72	99
25	<0.003	4.3	N/A	5.9	12

Vein 2

Pb [μg g^{-1}]	Th [μg g^{-1}]	U [μg g^{-1}]	Th/U [-]	Pb/U [-]	μ = ^{238}U/^{204}Pb [-]
44	0.67	26	0.03	1.7	43
64	14	140	0.10	0.46	160
24	4.0	36	0.11	0.69	100

Sample Grimsel-1

Pb [μg g^{-1}]	Th [μg g^{-1}]	U [μg g^{-1}]	Th/U [-]	Pb/U [-]	μ = ^{238}U/^{204}Pb [-]
130	0.12	190	0.001	0.68	100
150	7.6	180	0.04	0.83	85
170	0.15	270	0.001	0.64	110
150	0.99	230	0.004	0.67	110
130	0.47	79	0.01	1.6	44
130	<0.09~~4~~	130	N/A	1.0	70
150	0.82	350	0.002	0.44	160
97	0.07	60	0.001	1.6	44
170	0.71	130	0.01	1.3	52
87	0.30	140	0.002	0.64	110
170	0.56	240	0.002	0.72	99
150	2.6	100	0.03	1.4	49
170	0.47	220	0.002	0.78	91

93	4.9	100	0.05	0.90	79
190	0.81	140	0.01	1.4	50
78	1.9	160	0.01	0.49	140
180	0.14	260	0.001	0.68	104
93	0.04	54	0.001	1.7	41
150	0.84	140	0.01	1.1	65

Sample Grimsel-2

Pb [µg g⁻¹]	Th [µg g⁻¹]	U [µg g⁻¹]	Th/U [-]	Pb/U [-]	$\mu = {}^{238}U/{}^{204}Pb$ [-]
75	0.07	220	0.0003	0.34	210
68	0.27	160	0.002	0.43	170
75	0.20	150	0.001	0.49	140
51	<0.06~~1~~	120	N/A	0.42	170
62	<0.05~~48~~	120	N/A	0.53	130
74	0.07	160	0.0004	0.46	150
97	0.11	270	0.0004	0.35	200
95	0.13	270	0.0005	0.36	200
65	0.21	280	0.001	0.23	310
88	<0.02~~2~~	180	N/A	0.50	140
93	<0.03~~4~~	110	N/A	0.86	83
75	0.53	535	0.001	0.14	510
62	0.36	310	0.001	0.20	350

Sample Heyuan-1

Pb [µg g⁻¹]	Th [µg g⁻¹]	U [µg g⁻¹]	Th/U [-]	Pb/U [-]	$\mu = {}^{238}U/{}^{204}Pb$ [-]
19	0.48	8.4	0.06	2.2	32
12	0.30	18	0.02	0.68	100
16	0.38	8.7	0.04	1.8	39
15	0.42	8.4	0.05	1.8	39
27	0.67	7.5	0.09	3.6	20
16	0.05	13	0.004	1.2	57
21	17	24	0.70	0.86	82
20	38	34	1.10	0.58	120
26	0.08	18	0.004	1.4	50
17	0.15	7.0	0.02	2.4	29
16	1.4	9.7	0.14	1.7	42
19	0.13	13	0.01	1.5	49
23	18	30	0.62	0.78	90

17	0.12	9.1	0.01	1.8	39
17	1.3	7.0	0.19	2.4	29
24	0.16	14	0.01	1.6	43
22	2.2	9.9	0.22	2.2	32
8.2	0.04	22	0.002	0.37	190
18	0.88	8.3	0.11	2.2	31
12	0.22	2.6	0.08	4.4	16

2) ca. 1 mm wide epidote-quartz-plagioclase vein (Vein2). Epidote grains range between a few µm to 2 mm in diameter, most being fractured and euhedral to subhedral. Epidote grains of ca. 1–2 mm in diameter are mantled wrapped by thin layers of µm-sized anhedral epidote grains. Quartz subgrains resulting from recrystallization and plagioclase wrap the epidote grains. U contents of epidote are 26–140 µg g^{-1} (Table 4), and Th contents 0.67–14 µg g^{-1}. Pb contents range from 24–64 µg g^{-1}, Pb/U ratios from 0.46–1.7 and µ values from 43–160.

BSE images of epidote (Fig. 2a) reveal growth zoning and intra-grain veinlets resulting from interaction with a secondary fluid. Sample Albula-1 was selected for solution ICP–MS given the large size of epidote grains.

19
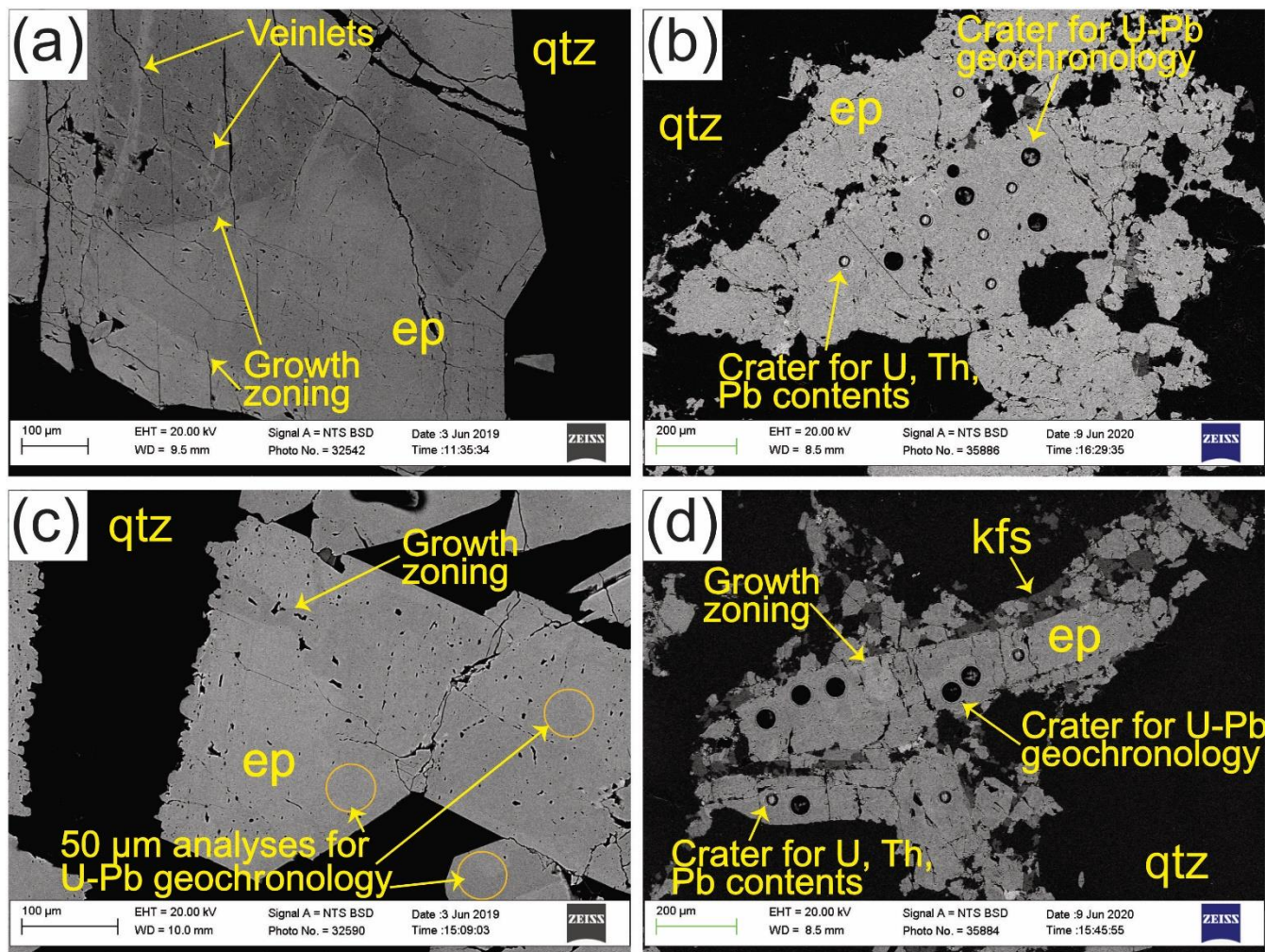
Figure 2: BSE images of (a) Albula-1, (b) Grimsel-1, (c) Grimsel-2 and (d) Heyuan-1 epidote. The specific epidote grain shown in panel (a) was not analyzed. The locations of the BSE images are indicated by the green rectangles in Fig. 1. bt = biotite; chl = chlorite; ep = epidote; kfs = K-feldspar; plg = plagioclase; qtz = quartz.

Sample Grimsel-1 (Fig. 1b) displays a folded epidote-quartz vein crosscutting a weakly deformed portion of the host rock. Epidote grains are generally prismatic and range between a few μm to ca. 2 mm in size. They are mostly subhedral to anhedral and cracked, and they form clusters with no preferential grain orientation. Quartz subgrains indicate dynamic recrystallization via subgrain rotation. Green biotite and rare chlorite are associated with the epidote-bearing vein. Epidote in BSE images (Fig. 2b) exhibits weak patchy zonations towards the rims and the presence of porosity. K-feldspar is recognized within epidote cracks. U contents are 54–350 μg g^{-1} (Table 4), and Th contents are 0.041–4.9 μg g^{-1}. Pb contents range between 79–190 μg g^{-1}, with Pb/U ratios from 0.45–1.7 and μ values between 41–160.

Sample Grimsel-2 (Fig. 1c) consists of an epidote-quartz-biotite vein cutting through a weakly deformed sector of the host rock. The vein boundaries are sharp and non-linear. Euhedral to subhedral epidote grains are cracked by stretching-induced

fracturing, with single fragments ranging from a few µm to ca. 3 mm in size. Epidote grains can be estimated to have had an aspect ratio up to ca. 6:1 before fracturing. Quartz is recrystallized by subgrain rotation. Biotite grain sizes range between ca. 100–500 µm. BSE images (Fig. 2c) show that epidote exhibits regular growth zoning. ~~U contents are~~Epidote contains 109–

370   535 µg g⁻¹ of U and ~~Th contents~~ 0.0~~7~~66–0.53 µg g⁻¹ of Th (Table 4). Pb contents range from 51–97 µg g⁻¹, Pb/U ratios are 0.20–0.86 and µ values 83–510.

Sample Heyuan-1 (Fig. 1d) is characterized by an epidote-quartz-K-feldspar-chlorite assemblage that fills pockets ~~whose boundaries~~ cut~~ting~~ through the granite-forming minerals or ~~follow their grain boundaries~~interstitial among the magmatic minerals. The ~~epidote bearing assemblage~~sample is crosscut by quartz ± hematite veins (see Fig. 4c in Tannock et al.,

375   2020b). Epidote is variably shaped, from elongated without preferential orientation to prismatic. Epidote ranges between tens of µm to ca. 2 mm in length and forms clusters of euhedral to anhedral crystals. Quartz associated with epidote is mostly recrystallized, as indicated by the presence of quartz subgrains. Some mm-sized quartz grains, however, display undulose extinction. Chlorite associated with epidote forms interstitial aggregates of ca. 500–1000 µm in size. Growth zoning of epidote is recognized from BSE images (Fig. 2d) and K-feldspar is intertwined with smaller-sized epidote grains along the

380   boundaries of larger ones, as well as with quartz filling epidote fractures. The measured U content~~s~~ ~~of Heyuan-1 epidote are~~ is 2.6–34 µg g⁻¹ (Table 4). Th contents range between 0.04~~2~~–38 µg g⁻¹~~;~~, with most analyses below 10 µg g⁻¹. ~~only 3 measurements out of 20 reach tens of µg g⁻¹ of Th (17, 18 and 38 µg g⁻¹ respectively).~~ Pb contents are 9.4–27 µg g⁻¹, Pb/U ratios range between 0.42–4.4 and µ values between 16–190.

~~A~~In summary, ~~a~~mong the four samples selected for U–Pb geochronology, measured U contents of epidote are highly

385   variable (2.6–530 µg g⁻¹; n = 80; Table 4), and the intra-sample variability in U concentrations is ca. one order of magnitude ~~in each sample~~ (Fig. 3). Samples Albula-1 and Heyuan-1 ~~overlap between~~both contain a few to tens of µg g⁻¹ of U~~.~~, ~~S~~whereas ~~s~~amples Grimsel-1 and Grimsel-2 ~~overlap at~~have higher U contents of hundreds of µg g⁻¹. Thorium concentrations span four orders of magnitude (0.0~~1~~09–38 µg g⁻¹; n = 56). Samples with similar U concentrations display different Th contents, creating variability in Th/U ratios. Pb contents are 3.9–190 µg g⁻¹~~.~~, and Pb/U ratios span between 0.14–10, each

390   sample varying to different extents. With only 4/88 Th measurements above 10 µg g⁻¹ (one in sample Albula-1 and three in sample Heyuan-1), Th–Pb geochronology is not viable. All epidote samples exhibit µ values well below 2000.

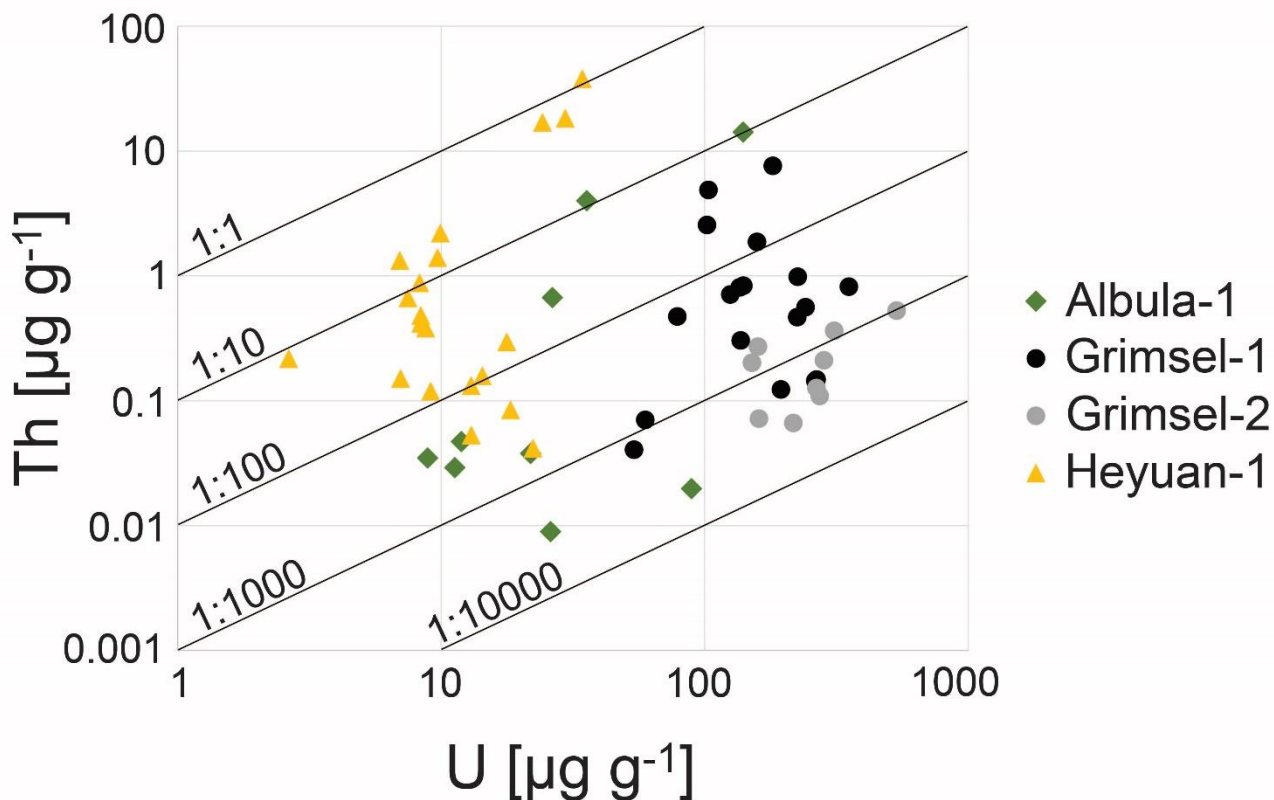**Figure 3: Th and U contents of the analyzed epidote samples.**
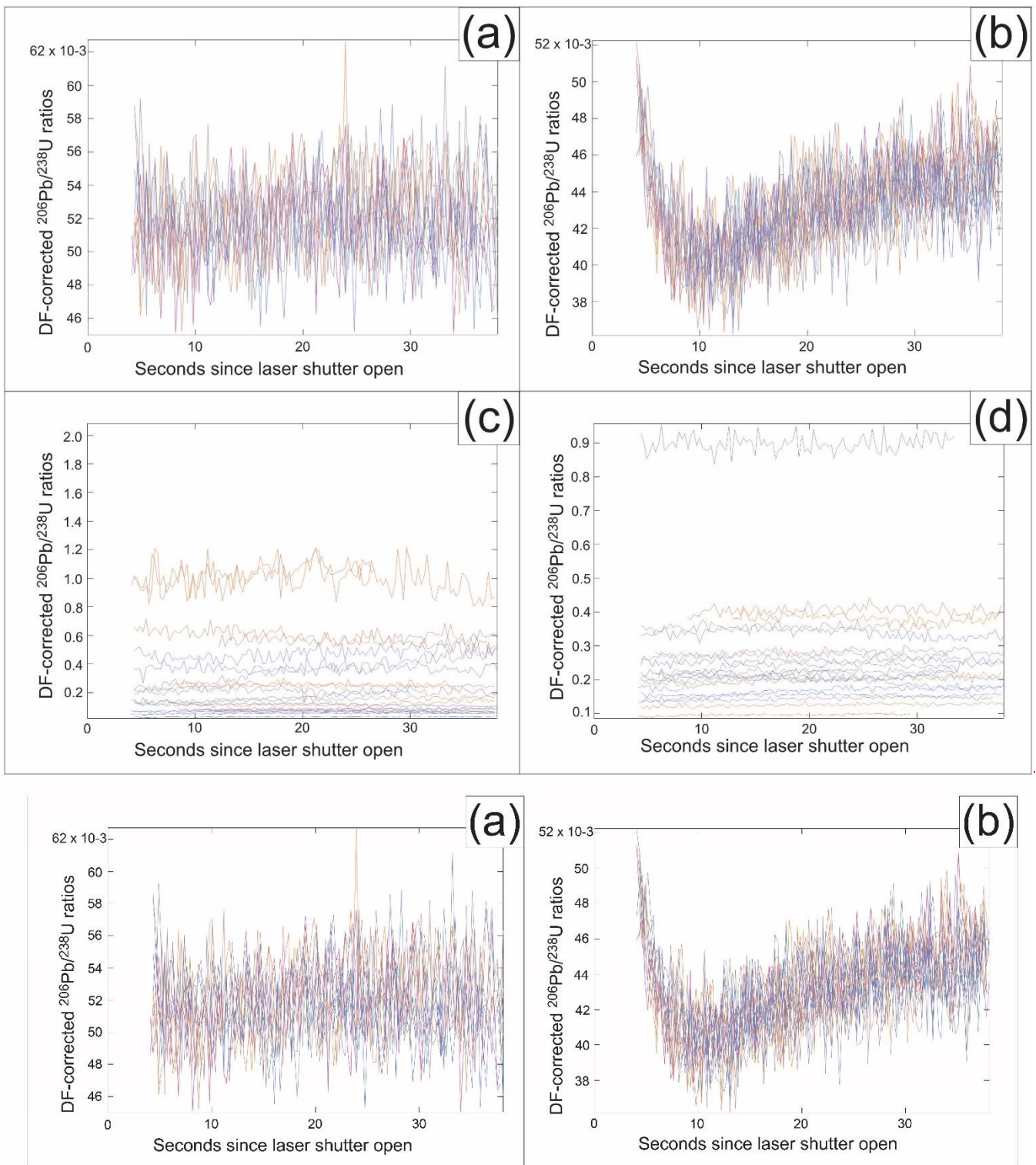
4.2 Testing Tara allanite as a reference material for epidote U–Pb geochronology

395   To assess the validity of allanite as primary reference material for epidote dating, we compared the DF correction of ^{206}Pb/^{238}U ratios over the ablation time using Tara allanite as reference for CAP[b] allanite (Burn et al., 2017) as matrix-matched (Fig. 4a), for Plesovice zircon (Sláma et al., 2008) as non-matrix-matched (Fig. 4b), and for epidote as closely matrix-matched (Fig~~s. 4 and~~ 5). An accurate correction for DF produces flat time-resolved lines of DF-corrected ^{206}Pb/^{238}U ratios for unknowns: sloping or more complex shaped curves ~~(Fig. 4b)~~ indicate <u>either zoning in initial Pb contents or</u> that the

400 DF correction is not compensating for the difference in matrix. ~~Parallel flat lines that plot below or above each other are indicative of variable initial Pb fractions, but still indicate proper correction for DF.~~ As expected, CAP[b] allanite has DF-corrected ^{206}Pb/^{238}U ratios that are flat when standardized to Tara allanite (Fig. 4a, both measured with a 50 μm spot). ~~T~~<u>Some of t</u>he DF--corrected ^{238}U/^{206}Pb ratios measured in Albula-1 and Grimsel-1 epidotes ~~with 50 (Fig. 4c–d) and even 30 μm spots are flat (Fig. 5a–b)~~ <u>did not display a flat trend, and we therefore applied a ^{208}Pb correction to verify if this was due</u>

405 <u>to zoning in initial Pb contents. The fact that the majority (122 out of 127 analyses) of ^{208}Pb- and DF-corrected time-resolved ^{206}Pb/^{238}U ratios are flat (Fig. 5)</u> ~~This~~ indicates similar ablation behavior and downhole fractionation of U from Pb between

22

epidote and allanite for our analytical setup, and accurate correction for DF in epidote by using Tara allanite as primary reference material with both 50 µm (Fig. 5a-d) and 30 µm (Fig. 5e-f) spot sizes. The analyses whose [208]Pb- and DF-corrected time-resolved $^{206}Pb/^{238}U$ ratios are not flat or do not overlap with all other analyses were excluded from age calculation (see Sect. 4.3) as they could indicate either analytical instability during ablation or a different initial Pb isotopic composition. In contrast, the distinct ablation behavior of (Plesovice) zircon is revealed by complex shaped DF-corrected $^{238}U/^{206}Pb$ ratios even with a 50 µm spot (Fig. 4b; also see Fig. 6 of Burn et al., 2017).

415   **Figure 4:** $^{206}Pb/^{238}U$ **ratios measured by LA–ICP–MS corrected for downhole fractionation (DF) of (a) CAP[b] allanite, and (b) Plesovice zircon~~, (c) Albula-1 and (d) Grimsel-1 epidote~~ with Tara allanite as primary reference material. Each individual line represents one analysis. Measurements are with a 50 µm spot size. The DF-corrected $^{206}Pb/^{238}U$ ratios include both initial and radiogenic Pb. ~~Lines that are not overlapping in (c) and (d) indicate variable amounts of initial Pb in each measurement.~~**
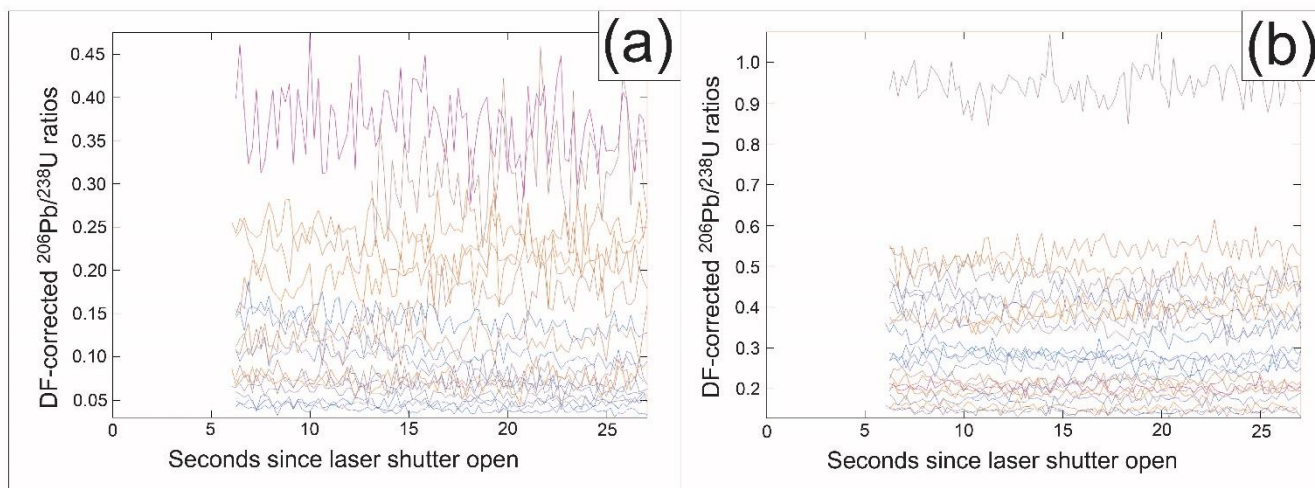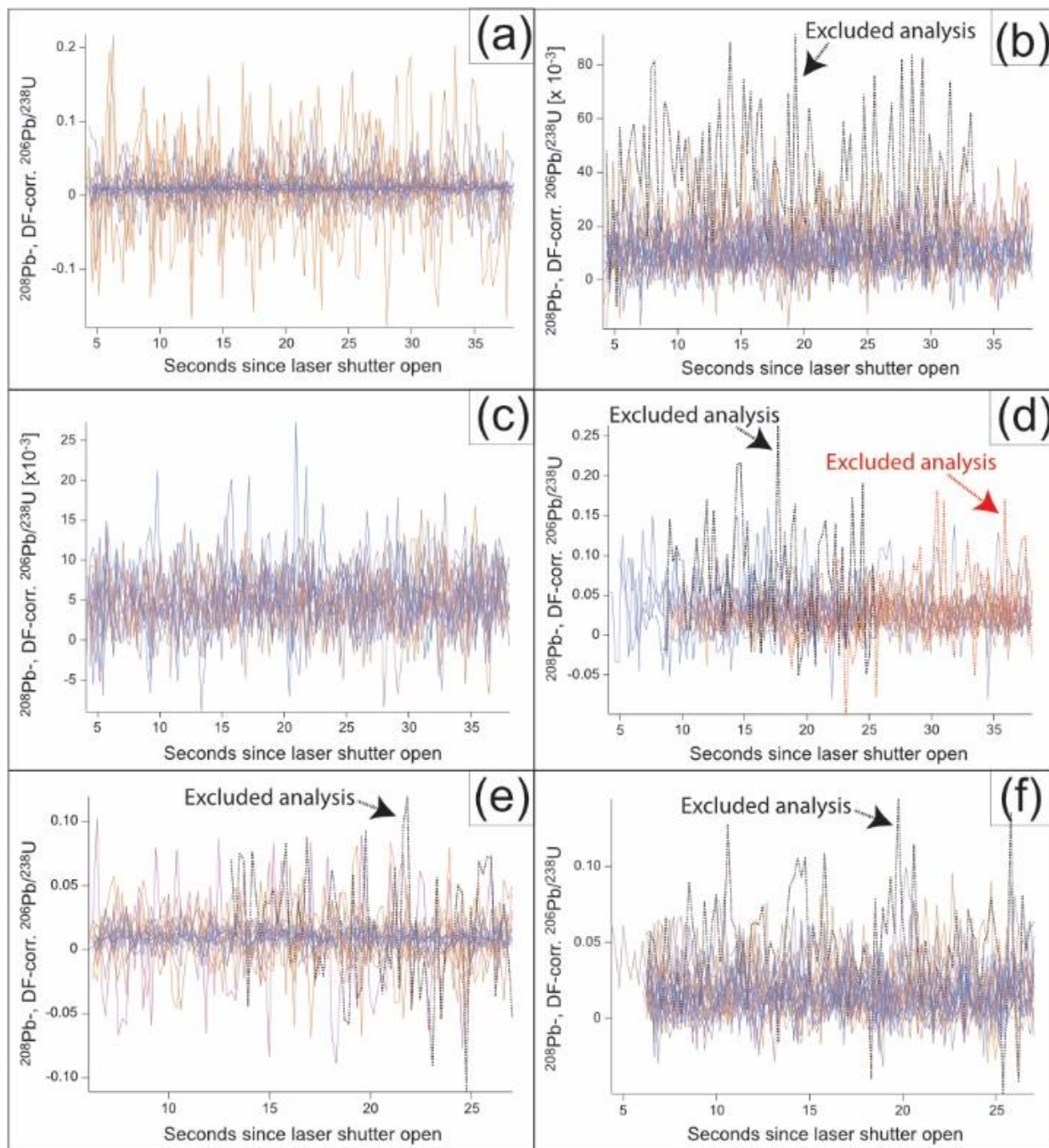
Figure 5: **208Pb-corrected** **206Pb/238U** ratios measured by LA–ICP–MS corrected for downhole fractionation (DF) of (a) Albula-1, ~~and~~ (b) Grimsel-1**, (c) Grimsel-2, (d) Heyuan-1, (e) Albula-1 and (f) Grimsel-1** epidote **samples** with Tara allanite as primary reference material. **Each individual line represents one analysis. Measurements are with spot sizes of 50 µm (a-d) and of 30 µm (e-f).** ~~Measurements with a 30 µm spot size. The DF-corrected 206Pb/238U ratios include both initial and radiogenic Pb. Lines that are not overlapping indicate variable amounts of initial Pb in each measurement.~~

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4.3 Laser ablation ICP–MS U–Pb data of unknown samples

Uncertainties on LA–ICP–MS $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios are 2 standard errors (2 SE), and all age uncertainties calculated with Isoplot are 95 % confidence.

430   **Table 5:** $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios, and their uncertainties as 2 standard errors (2 SE) measured by LA–ICP–MS. f_206 is calculated using the initial $^{207}Pb/^{206}Pb$ indicated by the Tera–Wasserburg diagrams. ~~Used spot size is indicated in brackets.~~(a) = 50 μm spot size; (b) = 30 μm spot size.
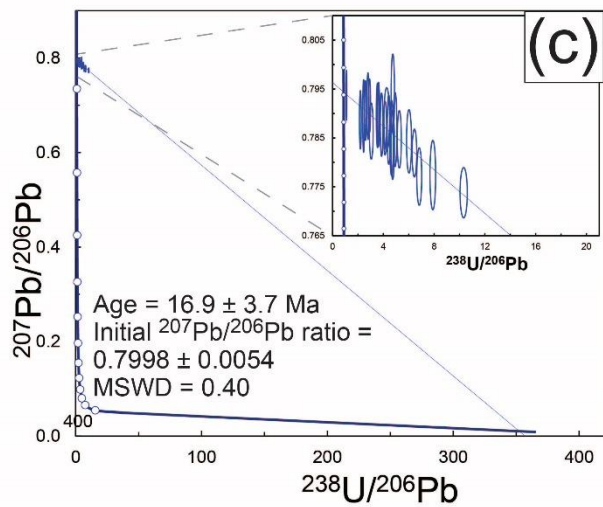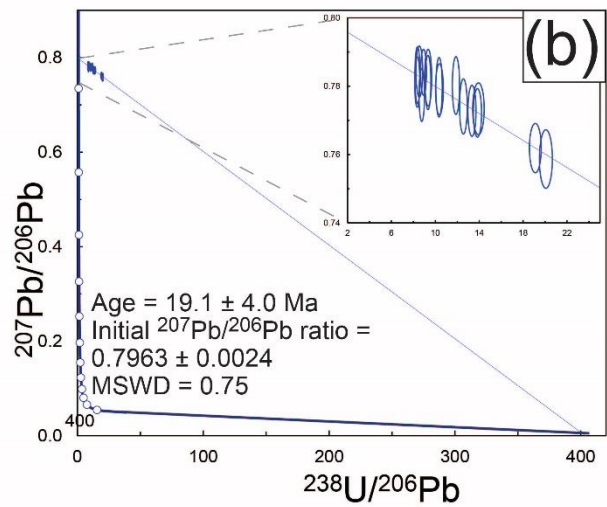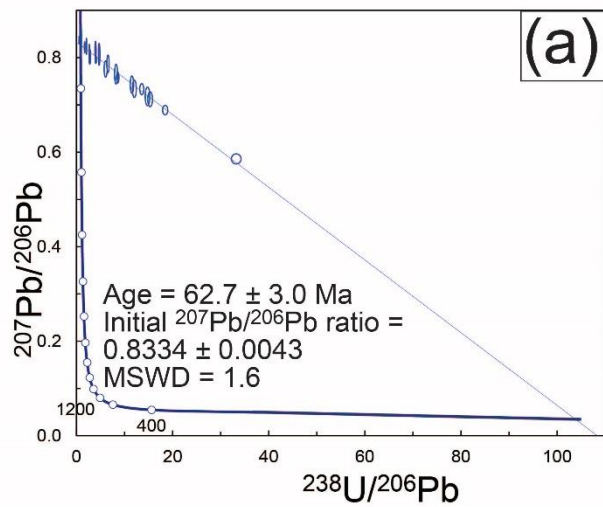
	Sample Albula-1 (a) Vein1				
Analysis	$^{238}U/^{206}Pb$	**2 SE**	$^{207}Pb/^{206}Pb$	**2 SE**	**f_206**
1	12.05	0.33	0.734	0.015	0.87
2	8.237	0.258	0.765	0.017	0.91
3	3.953	0.103	0.815	0.016	0.98
4	0.535	0.013	0.8368	0.0067	1.0
5	0.996	0.028	0.841	0.016	1.0
6	0.952	0.025	0.820	0.013	0.98
7	1.691	0.046	0.8225	0.0079	0.99
8	1.707	0.041	0.8216	0.0098	0.98
9	15.33	0.40	0.712	0.013	0.85
10	4.024	0.097	0.7961	0.0069	0.95
11	6.540	0.188	0.787	0.015	0.94
12	11.53	0.29	0.743	0.015	0.89
13	4.710	0.129	0.807	0.019	0.97
14	2.747	0.128	0.802	0.013	0.96
15	2.076	0.056	0.824	0.014	0.99
16	14.77	0.39	0.718	0.016	0.85
17	2.675	0.068	0.810	0.015	0.97
18	6.053	0.253	0.776	0.014	0.93
	Vein2				
Analysis	$^{238}U/^{206}Pb$	**2 SE**	$^{207}Pb/^{206}Pb$	**2 SE**	**f_206**
19	13.59	0.33	0.7332	0.0096	0.87
20	33.24	0.83	0.5858	0.0088	0.69
21	18.46	0.44	0.689	0.0083	0.82
22	8.576	0.213	0.7578	0.0094	0.90
	Sample Albula-1 (b) Vein1				
Analysis	$^{238}U/^{206}Pb$	**2 SE**	$^{207}Pb/^{206}Pb$	**2 SE**	**f_206**
1	2.762	0.107	0.839	0.025	1.0

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
2	13.91	0.58	0.737	0.027	0.89
3	5.035	0.213	0.794	0.028	0.96
4	4.102	0.143	0.788	0.013	0.95
5	4.706	0.168	0.799	0.015	0.96
6	8.569	0.338	0.763	0.028	0.92
7	6.510	0.309	0.782	0.025	0.94
8	3.236	0.157	0.778	0.038	0.94
9	14.08	0.62	0.710	0.030	0.85
10	13.37	0.59	0.735	0.032	0.88

Vein2

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
11	17.79	0.70	0.686	0.015	0.83
12	21.90	0.81	0.639	0.017	0.77
13	14.99	0.54	0.703	0.015	0.85
14	10.54	0.77	0.740	0.017	0.89
15	9.940	0.356	0.743	0.016	0.89
16	21.70	0.80	0.658	0.018	0.79
17	26.21	0.96	0.639	0.017	0.77
18	7.107	0.263	0.776	0.013	0.93

Sample Grimsel-1 (a)

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
1	3.049	0.121	0.7864	0.0047	0.99
2	2.593	0.059	0.7906	0.005	0.99
3	4.929	0.114	0.7867	0.0062	0.99
4	10.33	0.23	0.7738	0.0042	0.97
5	7.896	0.181	0.7774	0.0058	0.97
6	4.268	0.178	0.7888	0.0053	0.99
7	2.443	0.055	0.7895	0.0061	0.99
8	2.189	0.057	0.7887	0.0049	0.99
9	3.615	0.081	0.7898	0.0054	0.99
10	4.429	0.098	0.7867	0.0058	0.99
11	2.789	0.062	0.7915	0.0056	0.99
12	3.542	0.080	0.7896	0.0054	0.99
13	4.647	0.119	0.785	0.0063	0.98
14	1.098	0.024	0.7937	0.0042	1.0
15	4.137	0.098	0.787	0.0045	0.99
16	6.826	0.158	0.7771	0.0048	0.97
17	2.912	0.067	0.7916	0.0045	0.99
18	5.258	0.127	0.7847	0.0048	0.98

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
19	4.737	0.112	0.7836	0.0058	0.98
20	6.449	0.145	0.7819	0.004	0.98
21	4.746	0.106	0.7941	0.0066	1.0
22	6.020	0.159	0.7843	0.0053	0.98
23	3.862	0.086	0.7877	0.0053	0.99

Sample Grimsel-1 (b)

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
1	5.018	0.166	0.7792	0.0096	0.99
2	2.533	0.090	0.7839	0.0094	1.0
3	6.575	0.220	0.785	0.011	1.0
4	2.674	0.086	0.7852	0.0089	1.0
5	5.266	0.180	0.763	0.012	0.97
6	2.089	0.070	0.7777	0.0074	0.99
7	4.640	0.155	0.783	0.011	1.0
8	1.895	0.065	0.7855	0.0091	1.0
9	5.339	0.177	0.7667	0.0085	0.98
10	4.684	0.158	0.781	0.0086	0.99
11	6.973	0.233	0.780	0.011	0.99
12	2.123	0.077	0.7867	0.0085	1.0
13	1.077	0.036	0.7842	0.007	1.0
14	2.168	0.070	0.783	0.01	1.0
15	2.913	0.093	0.7794	0.0085	0.99
16	2.461	0.079	0.7769	0.009	0.99
17	2.685	0.086	0.7874	0.009	1.0
18	2.357	0.078	0.7771	0.0098	0.99
19	3.840	0.131	0.777	0.010	0.99
20	7.032	0.232	0.7703	0.0095	0.98
21	5.862	0.196	0.7687	0.0099	0.98
22	3.611	0.117	0.7763	0.0065	0.99
23	4.572	0.178	0.7781	0.0099	0.99
24	3.636	0.132	0.7779	0.0090	0.99
25	3.347	0.123	0.7804	0.0080	0.99

Sample Grimsel-2 (a)

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
1	13.83	0.31	0.7722	0.0058	0.96
2	19.11	0.44	0.7619	0.0059	0.95
3	13.34	0.30	0.7728	0.0061	0.96
4	8.929	0.215	0.7841	0.0055	0.98

5	12.56	0.284	0.7741	0.0066	0.97
6	11.88	0.27	0.7802	0.0069	0.97
7	8.376	0.189	0.7832	0.0068	0.98
8	8.547	0.248	0.7843	0.0061	0.98
9	13.93	0.43	0.7734	0.0062	0.96
10	10.37	0.29	0.7791	0.0061	0.97
11	8.353	0.188	0.7812	0.0060	0.98
12	9.346	0.262	0.7825	0.0068	0.98
13	20.07	0.48	0.7587	0.0070	0.95
14	9.329	0.218	0.7811	0.0065	0.98
15	8.765	0.200	0.7774	0.0063	0.97
16	10.34	0.23	0.7797	0.0071	0.97

Sample Heyuan-1 (a)

Analysis	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE	f_{206}
1	5.040	0.155	0.764	0.016	0.93
2	3.565	0.108	0.772	0.012	0.94
3	5.907	0.174	0.734	0.017	0.89
4	4.958	0.160	0.757	0.012	0.92
5	2.655	0.071	0.785	0.013	0.96
6	5.244	0.187	0.742	0.012	0.90
7	3.499	0.098	0.764	0.016	0.93
8	6.676	0.209	0.716	0.019	0.87
9	4.409	0.132	0.757	0.013	0.92
10	2.793	0.117	0.777	0.014	0.95
11	9.578	0.349	0.678	0.016	0.82
12	3.772	0.119	0.775	0.016	0.95
13	4.751	0.165	0.759	0.016	0.93
14	5.525	0.217	0.749	0.019	0.91
15	5.827	0.180	0.739	0.017	0.90
16	1.513	0.050	0.797	0.016	0.98
17	2.252	0.081	0.794	0.015	0.97
18	1.570	0.052	0.801	0.016	0.98
19	18.25	0.57	0.596	0.02	0.71
20	1.595	0.064	0.795	0.019	0.97
21	2.453	0.078	0.775	0.017	0.95
22	0.753	0.021	0.805	0.014	0.99
23	1.435	0.047	0.809	0.016	0.99

A total of twenty-two spot analyses were measured in sample Albula-1 with a 50 µm spot (Table 5). ^{238}U/^{206}Pb ratios are
435   0.535–33.2 with uncertainties of 2–4 %. ^{207}Pb/^{206}Pb ratios are 0.586–0.837 ± 0.8–2 % (Table 5). No analyses were excluded
as all ^{208}Pb- and DF-corrected time-resolved ^{206}Pb/^{238}U ratios are flat and overlap (Fig. 5a). A Tera–Wasserburg regression
based on all data points (Fig. 6a) yields an ~~lower concordia~~ intercept age of 62.7 ± 3.0 Ma (MSWD = 1.6) with a ~~n upper~~
^{207}Pb/^{206}Pb intercept of 0.8334 ± 0.0043. The good spread of the data points along the regression line reflects variable
fractions of initial Pb (f$_{206}$ = 0.69–1.0; Table 5). The small MSWD value indicates that there is no resolvable age difference
440   between the two veins at the stated ~~present~~ analytical precision. In fact, if the analyses from the two veins are considered
separately, the Tera–Wasserburg ages of Vein1 and Vein2 are 67.6 ± 5.0 Ma (n = 18) and 58.9 ± 3.8 Ma (n = 4), which
overlap within uncertainty. The initial ^{207}Pb/^{206}Pb ratio of Albula-1 epidote indicated by the Tera-Wasserburg diagram is
within uncertainty of the model~~ed~~ value ~~of initial ^{207}Pb/^{206}Pb~~ of 0.840 ± 0.015 at 63 Ma (Stacey & Kramers, 1975). By using
this model~~ed~~ initial ratio for a ^{207}Pb-correction, the weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb age is 65.0 ± 2.5 Ma
445   (MSWD = 0.91). Eighteen additional measurements were carried out in sample Albula-1 (10 in Vein1 and eight in Vein2)
with a spot size of 30 µm ~~(Table 5)~~. Analysis 8 (Table 5) was excluded from age calculation because it was considered
unreliable based on its ^{208}Pb- and DF-corrected time-resolved ^{206}Pb/^{238}U ratio (Fig. 5e). The Tera–Wasserburg diagram based
on ~~all~~17 ~~30 µm~~ analyses with a 30 µm spot yields an intercept age of 65.~~9~~4 ± 4.6 Ma and a ^{207}Pb/^{206}Pb intercept of
0.8~~308~~297 ± 0.008~~7~~6 (MSWD = 1.4). Both values are within uncertainty of those obtained with a spot size of 50 µm. By
450   combining the 50 and 30 µm datasets, an intercept age of 63.9 ± 2.6 Ma is obtained with an initial ^{207}Pb/^{206}Pb ratio of 0.8331
± 0.0039 (MSWD = 1.6). Given the consistency of the measured U–Pb data (i.e. no isotopic heterogeneity given by fluid
inclusions and zonation even with different spot sizes), sample Albula-1 is considered suitable for solution ICP–MS (see
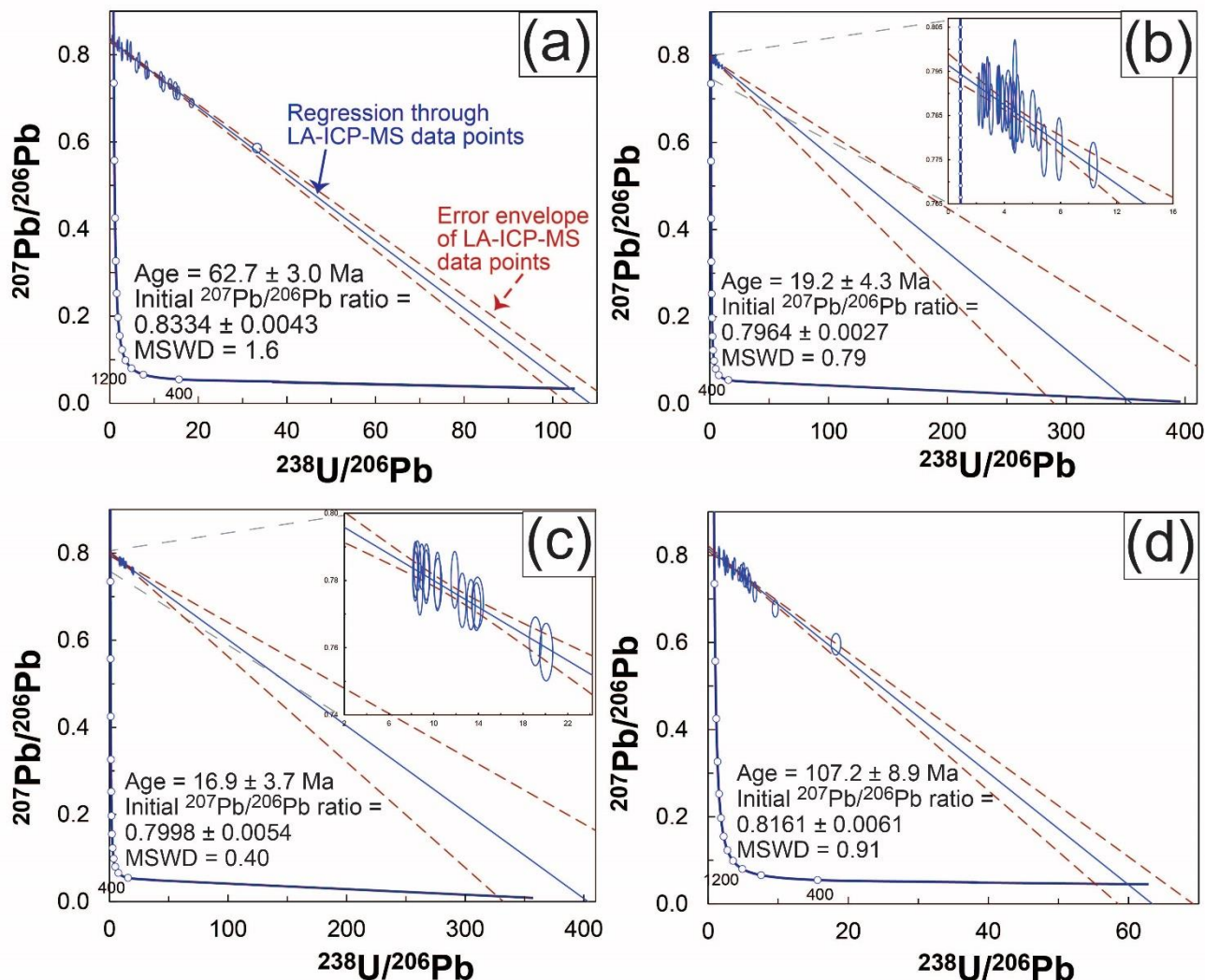Sect. 4.4).

32

Figure showing four Tera-Wasserburg concordia diagrams (a–d) plotting $^{207}Pb/^{206}Pb$ versus $^{238}U/^{206}Pb$.

(a) Age = 62.7 ± 3.0 Ma
Initial $^{207}Pb/^{206}Pb$ ratio = 0.8334 ± 0.0043
MSWD = 1.6

(b) Age = 19.1 ± 4.0 Ma
Initial $^{207}Pb/^{206}Pb$ ratio = 0.7963 ± 0.0024
MSWD = 0.75

(c) Age = 16.9 ± 3.7 Ma
Initial $^{207}Pb/^{206}Pb$ ratio = 0.7998 ± 0.0054
MSWD = 0.40

(d) Age = 108.1 ± 8.4 Ma
Initial $^{207}Pb/^{206}Pb$ ratio = 0.8170 ± 0.0055
MSWD = 0.92
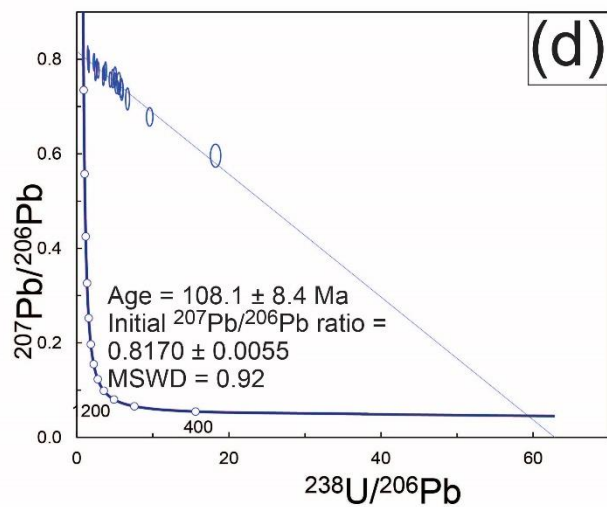
Figure 6: Tera–Wasserburg diagrams of (a) Albula-1, (b) Grimsel-1, (c~~b~~) Grimsel-2 and (d) Heyuan-1 epidote <u>samples</u> with 50 µm measurements. <u>All ratios are uncorrected for initial Pb.</u> Ages are calculated from the lower intercept of the regressions through the analyses with the concordia, whereas initial $^{207}Pb/^{206}Pb$ <u>ratios</u> are calculated from the upper intercept of the regressions with the y-axis. Data-point error ellipses are 2σ and age uncertainties are 95 % confidence. <u>Error envelopes are plotted with Isoplot 3.7.5 (Ludwig, 2012).</u>

Twenty-three 50 µm analyses were carried out in sample Grimsel-1. <u>Analysis 14 (Table 5) was excluded as its ^{208}Pb- and DF-corrected time-resolved $^{206}Pb/^{238}U$ ratio does not overlap with all other analyses (Fig. 5b), possibly indicating a different initial Pb isotopic composition.</u> ~~and~~<u>Twenty-two analyses</u> define a regression in a Tera–Wasserburg diagram (Fig. 6b) with an intercept age of 19.2~~1~~ ± 4.3~~0~~ Ma (MSWD = 0.79~~5~~) and a $^{207}Pb/^{206}Pb$ intercept of 0.796~~43~~ ± 0.002~~7~~4. All data points plot close to the y-axis ($^{238}U/^{206}Pb$ ratios = 1.10–10.3 ± 2–4 %; $^{207}Pb/^{206}Pb$ ratios = 0.774–0.794 ± 0.5–0.8 %; Table 5), indicating high and ~~poorly~~ <u>nearly in</u>variable initial Pb fractions <u>(f_{206} = 0.97–1.0; Table 5)</u> in all measurements. The initial $^{207}Pb/^{206}Pb$

34

value is outside uncertainty of the modeled initial ^{207}Pb/^{206}Pb ratio of 0.837 ± 0.015 at 19 Ma of Stacey and Kramers (1975). Hence, a ^{207}Pb-correction with the modeled ratio would yield an inaccurate weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb age; thus this sample can only be dated by the Tera–Wasserburg approach. Twenty-five additional measurements were made with

470   a spot size of 30 µm (Table 5). Analysis 13 (Table 5) is excluded based on its ^{208}Pb- and DF-corrected time-resolved ^{206}Pb/^{238}U ratio not overlapping with the other analyses (Fig. 5f). The Tera–Wasserburg age based on 22 analyses is 17 ± 10 Ma with MSWD of 1.3. The initial ^{207}Pb/^{206}Pb of 0.7863 ± 0.0049 is slightly outside uncertainty of that obtained with a spot size of 50 µm. The age obtained by combining the analyses with 50 and 30 µm spot sizes is 15.2 ± 6.5 Ma with an initial ^{207}Pb/^{206}Pb ratio of 0.7918 ± 0.0037. However, MSWD of the combined dataset is 2.6, much higher than those obtained from

475   the analyses with each spot size, indicating that the two datasets should not be combined and should be treated separately. Four data points are rejected as outliers as they cause higher MSWDs and lower age precision if included in the Tera–Wasserburg diagram. The regression based on 21 analyses intercepts the concordia at 24 ± 11 Ma (MSWD = 0.80) with a ^{207}Pb/^{206}Pb intercept of 0.7884 ± 0.0047. The age remains within uncertainty of that calculated with a 50 µm spot size.

Sixteen 50 µm analyses of sample Grimsel-2 define a regression in the Tera–Wasserburg diagram (Fig. 6c) yielding an age

480   of 16.9 ± 3.7 Ma (MSWD = 0.40). No analyses were excluded before age calculation (Fig. 5c). The spread along the regression is limited poor and the data points are close to the y-axis (^{238}U/^{206}Pb ratios = 8.35–20.1 ± 2–3 %; ^{207}Pb/^{206}Pb ratios = 0.759–0.784 ± 0.7–0.9 %; Table 5), indicating high and similar fractions of initial Pb in all analyses (f_{206} = 0.95–0.98; Table 5). The initial ^{207}Pb/^{206}Pb ratio of 0.7998 ± 0.0054 is outside uncertainty of the modeled initial ^{207}Pb/^{206}Pb value of 0.837 ± 0.015 at 17 Ma (Stacey and Kramers, 1975), which cannot be used for a ^{207}Pb-correction. The Tera–Wasserburg

485   approach is therefore the only viable to date this sample.

Twenty-three analyses were carried out in sample Heyuan-1 with a spot size of 50 µm, and analyses 22 and 23 (Table 5) were excluded based on the anomalous ^{208}Pb- and DF-corrected time-resolved ^{206}Pb/^{238}U ratios (Fig. 5d)., defining Twenty-one analyses define a regression (Fig. 6d) with an age of 10 7.2 8.1 ± 8.9 4 Ma (MSWD = 0.91 2). Initial Pb fractions are highly variable in the different measurements (f_{206} = 0.71–0.99; Table 5) yielding appreciable spread along the regression

490   (^{238}U/^{206}Pb ratios = 0.753–18.2 ± 3–4 %; ^{207}Pb/^{206}Pb ratios = 0.596–0.809 ± 2–3 %; Table 5). The initial ^{207}Pb/^{206}Pb ratio of 0.816 170 ± 0.006 155 indicated by the upper intercept is outside uncertainty of the modeled initial ^{207}Pb/^{206}Pb value of 0.843 ± 0.015 at 10 78 Ma (Stacey and Kramers, 1975). Thus, the age of this sample can only be is best determined from the Tera-Wasserburg diagram regression.

On a final note, we have calculated Tera–Wasserburg regression ages of the presented epidote samples by using a different

495   primary reference material: CAP[b] (June 2019; reference values from Burn et al., 2017) and CAP (July 2019 and January 2020; reference values from Barth et al., 1994) allanite as primary reference materials to assess if the calculated epidote U–Pb ages change when implementing a different allanite as primary reference material. The resulting epidote U–Pb ages remain within uncertainty identical to of those calculated with Tara allanite as primary reference material (Appendix C).

4.4 Solution ICP–MS U–Pb data

500   Uncertainties on solution ICP–MS $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios are 2 standard errors (2 SE).

Table 6: $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios measured by solution ICP–MS. Uncertainties are given as 2 standard errors (2 SE).

Sample	$^{238}U/^{206}Pb$	2 SE	$^{207}Pb/^{206}Pb$	2 SE
Albula-1_A	3.67	0.03	0.81319	0.00004
Albula-1_B	3.61	0.04	0.81337	0.00003
Albula-1_C	3.04	0.04	0.81674	0.00003
Albula-1_D	3.08	0.05	0.81674	0.00003

For measurements by solution ICP–MS of $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios in Albula-1 epidote, ca. 30 mg of material were
505   necessary to ensure ca. 300 ng of total Pb. $^{238}U/^{206}Pb$ ratios range between 3.04–3.67 with uncertainties between 0.8–1.6 %,
and $^{207}Pb/^{206}Pb$ ratios between 0.81319–0.81674 ± 0.03–0.04 ‰ (Table 6). The uncertainties on solution ICP–MS $^{238}U/^{206}Pb$
ratios are lower than those measured by LA–ICP–MS with a 50 μm spot size by a factor of 2.5, and a decrease by a factor of
13–100 occurs in analytical uncertainties on $^{207}Pb/^{206}Pb$ ratios. The two aliquots from each epidote micro-separate (A–B and
C–D in Table 6) yield identical ratios within uncertainty. $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios display minor ~~meager~~ spread in a
510   Tera–Wasserburg diagram (Fig. 7). In comparison to LA–ICP–MS data, the intra-sample variability of the solution ICP–MS
$^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios is only 2 % and 14 % respectively, attesting to homogenization of initial Pb fractions in the
micro-separates. This confirms that no statistically robust Tera-Wasserburg regression can be calculated from the solution
ICP–MS data alone. The $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios measured by solution ICP–MS overlap with individual LA–ICP–
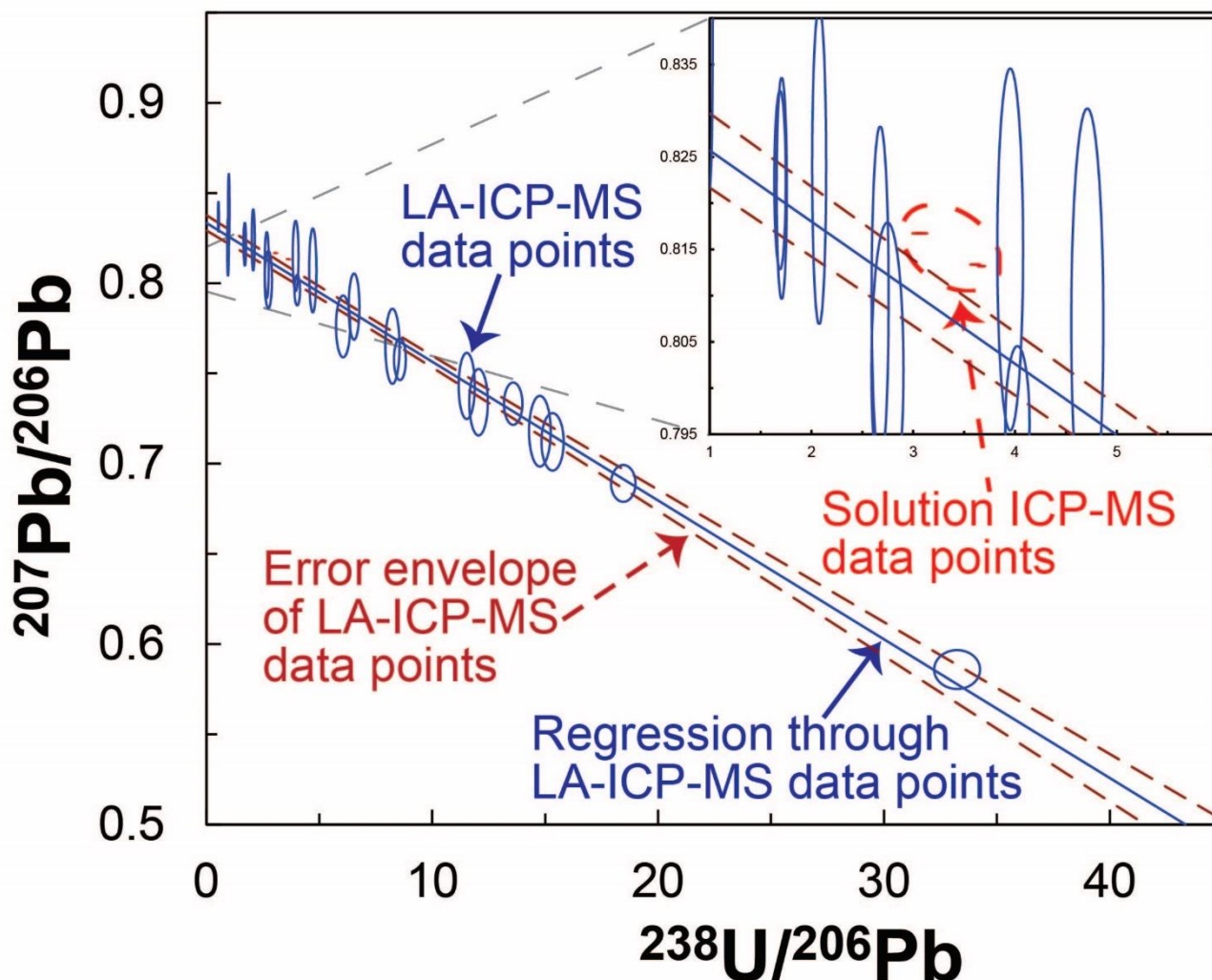MS data points ~~within their error envelope in a Tera–Wasserburg diagram~~ (50 μm spot; Fig. 7).

36

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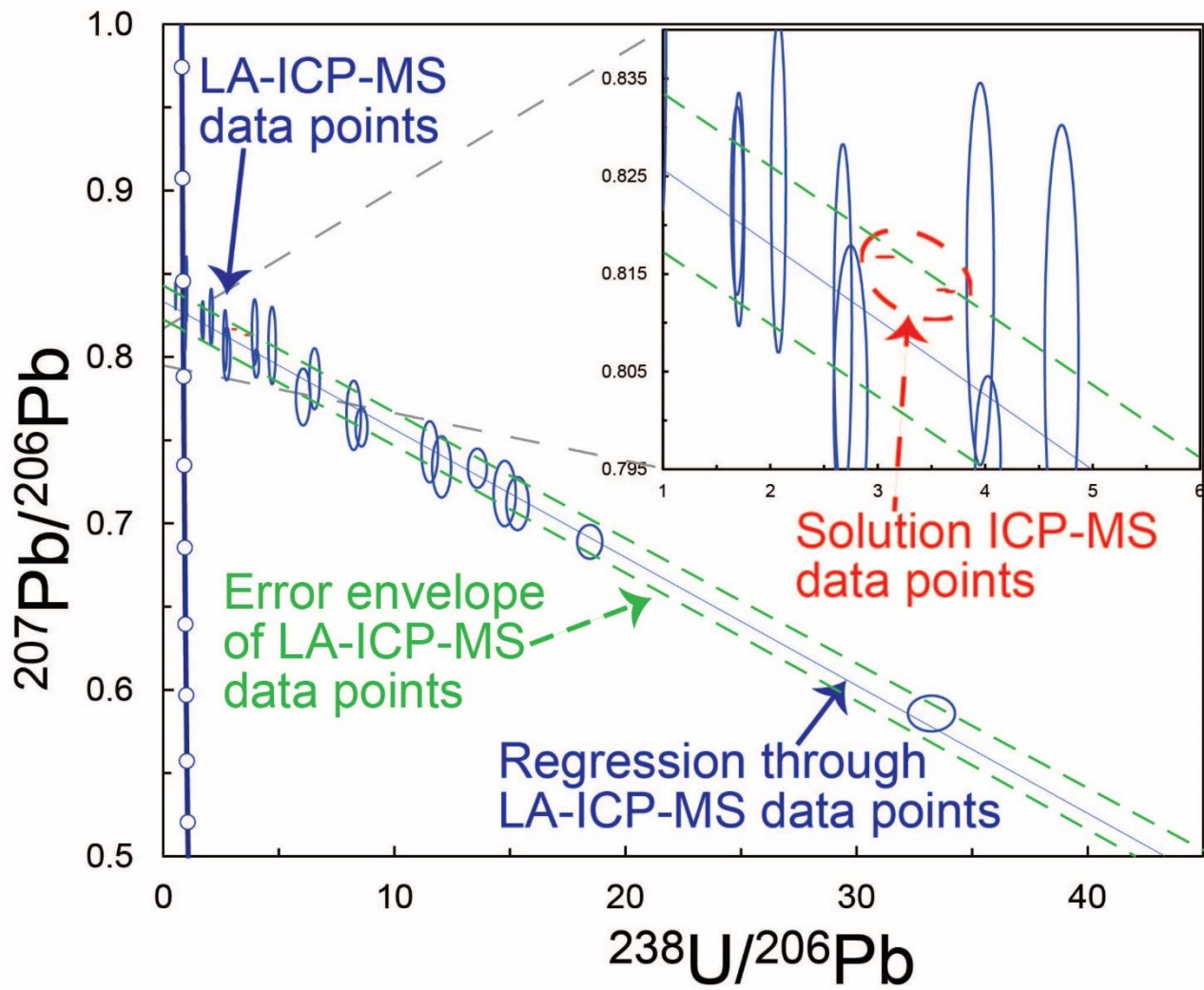
Figure 7: Tera–Wasserburg diagram showing the comparison between laser ablation ICP–MS and solution ICP–MS data points. The error envelope of LA–ICP–MS data points is ~~calculated with a MatLab script and is based on the scatter of the data points~~plotted with Isoplot 3.7.5 (Ludwig, 2012). All ratios are uncorrected for initial Pb. Data-point error ellipses are 2σ.

5 Discussion

5.1 CAP[b], CAP and AVC allanite as quality control

Although allanite geochronology is beyond the scope of this contribution, analyses of CAP[b], CAP and AVC allanite provide a quality control on U–Pb measurements during the analytical sessions. ~~Since t~~The epidote samples analyzed in this study contain too little Th for Th–Pb geochronology and we only explore epidote as a U–Pb geochronometer.~~, w~~For this reason, although the usual reference ages for allanite are Th–Pb ages, we check the reliability of our U–Pb measurements of allanite

secondary reference materials by comparinge ~~our measured allanite data~~them to published U–Pb ages (see Table 2) rather than their Th–Pb reference ages. ~~because~~ In fact, ages from the two systems differ for these allanite samples ~~(Barth et al., 1994; Gregory et al., 2007; 2012; Darling et al., 2012; El Korh, 2014; Smye et al., 2014; Burn et al., 2017)~~ likely due to excess ^{206}Pb and open-system behavior of the U–Pb system as opposed to the Th–Pb one (Barth et al., 1994; Oberli et al., 2004; Gregory et al., 2007; 2012; Darling et al., 2012; El Korh, 2014; Smye et al., 2014; Burn et al., 2017). Although this is a relevant issue in allanite geochronology per se, it does not impact the usefulness of allanite as secondary reference material for U–Pb dating in that it is the reproducibility of measured U–Pb ages in comparison with published values that confirms the reliability of U–Pb measurements. Tera–Wasserburg and weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb ages determined from our analyses of CAP^{b}, CAP and AVC allanite (Table 3) in all analytical sessions are overall consistent with their published U–Pb ages, attesting to ~~reliable~~ the reliability of our U–Pb measurements. AVC allanite analyzed in two sessions provided Tera–Wasserburg ages of 292.4 ± 3.7 Ma and 285.2 ± 4.5 Ma and identical weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb ages. Our AVC allanite ages are within uncertainty of the Tera–Wasserburg age of 289.6 ± 5.6 Ma of Gregory et al. (2007). CAP^{b} allanite (Burn et al., 2017) was used in one session, yielding a Tera–Wasserburg age of 284.2 ± 2.6 Ma and a weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb age of 284.2 ± 2.0 Ma, both within uncertainty of those calculated by Burn et al. (2017) of respectively 284.9 ± 2.8 Ma and 283.8 ± 2.8 Ma. CAP allanite was used in two sessions returning intercept ages of 288.5 ± 2.9 Ma and 283.0 ± 3.4 Ma, with comparable weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb ages. Our CAP U–Pb ages are within uncertainty of or close to the U–Pb age of 275.0 ± 4.7 Ma determined by SHRIMP by Gregory et al. (2007). The ages of CAP^{b}, CAP and AVC allanite obtained from unanchored Tera-Wasserburg regressions through our data are identical to those obtained from the anchored regressions but less precise (Table 3). We acknowledge that the Tera–Wasserburg age of 288.5 ± 2.9 Ma obtained from CAP allanite in the July 2019 session is slightly outside uncertainty of that reported by Gregory et al. (2007). However, we do not regard this difference outside uncertainty of ca. 2 % as significant given the complications of U–Pb age determinations of CAP allanite (e.g. Barth et al., 1994; Burn et al., 2017), and given the fact that AVC allanite used in the same session yielded an age within uncertainty of that measured by Gregory et al. (2007), attesting to reliable U–Pb measurements.

The values of excess variance calculated by Isoplot 3.7.5 (Ludwig, 2012) from the ^{207}Pb-corrected ages of CAP and AVC allanite samples in all analytical sessions conducted between July 2019 and October 2020 are respectively 1.9 and 2.2 % (2σ). These values are considered reasonable estimates of the long-term reproducibility, but they are not propagated onto our epidote ages because 1) they are not directly applicable to Tera–Wasserburg regression ages and 2) the effect of the propagation would be negligible.

~~The secondary reference materials are also used to calculate the systematic uncertainty of analyses, which should be propagated with the age uncertainty of the samples (see Fig. 1 in Horstwood, 2016). Since no long-term repeated measurements of U–Pb ages of our allanite secondary reference materials are available on the used LA–ICP–MS system, this step cannot be done for our epidote samples. However, a worst-case scenario can be envisioned by considering a systematic uncertainty of 5 %, which is the difference between the Tera–Wasserburg age measured in CAP during the July 2019 session~~

and its reference Th–Pb age. The age and its propagated 2 SE would be 62.7 ± 4.3 Ma for Albula-1 epidote, 19.1 ± 4.1 Ma for Grimsel-1 epidote, 16.9 ± 3.8 Ma for Grimsel-2 epidote and 108.1 ± 10 Ma for Heyuan-1 epidote. Therefore, even if the difference of 5 % between the CAP allanite age in the July 2019 session and the reference U–Pb age of Gregory et al. (2007) could be regarded as systematic uncertainty, it would not have a significant effect on our epidote U–Pb age uncertainties.

5.2 Tara allanite as reference material for LA–ICP–MS ~~standardization~~ dating of epidote

565 The presented data confirm that Tara allanite is an appropriate primary reference material for U–Pb dating of epidote by LA–ICP–MS in spot-analysis mode. The primary reference material is used to ~~normalize~~ correct the measured isotopic ratios ~~to real values after correcting them~~ for DF, which is crucial to obtain reliable U–Pb geochronology by LA–ICP–MS (Horstwood et al., 2016). In this respect, ~~the~~122 out of 127 analyses of epidote yield ^{208}Pb- and DF-corrected ^{206}Pb/^{238}U ratios ~~of epidote display a~~that are flat and that overlap ~~trend~~ throughout ablation time, demonstrating that the correction for

570 DF is accurately carried out by using Tara allanite with a spot size of 50 μm ~~(Fig. 4c–d)~~ and even 30 μm (Fig. 5). This is corroborated by the fact that the Tera–Wasserburg ages and initial ^{207}Pb/^{206}Pb ratios of Albula-1 and Grimsel-1 epidotes with a 30 μm spot remain consistent with the dataset with a 50 μm spot size. However, in both epidote samples age precision decreases with a spot of 30 μm. In the case of Grimsel-1 epidote, this is expected because the poor spread in ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios, ~~gets~~ combined with larger analytical uncertainties of the 30 μm measurements, lead~~sing~~ to an even more

575 poorly constrained regression than that with a 50 μm spot size. Thanks to the larger spread in plotted ratios of Albula-1 epidote, the effects of the lower analytical precision with a 30 μm spot size are less dramatic but still noticeable. The flat and overlapping trends of most ^{208}Pb- and DF-corrected time-resolved ^{206}Pb/^{238}U ratios of sample Grimsel-1 (Fig. 5b and f) indicate that the fact that its initial ^{207}Pb/^{206}Pb ratios are slightly outside uncertainty when measured with different spot sizes cannot be due to inaccurate correction for DF.

580 **5.3 Validation of ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios by solution ICP–MS and considerations on analyzed volumes versus age precision**

The consistency between the ~~differently acquired~~ datasets acquired by different techniques lands support to the accuracy of our LA–ICP–MS data and of the calculated Tera–Wasserburg ages. The ~~much more limited~~minor variability of ^{238}U/^{206}Pb ratios measured by solution ICP–MS data despite the high analytical precision with respect to LA–ICP–MS acquisitions is

585 expected because sample preparation for solution ICP–MS requires homogenization of ca. 9×10^9 μm^3 (ca. 30 mg of material). By comparison, with LA–ICP–MS homogenization occurred over a volume of ca. 20–24×10^3 μm^3, as the measured depth of the LA–ICP–MS craters is between 10–12 μm. ~~In fact, the intra-sample variability of solution ICP–MS data is limited to the extent that the two aliquots from each epidote micro-separate yield indistinguishable ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios despite the high analytical precision.~~

590 With decreasing spread in the plotted LA–ICP–MS ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios, the ~~extrapolation of the lower intercept of the regression with the concordia~~regression becomes less constrained. Epidote samples Grimsel-1 and Grimsel-2 give

~~larger uncertainties than~~ Albula-1 and Heyuan-1 epidote because of the more limited spread in their LA–ICP–MS data points despite having higher U and Pb contents and hence better counting statistics. ~~display the largest spreads in LA–ICP–MS data points and their age uncertainties are 5 % and 8 % respectively. Analyses in Grimsel-1 and Grimsel-2 epidote define small spreads and give large uncertainties on the Tera–Wasserburg ages (21 % and 22 % respectively). Notably, samples Grimsel-1 and Grimsel-2 have the highest U contents (hundreds of µg g^{-1} versus tens of µg g^{-1} in samples Albula-1 and Heyuan-1) and hence the best counting statistics.~~ This suggests that higher analytical precision alone does not ensure ~~the best possible~~better age precision unless it is accompanied by a large-enough data-point spread on the Tera Wasserburg diagram. It also confirms that epidote samples with relatively low U and Pb contents should not be automatically considered unsuitable for U–Pb geochronology.

~~From the considerations on analyzed volumes by both LA– and solution ICP–MS versus data point spread in Tera–Wasserburg diagrams, combined with those on age uncertainties and statistical robustness of regressions, i~~It is therefore crucial that the spot size of ~~the~~ LA–ICP–MS analyses represent a compromise ensuring ~~high enough~~sufficient analytical precision and the smallest extent possible of sample homogenization in order to preserve the variability in initial Pb contents. ~~As a result, the variability in initial Pb fractions is preserved, which is fundamental in determining large-enough spread along the Tera–Wasserburg regression and higher age precision.~~ It should be noted that the analyzed samples are characterized by variable Th/U ratios (Fig. 3~~2~~). The fractionation of Th from U is commonly attributed to oxidizing conditions (e.g. Frei et al., 2004). It ~~Although at the current state of research we cannot draw conclusions in this respect, it is~~ thus possible that the variability in initial Pb fractions of each individual epidote vein might be determined by physico-chemical conditions upon epidote crystallization, such as ~~the above-mentioned~~ oxidizing conditions or re-equilibration along fluid pathways.

5.4 Isotopic composition of initial Pb

Among the epidote samples analyzed in this study, only Albula-1 epidote gives an initial ^{207}Pb/^{206}Pb ratio that overlaps within uncertainty with the model~~ed~~ value of Stacey & Kramers (1975). Accordingly, ~~its~~the weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb age of sample Albula-1 is within uncertainty of its Tera–Wasserburg age. Epidotes from all other samples yielded Tera–Wasserburg initial ^{207}Pb/^{206}Pb ratios that deviate from model~~ed~~ values, indicating non-negligible additions of inherited radiogenic components to the initial Pb. Radiogenic Pb components can be inherited by the fluid at its source and/or during circulation and re-equilibration with rocks along its pathway containing U-Th-bearing minerals (e.g. Romer, 2001). The weighted average ^{207}Pb-corrected ^{238}U/^{206}Pb ages of epidote Grimsel-1, Grimsel-2 and Heyuan-1 calculated by assuming a model~~ed~~ initial ^{207}Pb/^{206}Pb ratio would be grossly inaccurate, implying that these three samples can only be dated with a Tera–Wasserburg ~~diagram~~regression. These considerations confirm the Tera–Wasserburg approach as the most suitable – and often the only viable – for accurate U–Pb dating of low-µ phases such as epidote (see Romer, 2001; Romer and Xiao, 2005; Odlum and Stockli, 2019; 2020).

41

5.5 Geological constraints on epidote U–Pb ages

To evaluate the geological accuracy of the U–Pb ages calculated from epidote in the veins presented above we consider other geochronological constraints on the deformation history of their respective host rocks. Albula-1 epidote gives a Paleocene age of 62.7 ± 3.0 Ma. Although, to our knowledge, no isotope geochronology is available in the Albula region, our epidote U–Pb age is consistent with geodynamic events taking place in its surroundings. For example, the Err–Platta system was investigated by Handy et al. (1996) and their D2 – in the stability field of epidote – is dated 80–67 Ma (K–Ar on white mica); epidote growth is also observed in the post-D2 deformation (Handy et al., 1996). A rutile U–Pb age of 63.0 ± 3.0 Ma was calculated by Picazo et al. (2019) from the Malenco–Margna boundary (Passo d'Ur, ca. 90 km south-southeast of the Albula area; Fig. 1a in Picazo et al., 2019) dating the stacking of the nappes associated with metamorphism at high pressure. Sample Grimsel-1 yielded initial $^{207}Pb/^{206}Pb$ ratios that differ outside uncertainty when measured with different spot sizes (50 vs. 30 μm). Although minimal, the difference in initial $^{207}Pb/^{206}Pb$ ratios given by the 50 and 30 μm measurements might indicate isotopic heterogeneity or unreliability of the 30 μm dataset. The 30 μm analyses were carried out in the same epidote grains as the 50 μm ones and no textural evidence (e.g. zoning) supports isotopic heterogeneity. Therefore, we regard the 30 μm dataset as questionable from a technical standpoint and only discuss the results obtained from the 50 μm dataset. Epidote U–Pb ages in samples Grimsel-1 and Grimsel-2 yield (early) Miocene ages of 19.2~~1~~ ± 4.3~~0~~ Ma and 16.9 ± 3.7 Ma respectively. These ages are within uncertainty of each other and can be attributed to the early deformation in the area between 22–17 Ma (Handegg phase; Challandes et al., 2008; Rolland et al., 2009). This is corroborated by the presence of green biotite associated with epidote in the epidote-bearing veins (Challandes et al., 2008; Rolland et al., 2009; Herwegh et al., 2017; Wehrens et al., 2017). Notably, Grimsel-1 and Grimsel-2 epidote samples yield initial $^{207}Pb/^{206}Pb$ ratios that are identical within uncertainty and indicate an inherited radiogenic component. This implies that the Pb isotopic signature of the circulating fluid(s) was homogenously re-equilibrated over a ca. ~~2~~100 m distance.

Epidote of sample Heyuan-1 yields an age of 10~~8.1~~7.2 ± 8.~~4~~9 Ma, which is (early) Cretaceous~~. Since the sample is crosscut by an earliest-generation quartz vein associated with hematite (Tannock et al., 2020a; 2020b), this age is~~ and consistent with the earliest movements of the Heyuan Fault. This is supported by the sample being crosscut by an earliest-generation quartz vein associated with hematite, as the formation of quartz veins post-dates that of epidote veins across the Heyuan fault but is related to the early phases of faulting (Tannock et al., 2020a; 2020b).

5.6 Epidote ages as time of crystallization in low-temperature veins

Having established that the calculated epidote U–Pb ages are consistent with geological events that affected the host rocks, we now discuss whether these ages can be truly considered ~~as~~ representative of epidote crystallization. The highest temperatures recorded by the deformation events that affected the meta-granitoid rocks hosting the analyzed epidote veins at Albula Pass, at Grimsel Pass and at the Heyuan Fault are respectively 300 °C (Mohn et al., 2011), 450 ± 30 °C (Challandes et al., 2008; Goncalves et al., 2012) and 330 °C (Tannock et al., 2020a). All these temperatures are well below 685–750 °C,

655 proposed by Dahl (1997) as the range for the closure temperature of Pb diffusion in epidote. Nevertheless, resetting of the U–Pb geochronometer can occur independently of temperature-controlled diffusion via fluid-mediated dissolution–precipitation processes, which can be assessed with BSE imaging. Albula-1 and Grimsel-2 epidotes display growth zoning, which is regarded as primary zoning and thus lack of significant elemental diffusion (Franz and Liebscher, 2004). Since care was taken to avoid mixing of different zoning domains in each single analysis – including those associated with secondary

660 veinlets – and considering that the MSWDs of the calculated epidote ages are all close to or below 1 (i.e. only one epidote generation can be distinguished at the ~~current~~ stated analytical precision), we can conclude that the ages of Albula-1 and Grimsel-2 epidote date their crystallization and therefore the formation of the epidote-bearing veins.

The epidote-bearing vein in sample Grimsel-1 is folded; epidote does not display prominent zoning, and it is fractured and porous. This may raise questions as to whether the age of 19.2~~1~~ ± 4.3~~0~~ Ma ~~represents~~dates the formation of Grimsel-1

665 epidote or the ~~complete~~ resetting of the U–Pb geochronometer by interaction with a fluid assisting the Alpine deformation. However, epidote is associated with green biotite~~ and chlorite is locally present~~, hinting that the vein epidote formed ~~at 19.1 ± 4.0 Ma~~ during the Handegg phase (22–17 Ma) in the stability field of green biotite (Challandes et al., 2008; Rolland et al., 2009; Herwegh et al., 2017; Wehrens et al., 2017). Therefore, the age of 19.2 ± 4.3 Ma is interpreted as the crystallization age of epidote. The minor presence of chlorite may indicate that the subsequent folding of the vein may have occurred at the

670 end of the Handegg phase or at the beginning of the Oberaar phase with the onset of chlorite crystallization (Herwegh et al., 2017; Wehrens et al., 2017).

In sample Heyuan-1, epidote is present in pockets filled by an epidote-quartz(-chlorite) assemblage. This microstructure might suggest a magmatic origin of epidote, and consequently that epidote might have formed in the Jurassic as a magmatic mineral and that the U–Pb system was reset by ingression of fluids related to the first movements of the Heyuan Fault.

675 However, a magmatic origin of the epidote can be ruled out based on the association of epidote with chlorite instead of biotite (the magmatic phyllosilicate stable in the Xinfengjiang pluton; Li et al., 2007; Tannock et al., 2020a; 2020b)~~.~~ Coexistence with chlorite ~~the former also~~is consistent with the temperature of mylonitization during Heyuan normal faulting (330 °C; Tannock et al., 2020a). Furthermore, the Th/U ratios measured in Heyuan-1 epidote are << 1, whereas the Fogang Batholith – which comprises the Xinfengjiang pluton – has Th/U ratios >> 1 (Li et al., 2007). This lands support to a non-

680 magmatic origin of the studied epidote because epidote generally reflects the trace element composition of its host rock (Frei et al., 2004). We thus conclude that all epidote U–Pb ages presented in this study date the crystallization of the epidote grains that formed during low-temperature fluid circulation.

6 Concluding remarks and future prospects

This contribution presents a protocol to ~~obtain~~ determine U–Pb ages and initial ^{207}Pb/^{206}Pb compositions ~~from~~ of epidote (i.e.

685 epidote–clinozoisite solid solution), that is ~~monoclinic epidote, a mineral~~ highly but variably enriched in initial Pb. This includes preliminary screening of the material to verify the presence of sufficiently high U contents (mainly between 7–310

µg g^{-1} in our samples) and intra-sample chemical variability. If these geochemical characteristics are ascertained, measurements by spot-analysis LA–ICP–MS using a quadrupole mass spectrometer can allow U–Pb ages to be determined with uncertainties between ca. 5–20 %, the lowest precision being related to poor variability in initial Pb fractions. It is

690 demonstrated that epidote and allanite have similar downhole fractionation of Pb from U during LA–ICP–MS spot analysis, and the consistency between the data measured by LA–ICP–MS and solution ICP–MS corroborates the accuracy of ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios for epidote samples determined by using Tara allanite as primary reference material. We have shown that all effects due to downhole fractionation are accurately corrected for even with a spot size as small as 30 µm by using Tara allanite as primary reference material. Therefore, the lack of a standard that is perfectly matrix-matched to

695 epidote does not prevent U–Pb dating of ~~monoclinic~~ the epidote–clinozoisite solid solution by spot-analysis LA–ICP–MS with precision between ca. 5–20 %. The ~~reliability~~ geological significance of the ages ~~data~~ is ~~also~~ verified against ~~by the fact that they fit well in~~ the geological evolution of the areas of origin of the epidote samples~~., and it has been demonstrated that the presented epidote ages date~~ In each sample, the obtained ages are interpreted as dating epidote crystallization during hydrothermal-vein formation.

700 The key strategy for U–Pb dating of epidote is the Tera–Wasserburg ~~diagram~~ regression through data uncorrected for initial Pb. U–Pb geochronology of epidote is most successful when the epidote samples display large-enough variability in initial Pb fractions – even when high analytical precision is achieved – which may be related to variable physico-chemical conditions during the crystallization of vein-filling epidote. Although it is recommended that the largest spot size possible be used to ensure good counting statistics, it is imperative that geochemical heterogeneity be preserved among the different

705 analyses in order to obtain a well-constrained Tera–Wasserburg regression and a small age uncertainty. An unexpected perk highlighted by the present study is that relatively low U contents (i.e. tens of µg g^{-1}) do not necessarily hamper age determinations at a geologically useful precision provided that the spread of ^{238}U/^{206}Pb and ^{207}Pb/^{206}Pb ratios is large enough. This study presents a protocol that can be readily applied to date epidote-bearing hydrothermal veins and to assess initial Pb isotopic variability of the epidote-forming fluid. Better insight can now be gained from the application of epidote U–Pb

710 dating into the mechanisms that led to the hydration of the continental crust in the Aar Massif and in the Err nappe. This study represents the base from which further developments may allow to date high-P epidote-bearing veins in subducted oceanic units and to determine at the same time where the vein-forming fluid originated ~~from~~ thanks to the combination of trace element, age and isotopic data measured in epidote. Multiple phases of fault re-activation may be identified in fault-plane epidote. Whether or not plagioclase recrystallization in metamorphosed granitoid rocks is linked to the formation of

715 epidote-bearing veins may be solved by measuring U–Pb ages and initial Pb isotopic compositions in epidote, which has proven its potential to become an invaluable geochemical, isotopic and geochronological tool.

Appendix A

Contents of major elements were measured by electron probe micro-analyses (EPMA) using a JEOL-8200 microprobe at the Institute of Geological Sciences (University of Bern) with 15 KeV accelerating voltage, 10 nA specimen current and 2 μm electron beam diameter. The following natural and synthetic standards were used for calibration: wollastonite (SiO_2), olivine (MgO), anorthite (CaO, Al_2O_3), garnet (FeO), Topaz (F), tephroite (MnO), tugtupite (Cl), rutile (TiO_2) and celestite (SrO). Structural formula was calculated based on 12.5 oxygen cations.

REE, U, Th and Pb contents of epidote samples were measured on thin (30 μm) or thick (50–60 μm) sections, pre-cleaned with ethanol. Concentrations in sample Albula-1 were measured on a Geolas Pro 193 nm ArF excimer laser (Coherent, USA) coupled with an ELAN DRCe quadrupole ICP–MS (QMS; Perkin Elmer, USA) at the Institute of Geological Sciences (University of Bern). Instrument optimization and measurement procedures [similar to those reported in Pettke et al. (2012)] employed an ablation rate of ca. 0.1 μm per laser pulse, 10 Hz, and beam sizes of between 24 and 60 μm, the largest possible to minimize limits of detection and to avoid inclusions and fractures. Ablation was done in a 1 l min^{-1} He–0.008 l min^{-1} H_2 atmosphere. Concentrations in samples Grimsel-1, Grimsel-2 and Heyuan-1 were measured on a RESOlutionSE 193 nm excimer laser system (Applied Spectra, USA) equipped with a S-155 large-volume constant-geometry chamber (Laurin Technic, Australia) coupled with an Agilent 7900 ICP–QMS. Ablation was carried out in He atmosphere, which was allowed to mix with Ar carrier gas for transport to the ICP–MS. Repetition rate was 5 Hz, at spot sizes between 20 and 50 μm. On both systems, analytical conditions were optimized on NIST SRM612 so as to keep ThO production rate < 0.2 % and Th/U sensitivity ratio of 0.97–1.0, the latter indicative of robust plasma conditions. GSD-1G from USGS was employed as the external standard whereas quality control was monitored by measuring SRM612 from NIST measured as an unknown. A true-time linear drift correction was applied by bracketing standardization. Data acquired on both systems were reduced off-line using SILLS (Guillong et al., 2008), with the sum of measured total oxides (98.3 % for epidote and 100 % for SRM-NIST 612) used for internal standardization (compare Halter et al., 2002). Limits of detection were rigorously calculated for each element in each analysis employing the formulation detailed in Pettke et al. (2012).

Appendix B

Tera–Wasserburg diagrams of allanite secondary reference materials. All regressions are anchored to a $^{207}Pb/^{206}Pb$ intercept of 0.854 ± 0.015 at 275 Ma following Stacey and Kramers (1975) and all age uncertainties are 95 % confidence.
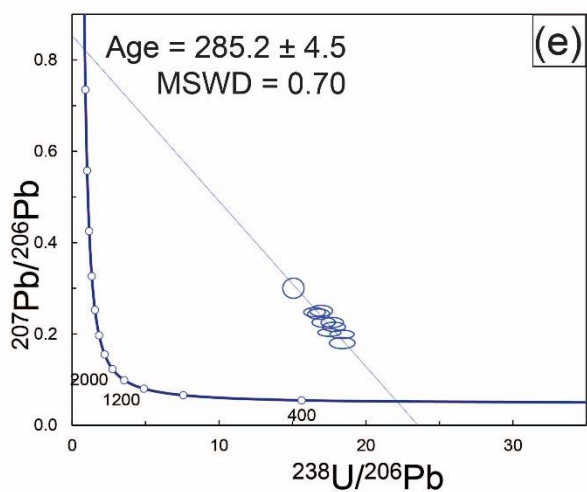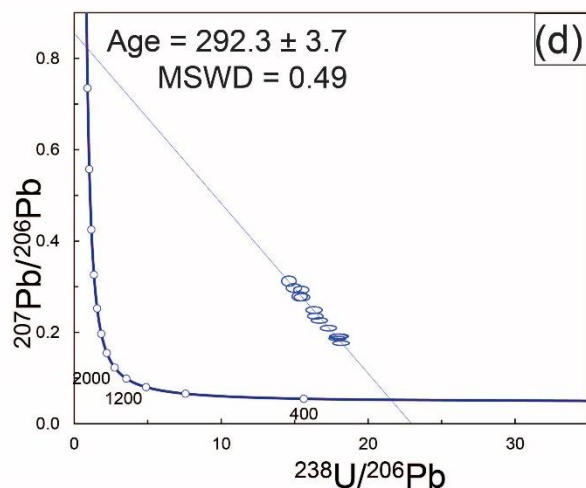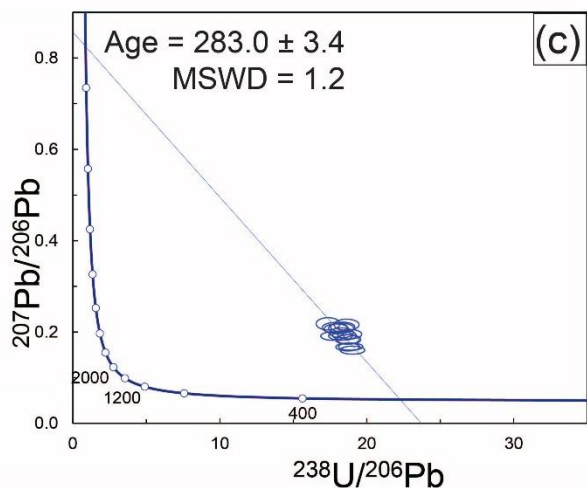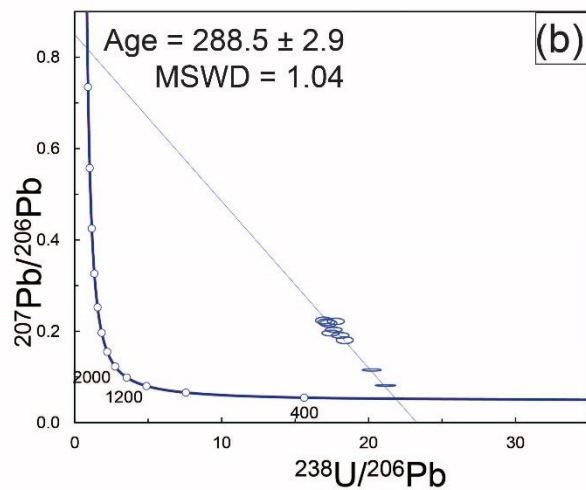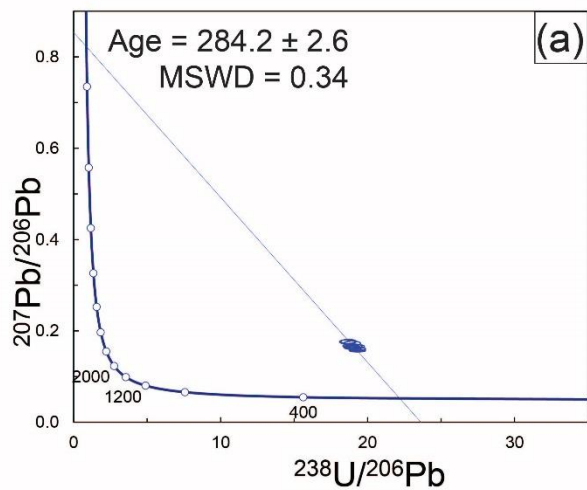
Figure B1: Tera–Wasserburg diagrams of allanite secondary standards. (a) CAP[b] allanite, 14 June 2019 session; (b) CAP allanite, 23 July 2019 session; (c) CAP allanite, 16 January 2020 session. (d) AVC allanite, 23 July 2019 session; (e) AVC allanite, 16 January 2020 session. <u>All ratios are uncorrected for initial Pb.</u> Data-point error ellipses are 2σ and age uncertainties are 95 % confidence.

Appendix C

Table C1: U–Pb ages of epidote samples with CAP[b] (14 June 2019) and CAP (23 July 2019) allanites as primary reference materials. <u>Measurements are with a 50 μm spot size.</u> Age uncertainties are 95 % confidence.

Sample	14 June 2019 Tera–Wasserburg U–Pb age [Ma]	23 July 2019 Tera–Wasserburg U–Pb age [Ma]
Albula-1	61.1 ± 2.8 MSWD = 1.6 n = 22	-
Grimsel-1	18.87 ± 4.33.9 MSWD = 0.784 n = 223	-
Grimsel-2	16.5 ± 3.5 MSWD = 0.39 n = 16	-
Heyuan-1	-	101.72.5 ± 8.94 MSWD = 0.87 n = 213

Author contribution

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Competing interests

The authors declare that they have no conflict of interest.

Code/data availability

All data are included in the manuscript (see tables).

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