

# ***Interactive comment on “U–Pb geochronology of epidote by LA–ICP–MS as a tool for dating hydrothermal-vein formation” by Veronica Peverelli et al.***

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This paper presents results of LA-ICP-MS dating of epidote veins from three geological settings: Albula (eastern Swiss Alps), Grimsel (central Swiss Alps), and along the Heyuan fault (China). The goals are to demonstrate the viability of epidote LA-ICP-MS dating and provide ages that are useful in interpreting the tectonics of these regions. The paper describes both technique development and application. In terms of technique development, the paper does not seek to reproduce epidote ages from known standards. Instead, it uses radiogenic allanite (an epidote group mineral) as a standard to date epidote of unknown ages. Overall, their use of the Terra-Wasserburg plot

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appears useful and applies to epidote, which contains low amounts of radiogenic elements and higher amounts of common Pb. It is promising that the unknown LA-ICP-MS ages yields results consistent with the tectonics of these regions. However, two issues to address are: (1) the secondary standards (CAP and AVC) appear to yield ages >10 m.y. older than what is reported for these grains (Table 3), and (2) the primary standard (Tara) is heterogeneous in age (e.g., Liao et al. 2020 JAAS). Overall, the approach described here would be of use to those seeking to generate epidote ages from regions that have experienced a simple tectonic history (i.e., epidote crystallization and no subsequent deformation/recrystallization events).

Some specific comments: Lines 52-53: “However, none of these techniques are in situ, and they cannot target different microstructural and textural domains.” It is possible to microdrill different domains of epidote, especially as it forms larger crystals and zones in the types of rocks under investigation. The authors also date one of the unknown epidote grains using solution ICP-MS, which seems at odds with this statement. Lines 104-107: “However, in recent years, magmatic allanite 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 several allanite samples have been proposed as suitable primary reference materials (e.g. Gregory et al., 2007; Smye et al., 2014).” Allanite has been shown to reproduce TIMS ages using SIMS as early as 2000 (Catlos et al., 2000, Am. Min.). Lines 110-115: “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  $^{206}\text{Pb}$  due to incorporation of  $^{230}\text{Th}$  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.” Allanite can be incredibly complex, as shown in numerous BSE images available throughout the literature. It is likely that a careful understanding of its chemistry in terms of compositional

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analyses could be included here. I don't think any of the issues described above can be avoided, and the authors should be more precise in their description of problematic issues. Lines 128-129: "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)." It is unclear if the sample numbers also correlate to samples described in these references. They should perhaps provide GPS locations if the authors do not want to make geological maps of the areas. Lines 130-131: "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." An overprint would suggest that alteration is possible. "Weak" is a relative term—it would be helpful to include particular P-T conditions. Lines 132-133: "The Heyuan Fault was selected because structural constraints allow to assess if the calculated U–Pb age is reasonable for epidote crystallization." Anticipated absolute ages for the samples are not provided. It would be helpful to indicate what they could be here or in further paragraphs. Lines 157-158: "As these veins are only visible within the tunnel, their relationships with Alpine structures and between each other are not understood." If the epidote ages from this area are unknown is at odds with the impression of this manuscript up until this point that the technique will reproduce epidote ages to a degree of helpful precision. Lines 201-203: "...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 (Smye et al., 2014)." One would hope that all of the standards are homogenous in terms of U-Th-Pb isotopes, which translate to their ages. The CAP and AVC allanites are incredibly useful materials. They are compositionally heterogeneous, but they are incredibly well-characterized in terms of their ages. There is no need for qualitative judgments regarding allanite standards. Lines 203-205: "Tara allanite reference isotopic ratios and their uncertainties (Table 2) were calculated by averaging five ID–TIMS measurements reported by Smye et al. (2014), excluding the measurement that yielded the youngest U–Pb age outside 205 uncertainty (Smye et al., 2014)." No need to repeat the Smye reference twice in the sentence. The age and uncertainty that

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they obtained from the standard should be reported. From my understanding, the Tara allanite age has a more considerable uncertainty compared to CAP and AVC (e.g., see Liao et al. 2020 JAAS). See also their concerns about the homogeneity of this grain and problems regarding the reproducibility of its ages. All of the allanite standards have ages that differ significantly from the age of the “unknowns.” It would be helpful to comment on this observation. Line 302-303: “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.” This sample appears affected by secondary fluid interaction, but that was not considered problematic in terms of interpreting its solution ICP-MS result. Line 343. “. . .CAPb.” I am not sure what CAP superscript b is exactly. It is likely explained somewhere, but I could not find it. Line 445: “overall consistent with published U–Pb ages, attesting to reliable U–Pb measurements. . .” It would be helpful to indicate what the U-Pb ages are and reference those results. Lines 512-13: “These considerations confirm the Tera–Wasserburg approach as the most suitable – and often the only viable – for accurate U–Pb dating of low- $\mu$  phases such as epidote (see Romer, 2001; Romer and Xiao, 2005).” The approach applied is very similar to that done for apatite by others (Oldum and Stockli, 2019, Tectonics and 2020 EPSL). Table 1. Is difficult to read. Similar parameters for each session can be placed in a footnote. There is a footnote b at the last row that is not explained. Table 2. Reference data for the other standards could be provided as well. Please include the ages. Table 3. The CAP and AVC ages reported here are 10 m.y. older than their TIMS ages (Barth, 1994, also Liao et al. 2020). Table 4 and Table 5. Are difficult to read in terms of which dataset belongs to which sample. Could place the sample names in rows. Figure 2. Are the BSE images located in the petrographic images in Figure 1? No spots are shown in panel a1, so I assume it was not also dated using LA-ICP-MS. I think the contrast can be enhanced in some of the images to enhance the zoning.

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