<u>Review of the manuscript (n. gchron-2023-11)</u>: "Volcanism straddling the Mio-Pliocene boundary on Patmos (East Aegean Sea): Insights from new ⁴⁰Ar/³⁹Ar ages" *by K. Boehm et alii*

General comment

This is an interesting and well written manuscript reporting a significant set of Ar/Ar data performed by a new generation multi-collector noble gas mass spectrometer on volcanic rocks from Patmos and the nearby Chilomodi Island (Aegean Sea). Results significantly strengthen the limited set of existing data and permit a detailed reconstruction of volcanism at Patmos, also allowing a revised tectonic reconstruction. Furthermore, data allow general considerations on the reliability of Ar/Ar data from biotite of volcanic rocks. Although for volcanic rock samples it would be preferable to analyse alkali-feldspars, in some chronostratigraphically relevant tephra, biotite is the only K-rich mineral that can be analyzed. Therefore, improving our knowledge about the reliability of biotite in geochronological studies of volcanic rocks, through the comparison of Ar/Ar data from coexisting biotite and sanidine, is of great and broad utility.

The main objection I have on the MS in its present form concerns the uncertainties on Ar/Ar ages (weighted means). The Author state they have conducted an investigation at a high resolution but report uncertainties on the weighted mean ages up to ~2%, quite high for modern geochronology based on multicollector mass spectrometry and using astronomically calibrated reference minerals. First, I recommend that Authors use internal uncertainties (i.e., including analytical errors and uncertainties on the fluence monitor) for inter-sample comparisons of Ar/Ar ages and not the full external uncertainty, which in fact also includes systematic errors (i.e., the uncertainty on the age of the reference material and on ⁴⁰K total decay constant) and which affect the calculated ages from the different samples in the same way. If the authors deem it necessary to report the total uncertainty for each age value, I suggest adding it in parentheses after the internal uncertainty. I also suggest to report the first two significant decimal digits both in the age value and in the relative uncertainty. Second, full external uncertainties of up to ~2 % starting from internal uncertainties in most cases of ~0.4-0.5% and using the astronomical calibration for the reference material Fish Canyon sanidine (Kuiper et al. 2008) seem quite high.

My comments mainly focused on Ar/Ar geochronology and I recommend a specific review for the remaining topics. In conclusion, the manuscript needs some work addressing the general comment above and some specific points listed below and after revision, should be publishable in the journal.

Specific points

Line 19 pag. 2: here and through the whole MS replace full external uncertainties with (or add) the 2σ internal uncertainty. The use of the full external uncertainty makes sense only for comparison of Ar ages with those obtained from other radioisotopic systems or non–radioisotopic techniques. See also general comment above.
Line 132 pag. 6: replace "between 5.7 and 6.0" with "between ~5.7 and ~6.0".

- Lines 133-134: replace "from 5.2 Ma to 5.4 Ma" with "from ~5.4 Ma to ~5.2 Ma".
- Line 135 pag. 6: "rather low K contents"... it is just another phase, anorthoclase.
- Line 149 pag. 6: Why was biotite analysed if it is so altered?

- Line 162 pag. 7: "a biotite age that is ~0.21Ma older" replace with "a biotite age that is 0.219±0.056 Ma older".

- Lines 164-167 pag. 7: "Recoil from K-depleted cleavage zone"... I don't really agree that recoil processes from chloritized levels alone can justify a significant increase in the age of biotite with respect to that of coexisting sanidine. It is well known that chloritization processes induce rejuvenation of total gas ages from biotite (e.g., Roberts et al. 2001; Di Vincenzo et al. 2003).

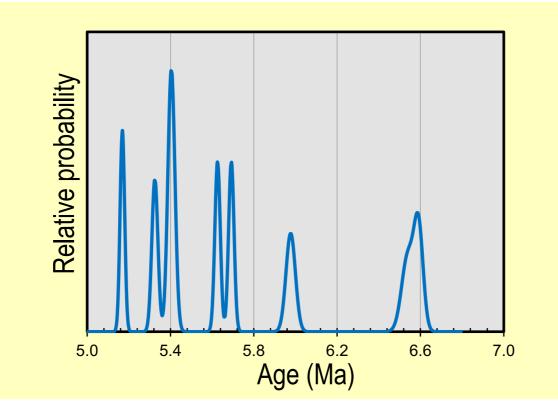
- Lines 171-172 pag. 7: "on cooling rates at the time of the eruption". In my opinion the cooling rate for an effusive/explosive volcanic rocks is irrelevant in this case. In my opinion the most important cause for older biotite ages with respect to those of coexisting sanidine has not been mentioned: i.e., the presence of excess Ar (parentless ⁴⁰Ar), preferentially partitioned into biotite with respect to coexisting sanidine by virtue of its higher mineral/melt partition coefficients (Kelley 2002). I am not saying that extraneous Ar present in biotite P7 cannot be, at least in part, inherited Ar but that excess Ar may be a possible cause and needs to be mentioned.

- line 192 pag. 7: "resp.", make explicit.

- line 193 pag. 8: "we conclude that", this not a conclusion but a finding.

- line 202 pag. 8. The period of activity is 1.370±0.063 Ma (excluding data KB11) or ~1.4 Ma.

- lines 202-203 pag. 8: "with at least three distinct interval of activities", what I see from Ar/Ar data on sanidine (and using $\pm 2\sigma$ internal uncertainties) is an onset of volcanism at ~6.5 Ma followed by several pulses down to ~5.2 Ma (see the cumulative probability plot below).



- Line 299 pag. 11: rephrase in "We provide 12 new sanidine and 3 new biotite".

- Fig. 3: Caption, rephrase in "Individual fusion ages with 2σ analytical uncertainties…". I suggest to include in the figure the weighted mean ages followed by the respective internal and full external uncertainties for each mineral separate. Also explain in the caption what are the white dots and why they were excluded (I expect) from the weighted mean calculation.

References

Di Vincenzo, G., Viti, C., Rocchi, R. (2003). The effect of chlorite interlayering on ⁴⁰Ar–³⁹Ar biotite dating: An ⁴⁰Ar–³⁹Ar laserprobe and TEM investigation of variably chloritised biotites. Contrib. Mineral. Petrol., 145, 643–658.

Kelley S.P. (2002). Excess Ar in K-Ar and Ar–Ar geochronology. Chem. Geol. 188, 1–22.

Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R., Wijbrans, J.R., 2008. Synchronizing rock clocks of Earth history. Science 320, 500–504.

Roberts H.J., Kelley S.P., Dahl P.S. (2001). Obtaining geologically meaningful ⁴⁰Ar–³⁹Ar ages from altered biotite. Chem. Geol. 172, 277–290.