

Thank you very much for carefully reviewing our manuscript, providing helpful and valuable comments. The minor comments on writing errors or cited reference have been directly corrected in the text. An answer is addressed below each point that needed further discussion.

Regards,  
Marie Gérardin

Line 31. Point (1) is not strictly true. There is evidence that electron capture is affected by pressure, but this does not affect any "real" dating by the K-Ar method.

Line 32. Point (2) is erroneous. The  $^{40}\text{K}/\text{K}$  ratio decreases over time; this is the basis of the K-Ar geochronometer. The authors mean that it is constant for all samples at present, which is also strictly false, but within the margins of error currently achievable, it can be considered true.

Line 32. Point (3) needs to be worded a little differently, as stating that all  $^{40}\text{Ar}$  comes from the decay of  $^{40}\text{K}$  does not exclude  $^{40}\text{Ar}$  trapped during the rock's formation and originating from the decay of  $^{40}\text{K}$  before the system closed. The later point (5) also does not eliminate this case. Saying that  $^{40}\text{Ar}$  comes from the decay of  $^{40}\text{K}$  within the mineral will solve the problem.

Line 33. Point (4) we know is false, but we must assume it for atmospheric correction. In any case, most of the air in the extraction lines has a modern atmospheric composition. A different case occurs when measuring very old samples with trapped air bubbles (fluid inclusions) that could give values different from modern air (and that have been studied for this reason).

Line 34. As mentioned, point (5) does not exclude radiogenic argon trapped during rock formation.

Reply: Thank you for sharing clarifications about the 5 points that must be addressed to apply K-Ar method. As written in the text, those 5 points are assumptions that we need to consider to apply the method but we know some of them are strictly false, as you rigorously mentioned. I made some modification in the text following your suggestion and added "It is considered that..." to avoid confusion.

Line 61. The word "desorption" introduced here and used later raises some doubts. The Merriam-Webster dictionary defines it as "to remove (a sorbed substance) by the reverse of adsorption or absorption." But this is not what happened with argon; argon was not absorbed. It would be better to name it 'the extraction line,' but I will leave it to the authors' discretion.

Reply: I agree with this comment, Ar is not physio-sorbed on the surface of micas but trapped in the interlayer. I will replace the word "desorption" by "extraction", more adapted to radiogenic argon.

Table 1. The lambda-beta value of Steiger and Jäger is 4.962. Where do the errors come from? They are not specified in the Steiger and Jäger publication.

Reply: Thank you for pointing out this mistake. At the beginning of the writing, I evaluated the contribution of an error on the decay constants on the age. I probably took the error mentioned in Guillou et al. (2021). I found that this contribution is negligible compared to the error on the Ar measurement and especially on %K<sub>2</sub>O. The errors has been removed.

Line 85. From here to the end of the article, including the tables, it is unclear whether the errors are expressed as one or two standard deviations. If the deviations differ, they should be stated now or noted on each occasion.

Reply: One sentence has been added in section 2.1: "If not specified, all errors reported in this paper are expressed as one standard deviation."

Lines 114-116. "To compare one analysis to another ... and a charcoal trap." Is there a lot of volume change in the complete line? I assume the problem is the furnace.

Reply: I'm afraid I don't understand this comment and especially what stands for "volume change". The gas in the line travels through multiple volumes from the furnace to the MS and is sorbed on a charcoal trap (either to purify the gas or to attract the gas near the MS). In order to compare one MS measurement to another, we need to perform the analysis in an equivalent volume. I choose this volume to be the one of the MS + one "introduction" volume before entering MS.

Line 117. According to the published graphs by physicists, the highest cross-section of electronic impact ionization for argon is 80-100 eV, so why is the source regulated at 60 eV? To diminish the background?

Reply: Thank you for raising this question. I was not aware of these studies about the optimal energy to ionize argon. The source is regulated at 60 eV to reduce the proportion of double ionizations ( $\text{Ar}^{++}$ , i.e.  $m/z = 20$ ). I will run some tests in the energy range of 80-100 eV.

Line 125. The sensitivity of the spectrometer also depends on the transmission, typically controlled by the slit widths and the quality of the focus given by the ion source, the magnet, and additional electrical filters, if any.

Reply: Thank you for those details that are definitely included in the "black box" that I called in the text: "the ionization capacities of the source". I did not risk to make an exhaustive list of all parameters influencing the ionization capacities because it could be interpreted as if we can control all of them.

Line 139. Figure 4 and equation (2). The Y-axis value of Figure 2 is given in pA, but equation (2) seems to provide the values in fA. This should be stated in the text or Figure 2 modified accordingly. What is the relationship between the  $^{40}\text{Ar}$  intensity of -644 fA when  $\text{DE}=0$  (i.e., no gas) deduced from equation (2) and the values of the analytical blank in Table 2, discussed below? The correlation in Figure 2 is very good, but I would expect the intersection to be positive, implying a positive analytical blank (atmospheric or otherwise). Is there any correction somewhere in the calculation?

Reply: All intensities have been changed in pA in eq. 2. Eq. 2 is an empirical equation based on the signal obtained at  $n\text{DE}$  ( $n \geq 1$ ). This equation is meant to correct the signal from pressure effect in the source. Then it has no meaning when there is no gas in the mass spectrometer. The signal at 0 DE (blank) is then not included in the data to build the equation. The following sentence is added in the text: "Note that this equation is valid when  $I(^{40}\text{Ar}) > 0.01$  pA corresponding to the lowest signal measurable in the mass spectrometer (see the blank measurements at section 2.6)." This condition concerns the signal intensity because this is what we measure. The DE is calculated from I.

Line 150, Figure 5. It seems to me there is some error in the equations under the figure. Perhaps it needs to be explained better how the equations are derived, particularly (3); see the comment below.

Reply: The paragraph above Fig.5 has been changed. Hopefully, this will help the reader to better understand the calculation performed after each step of the analysis.

Lines 163-164. Is the oxygen peak sufficient to know that there is not still too much water, hydrogen, carbon dioxide, or hydrocarbons in the line? If the spectrometer is used to scan, it means the sample has already been introduced; does this not delay the first argon reading too much from time zero? Wouldn't it be better to have a "pipette" with a gas quadrupole in some section of the line to sample a small (but constant) volume of the gas before introduction? The information these instruments provide about the vacuum quality is very significant. Once you have tried one, you cannot work without it.

Reply: When the gas enters the MS, it is not in the scan mode. Argon 40, 38 and 36 are measured simultaneously during 200 s (one point every 2s). Then, we use the scan mode of the MS to measure the oxygen pics. The former analysis of argon can be disregarded if the oxygen pics are too high. Indeed it would be very interesting to work with a small quadrupole like a RGA to measure the quality of the purification before analysis into the MS.

Lines 167. "... the absence of radiogenic argon in the system ..." But there could also be hydrocarbons, or HCl at mass 36, that modify the  $^{36}\text{Ar}$  reading, not just radiogenic argon.

Reply: This is true that the mass 36 could be contaminated by hydrocarbons or HCl if the purification of the sample didn't operate properly. I complete the sentence by "or any hydrocarbons or HCl remaining in the system".

Lines 170-172 and Table 2. In my opinion, the composition of the electronic blank can be problematic. The values are certainly much lower than those of the furnace blank in the case of  $^{40}\text{Ar}$ , but in the case of  $^{36}\text{Ar}$ , the negative signal value is very close to the  $^{36}\text{Ar}$  of the furnace blank. Since it is unclear how the 4.7 fA of the furnace blank has been measured, I cannot confirm. However, suppose the value of 4.7 fA is directly the reading of the multimeter (or the equivalent conversion of voltage to current). In that case, the "base" value of -1.0 fA should be subtracted, giving 5.7 fA, which is not an atmospheric blank ( $^{40}\text{Ar}/^{36}\text{Ar} = 1358.8/5.7 = 238.4$ ). The furnace blank may have some atomic or molecular species at 36 Da that is not  $^{36}\text{Ar}$ . If the same calculation applies to the "1 DE" values, the 40/36 ratio would be 298.6, which is exactly the value of air. I think the AX amplifier should be adjusted; it surely has a circuit to adjust the zero (offset) with a potentiometer to leave it positive, not negative, to avoid possible confusion. These comments might seem exaggerated, but we must consider that the latest-generation spectrometers have very stable electronics and provide high-precision data, so these details are relevant. All this should be clarified in the manuscript.

Reply: A sentence has been added under Table2: "\* signals corrected from the electronic blank". Indeed, all signals presented in this paper are corrected from the electronic blank. It means that the intensity of the  $^{40}\text{Ar}$  in the furnace blank is measured at 1366.1 fA and the  $^{36}\text{Ar}$  is measured at 3.7 fA. In the future, I will adjust the signal to zero to avoid confusion.

Table 2. The furnace blank is quite high, approximately 0.1 V for  $^{40}\text{Ar}$ . In modern laser systems, the blank is much lower by two or three orders of magnitude. According to the text, I understand that this is compensated by the weight of the samples analyzed, which makes the signal, on average, about ten times larger than the analytical blank. Even so, reducing the furnace blank by an order of magnitude would be a good goal.

Reply: Indeed, the blank is low enough to allow the measurement of radiogenic argon from the samples but is still quite high. This will be reduced with further improvements on the heating device. A new furnace is expected in 2025 with higher heating performance. Notably, the furnace will reach high temperatures in less time limiting the gas release of the furnace surfaces.

Lines 337-338. Another explanation is that, at atmospheric pressure, heating oxidizes the  $\text{Fe}^{+2}$  that may be present, and the weight increases slightly, causing the weight loss due to water loss not to be so great. This phenomenon often occurs when determining the loss on ignition (LOI) of rock samples.

Reply: Thank you for this comment. I was not aware of the weight increase by  $\text{Fe}^{2+}$  oxidation. I added this hypothesis to explain my result in the Appendix.

Line 348-349, equation (5). What is the value of the sensitivity S? With the data provided in the article, I inverted the equation and obtained  $S=1.5\text{e-}11$  pA/at. Is this correct?

Reply: Yes, this value is around  $1.6 \times 10^{-11}$  pA/at. The sensitivity can also be calculated using the equation 4 and considering that  $I_{\text{aliquot}}(^{40}\text{Ar})$  is 50.68 pA.