

## ***Interactive comment on “Measurements of atmospheric He/N<sub>2</sub> as an indicator of fossil fuel extraction and stratospheric circulation” by Benjamin Birner et al.***

### **Anonymous Referee #2**

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Review AMT Manuscript "Measurements of atmospheric He/N<sub>2</sub> as an indicator of fossil fuel extraction and stratospheric circulation"

#### General assessment

The manuscript presents a method for analysis of the He mole fraction in large air samples, calibrated relative to a gas standard. The method allows much better precision than previous methods for He analysis in air. As far as I can tell from the manuscript, the analytical tests are reliable and demonstrate the instrumental performance of the method in a good way. However, in the current form of the manuscript, the scientific relevance of the new method remains unclear to me, and I have some technical ques-

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tions, which deserve more background explanation. If these points can be fixed in a revised version, I recommend publication of the manuscript in AMT.

#### Specific comments

\* The measurement yields the mole fraction of He in the sample gas matrix, normalized relative to the He mole fraction in a gas standard. However, the method is presented in the manuscript to yield the (absolute?) He/N<sub>2</sub> ratio of the sample. This is rather confusing, as N<sub>2</sub> is NOT part of the measurement (in fact, N<sub>2</sub> is removed from the gas sample before MS analysis). The conversion of the measurement result (He mole fraction) to the He/N<sub>2</sub> ratio is based on a simple mathematical manipulation and some assumptions about the composition of the gas matrix. This conversion seems trivial and is not related to the measurement technique; and I don't see the need for it. I suggest to avoid this confusion by removing He/N<sub>2</sub> (or He/O<sub>2</sub> etc.) as far as possible (from the title and most of the text), and to focus on the true nature of the measurement, i.e., on the (relative) He mole fraction.

\* The manuscript is missing a review/overview of existing techniques for He analysis in air (3He/4He, He/Ne, He mixing ratio). Without this background, it is difficult to understand on what grounds the new method was designed, and how it improves on previous methods, both in terms of instrumental techniques and scientific applications. The manuscript should be revised to better develop the link of the new method to existing techniques. What were the design targets for the new instrument? What was the design approach to achieve these targets? Why was the new method implemented in this way?

\* As it is, I am not convinced about the scientific utility of the new method: (1) Earlier work with static MS systems for He isotope analysis showed that their 0.2% precision was sufficient to resolve the expected atmospheric He variations (for example: Mabry et al, EPSL, 2015). Why exactly is a new method with approx. 100x better precision required to study the evolution of the atmospheric He? (2) Most publications on at-

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atmospheric He acknowledged that the quality of the historic/archived air samples put major limitations on the uncertainty of reconstructing the atmospheric He abundance (for an overview see for example: Brennwald et al, EPSL, 2013 / reference missing in the manuscript). Further improving the instrumental precision of the He analysis does not help with this fundamental issue. I am therefore not convinced that an improvement of the instrumental precision is very useful to study some of the effects noted by the authors. (3) With an analysis time of 6-8 hours and a sample gas consumption of 28 mL per minute, a single analysis requires about 10-14 L of sample gas. However, typical samples of historic/archived air are typically in the order of 0.1-100 mL (see refs. cited in the manuscript, and as given above), which is 2 to 5 orders of magnitude too low for the new method described in the manuscript. The large gas consumption of the new method therefore severely limits the technical applicability to large-volume gas archives, which are scarce and may not be readily available for consumption to a (destructive!) analysis. In order to illustrate the scientific potential of the new method, the manuscript should be extended with application examples targeted at the scientific questions described in the introduction. I suggest to add a few measurements of real-world historic/archived air samples to demonstrate the true utility and suitability of the new method to study the He change due to fossil fuel extraction (and analogous for stratospheric circulation).

\* What is the purpose of the cold traps at the gas inlet system? My guess is that they are meant to remove water vapor from the sample/standard gas streams, but I am not sure. This should be described better.

\* The intensity of the He ion beam in the MS is controlled by the sample/standard gas flow to the gas inlet system. As far as I can tell, the precision of the analysis result is therefore controlled crucially by the inlet system, and in particular by the cold traps and the pressure regulators: (1) Cold traps: the efficiency of the water removal from the gas streams is likely not stable over time, and will therefore introduce a variation of the He mixing ratio in the gases. How can the cold trap variation be avoided such that

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the He mixing ratio in the gas stream is stable to 10 per meg or better? (2) The gas pressure at the main capillary inlet directly controls the gas flow into the capillary, and hence the He flow into the MS. Similarly to the cold traps, this seems to imply that the pressure at the capillary inlet must be stabilized to 10 per meg or better. How is this technically possible? I don't have a strong background with large-volume dynamic MS gas analysis, so I may be overlooking something that may be obvious to the authors (I am mostly into static and low-volume dynamic MS). However, I believe it would be very difficult to achieve such tight stability controls over the gas inlet system, and there must be some way to avoid or compensate such variations in the gas inlet in order to achieve the 10 per meg precision in the He mixing ratio of the gas sample. I feel these points need to be explained better.

\* Title: "Measurements of ..." seems to indicate that the focus of the paper is to present new measurement data. I'd suggest to change focus to the new analysis method / technique.

\* Line 26/27: "...gases heavier than air in the stratosphere..." → what gases other than air are in the stratosphere? Also, does the gravitational separation only apply to heavier gases, not lighter ones?

\* Line 56/57: I'd assume that N<sub>2</sub> and other "noble" gases are seasonally variable due to atmosphere/ocean gas exchange, which is subject to the temperature dependence of N<sub>2</sub> solubility in the water (e.g., Keeling et al., Tellus 322–338, 2004). Note that the He solubility dependence on temperature is much less than for N<sub>2</sub>. While this effect may be relatively small, it should at least be noted in the text (if the N<sub>2</sub> normalization is not removed entirely, see above).

\* Line 83: Using the equations given above, I calculate  $\Delta(\text{He}/\text{N}_2) = -6.4$ , not 7.5 (note the sign!). Please check.

\* Line 95: "...no significant trend in atmospheric <sup>3</sup>He/<sup>4</sup>He has been observed..." → there are many different studies with different (and sometimes contradicting!) conclu-

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sions regarding the existence and size of the atmospheric  $^3\text{He}/^4\text{He}$  change. Considering the work cited in the manuscript it seems wrong to say "no significant trend was observed", and this argument needs to be revised. To this end, it might be useful to take a look at Brennwald et al, EPSL, 2013, which has a compilation and comparison of different studies on the atmospheric  $^3\text{He}/^4\text{He}$  change, and also presents some measurements on He changes observed in archived air samples.

\* Line 144: "...compared to the 30-second switching timescale." → what does this refer to? Switching of what?

\* Line 156: "Background concentrations..." → what "background" is this? "Blank"? "Residual"?  $m/z=4$  signal with analysis of He free gas? Or with the inlet to the MS closed? Please define.

\* Line 172: The geometry of the cold trap crucially controls the operation and performance of the cold trap. Is this a U shaped tube? Or a 'washing flask' type? Or something else? Please explain the details of the cold traps ("made from 1/4" stainless steel" is not sufficient).

\* Line 175–178: Why is the performance of the getter important (as long as it is not "dead" and works as a pump to draw the air matrix into the capillary)? As far as I can tell, the He flow rate into the MS is identical to the He flow rate into the getter. I therefore don't see how the getter can affect the He analysis (as long as the getter operation is stable between the analysis runs of the sample and standard gases). How does the getter affect the performance of the He analysis? Does the getter performance affect the He analysis at all? Please explain.

\* Line 201: What does "the 5% level" refer to? Is this a statistical "significance level"? What kind of statistics? Please explain.

\* Fig. 7 shows the measured zero effect, with a substantial scatter (about +/- 50 per meg or so). However, the discussion in the main text indicates a zero-effect uncertainty

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of only 6 per meg. I am confused because I don't understand how the +/- 50 per meg scatter is consistent with the 6 per meg uncertainty. I believe my confusion is due to some ambiguity in how the zero-effect is quantified and compensated during the analysis and data processing routines. This should be explained better.

\* Tab. 2: what is the meaning of "scaled" Xe peak heights? What kind of "scaling" was applied, and how? Please explain.

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