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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurements of atmospheric He/N_2 as an indicator of fossil fuel extraction and stratospheric circulation" *by* Benjamin Birner et al.

Anonymous Referee #3

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In this paper, the authors describe a new measurement system they developed to precisely measure atmospheric He/N2. It is my opinion that the unprecedented high precision achieved by the method will make a significant contribution to an increased understanding of the He budget and gravitational separation processes in the stratosphere. The authors' effort is to be congratulated. I have found the paper to be well written and should be published in Atmos. Meas. Tech.. However, listed below are some comments I would like the authors to address before the publication.

1) I think the analytical precisions of mass spectrometry can be classified into "internal precision", "internal reproducibility" and "external reproducibility" (see Bender et al.,

1994, Geochim. Cosmochim. Acta.). Internal precision indicates a standard error of xx cycles in a 1-block analysis, and internal reproducibility indicates a standard deviation of the repeated analyses of several blocks. I think the authors did not distinguish between internal precision and internal reproducibility in the paper, and the presented internal precision of $\pm$15 per meg for sample run of 1.5h and $\pm$8 per meg over 6h (line 186-187) are standard error (1sigma/sqrt(n), n = number of the total cycles $\sim$ about 1,800 and 7,200 for 1.5h and 6h, respectively). The internal precision is shown as error bars in Fig. 6, and the variability of every cycle measurements is presented in Fig. 3 (b) (the unit "per meg" is needed for the y-axis label of Fig. 3 (b)). I hope I have not misunderstood or misinterpreted the presentation.

2) Fig. 6 shows d(He/M) values of 8 (5) times repeated analyses of the 6-8h measurements of Cylinder A (B) against La Jolla air. I think it corresponds to the external reproducibility in the context of Bender et al., but I have some concerns: Is the La Jolla air identical to the "He/N2 reference material (line 163-165)", "standard gas cylinder (line 188)", and "reference (Fig. 2)"? Please clarify to avoid confusion. Assuming that the standard and La Jolla air are identical and used as the reference in Fig. 2, how do the authors ensure the short-to-long term stability of the La Jolla air? In other words, how long does it take to obtain the results of 8 or 5 times repeated measurements shown in Fig. 6? If it takes several days, then I agree that the stability of the standard is enough for the period, however, future work is needed to confirm much longer-term stability for the observations of seasonal and interannual variations in the atmospheric He/N2 ratio.

3) Please provide information related to the needed minimum and maximum inner pressures of the sample and reference gas to maintain the appropriate flow rate of 27-28 mL/min using capillary. In this regard, I sort of remember Scripps flask samples being collected at an atmospheric pressure. If so, I don't think these flasks can be used for the He/N2 analysis, as described in the present study. How do the authors collect pressurized air samples without significant fractionation of He and N2?

4) Related to the comment 3) above, there does not seem to be any discussion of the analyses of the locally pumped ambient air shown in Fig. 2. I would be very much interested in hearing from the authors some information regarding the ambient air analyses, since it will serve as an indicative evaluation of "true" external reproducibility, including air sampling procedures, such as inlet fractionation, and leakage or permeation of He through pump diaphragm.

5) I think the response of d(He/N2) measured by the mass spectrometer to the actual H2/N2 ratio of a sample air will likely be linear, but some checks are needed. Please provide some concrete evidence to that effect.

6) The potential application of He/N2 to evaluate interannual variability in the stratospheric circulation ($\pm$375 per meg/yr, expected value) is very interesting and is an excellent idea, considering that it can provide better signal-to-noise ratio than Ar/N2. In order to extract the gravitational fractionation signal of He/N2, it is necessary to subtract the He/N2 change due to chemical processes such as fossil fuel extraction (which yields 35 – 350 per meg/yr of secular He/N2 trend at the surface) from the observational results in the stratosphere. I guess the authors have plans to observe surface He/N2 variations, so that a precise secular trend in the troposphere will be achieved in the near future. However, as reported by Engel et el. (2009 Nature Geoscience), CO2 or SF6 age of the stratospheric air samples show interannual variability by about $\pm$1 years. This interannual variability of the age corresponds to $\pm$35 – $\pm$350 per meg of the stratospheric He/N2 change due to the fossil fuel extraction, if we ignore attenuation of the interannual variability from the surface to the stratosphere. Therefore, to evaluate the interannual variability in the stratospheric circulation based on gravitational fractionation of He/N2, precise determination of He/N2 age will be important. However, as Ray et al. (2017 JGR) and Sugawara et al. (2018 ACP) reported, CO2 age and SF6 age do not necessarily agree with each other. Given these issues, I would be very much interested in hearing how the authors are planning to determine the age of He/N2.

7) Line 198: "9 psi, 14 psi, and 16 psi. . ." should be changed to "9, 14, and 16 psi".

8) Line 202: "-9.61$\pm$7.2 per meg, 1$\pm$3.7 per meg, and -15.7 per meg. . ." should be changed to "-9.61$\pm$7.2, 1$\pm$3.7, and -15.7 per meg. . .".

9) References: Please change "2" in CO2, O2/N2, Ar/N2 and SF6 to subscripts.

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