Revision:

We thank for the careful reading of the revision and hope that we meet with our revision of the Appendix the expectations.

Thank you very much for your response. I appreciate the level of detail that you dedicate to the discussion of the conversion from O2 mole fraction to delta(O2/N2). I fully agree with your suggestion of modifying the introduction and to move the detailed discussion on the relation between O2 mole fraction and delta(O2/N2) to the Appendix. The first two paragraphs are very comprehensible. You could state before "Following equation 1 in Thojima ..." that no unique conversion factor exists if N2 or the other air components are not known.

Unfortunately, paragraphs 3 and 4 of the analysis and table A1 in the Appendix still lead to confusion and the two paragraphs need to be corrected/rewritten. I cite:

"Note that under the assumption the atmospheric N2 content is constant (i.e. N2sample equals N2reference), we convert relative changes in oxygen given in per meg following equation 1 to oxygen changes in parts per million (equivalent to micromol/mol) by multiplying by the O2 mole fraction (O2reference) expressed as 209500 ppm (the O2 mole fraction of atmospheric air) (Machta and Hughes, 1970). Hence 1 ppm corresponds approximately to 4.8 per meg, or 1 per meg to 1/4.8 (209500/106) ppm.
This is used in our approach since the Picarro ... in the following Table A1"

The above text seems to indicate that in your calculation you consider changes to O2 alone (thus keeping N2, CO2, Ar, ... const). If done correctly, this corresponds to case 3 in your table A1 (ΔO2 only), which indicates that the conversion factor is 6.04 per meg /ppm, but you derive 4.8 per meg /ppm from your calculation ! It is evident that there is an error or an undocumented approximation somewhere in your calculation. This contradiction needs to be resolved.

I might be wrong, but from your arguing, you take the value of 4.77 per meg / ppm as an ad hoc conversion factor somewhere in the range of values that might be observed (between 0 and 6.11 per meg / ppm). If this is true, you should present it in exactly this way. If this is not the case, please give another motivation that does not contradict the results in your Table A1.

Finally you mention the N2 mole fractions of your standards but you don't give them in Table 1. However, this seems to be very important information. With N2, O2, CO2 given, using reasonable Ar values and a measured data for H2O, much of the uncertainty in the conversion from mole fraction to delta should be very small. Please add these data if they are available.

We, have added a new table A1 that lists all the information for the scenarios displayed in table A2 for the conversion of mole fractions in delta O2/N2.

Minor corrections/suggestions

Following equation 1 in Thojima et al., 2000, the per meg to ppm conversion has a slope of 6.04 if only a change in oxygen is applied as seen in table A1.
->
Following equation 1 in Thojima et al., 2000, the per meg to ppm conversion has a slope of 6.04 if a change only in oxygen is applied as seen in table A1.

Corrected as suggested above

The fact that our supplementary plot shows slopes of 5.78 (for the first five standards) or 6.08 (for all standards except ST-7) is due to a mixed influence dilution effects.
->
The fact that our supplementary plot shows slopes of 5.78 (for the first five standards) or 6.08 per meg per ppm (for all standards except ST-7) is due to a mixed influence of dilution effects.

Corrected as suggested above

The lower slope of 5.78 documents particularly the influence of the CO2 dilution effect.
->
The lower slope of 5.78 per meg per ppm documents particularly the influence of the CO2 dilution effect.

Corrected as suggested above

For example a 10 ppm increase in CO2 lead to an incorrect value of -10 per meg in δO2/N2,est compared to the true δO2/N2,true value.
->
For example a 10 ppm increase in CO2 leads to a bias of -10 per meg in δO2/N2,est compared to the true δO2/N2,true value.

Corrected as suggested above

As you can see from table A1 an addition of N2 of 10 ppm leads to a reduced and opposite effect for the difference in δO2/N2 (true – est) because the dilution effect on O2 cannot compensate the change from the increase in nitrogen, therefore it scales with -10 ppm x (oxygen mole fraction/nitrogen mole fraction).
->
As can be seen from table A1, addition of 10 ppm of N2 leads to a reduced and opposite effect for the difference in δO2/N2 (true – est) because the dilution effect on O2 cannot compensate the change from the increase in nitrogen.

Corrected as suggested above

In our case this is given – but can certainly be improved – since we are comparing air composition to air standard compositions.
->
In our case this is given – but can certainly be improved – since we are comparing natural air to air standards.

Corrected as suggested above

Yet, determinations of the standards that has been used in this study have a range in N2 concentrations of -110 to +110 ppm for the ST-1 to ST-5, whereas ST-6 (+700 ppm) and ST-8 (-6200 ppm) are significantly off compared to our primary standard used for mass spectrometric determination.
->
Yet, determinations of the standards that have been used in this study have a range in N2 concentrations of -110 to +110 ppm for the ST-1 to ST-5, whereas ST-6 (+700 ppm) and ST-8 (-

6200 ppm) are significantly off compared to our primary standard used for mass spectrometric determination.

Corrected as suggested above

Table A1: ppm to per meg conversion calculations for air-like compositions
->
Table A1: mole fraction to delta conversion for air-like gas compositions according to different scenarios

Corrected as suggested above

δO2/N2,true: for instance measured by mass spectrometry; δO2/N2,est: for instance measured by 988 Picarro G-2207.
->
δO2/N2,true: calculated (eg Thojima et al., 2000); δO2/N2,est: use fixed conversion factor of 4.77 per meg / ppm

Corrected as suggested above

ΔO2 in line 4 of your Table A1 should be ΔN2

Corrected as suggested above

New Appendix:

Appendix: Uncertainty consideration during mole fraction (ppm) to delta (per meg) conversion for air-like gas compositions according to different scenarios

Generally, the Delta notation, as given in equation 1 of this publication (main text), is used in order to circumvent the influences of dilution by other gas components when determining oxygen mole fractions (see table A1). Yet, several instruments are measuring the oxygen mole fraction such as the paramagnetic cell, the UV-cell as well as the instrument by Picarro presented here. Therefore, a thorough consideration of the conversion from ppm (mole fraction) to per meg (Delta O2/N2 notation) is necessary which we do in this appendix.

Following equation 1 in Thojima et al., 2000, the per meg to ppm conversion has a slope of 6.04 if a change only in oxygen is applied as seen in table A2. It changes slightly to 6.11 per meg per ppm, when we talk about nitrogen changes only, or to a slope zero (horizontal line) when talking about any other changes of air components excluding oxygen and nitrogen. The fact that our supplementary plot shows slopes of 5.78 (for the first five standards) or 6.08 per meg per ppm (for all standards except ST-7) is due to a mixed influence dilution effects. The lower slope of 5.78 per meg per ppm documents particularly the influence of the CO2 dilution effect.

$$\delta\left(\frac{O_2}{N_2}\right)(per\ meg) = \left(\frac{(\frac{O_2}{N_2})_{sample}}{(\frac{O_2}{N_2})_{reference}} - 1\right) \cdot 10^6 \quad (1)$$

Note that under the assumption the atmospheric N2 content is constant (i.e. N2sample equals N2reference), we convert relative changes in oxygen given in per meg following equation 1 to oxygen changes in parts per million (equivalent to micromol/mol) by multiplying by the O2 mole fraction (O2reference) expressed as 209500 ppm. (the O2 mole fraction of atmospheric air) (Machta and Hughes, 1970). Hence 1 ppm corresponds approximately to 4.8 per meg, or 1 per meg to 1/4.8 $(209500/10^6)$ ppm.

This is used in our approach since the Picarro instrument gives us an O2 mole fraction which requires to be converted to an O2/N2 ratio. Since no information about N2 is available one assumes a constant value, i.e. N2 of the standard. Therefore, eq. 1 in the manuscript reduces to $(O_{2,SA}/O_{2,ST}-1)*10^6$ or $\Delta O_2/O_{2,ST}*10^6$. The value obtained is an estimated $dO2_{,norm}/N2_{,base}$ ratio, which indeed does not need to correspond to the true $dO2_{,norm}/N2_{,norm}$. The effect of water dilution (amount of water vapor is measured by the Picarro 2207 instrument) is taken into account as described in the manuscript. Yet any other dilution effect is not considered except if additional information is available, e.g. CO2 mole fraction measurements. Indeed this dilution effects can be significant and are displayed in the following table A2.

Table A1: Different dilution scenarios on their effects on air-like compositions

Mole fraction	base	original	normalized	original	normalized	original	normalized	original	normalized
N2, ppm	**780809**	780809	780801.192	780809	780801.192	780809	780801.192	780819	780811.192
O2, ppm	209451	209451	209448.906	209451	209448.906	209461	209458.905	209451	209448.906
Ar, ppm	9340	9340	9339.9066	9350	9349.9065	9340	9339.9066	9340	9339.9066
CO2, ppm	400	410	409.9959	400	399.996	400	399.996	400	399.996
Total	1000000	1000010	1000000	1000010	1000000	1000010	1000000	1000010	1000000
	base	original	normalized	original	normalized	original	normalized	original	normalized
Change		original	apparent	original	apparent	original	apparent	original	apparent
DCO2, ppm		10	9.9959	0	-0.0040	0	-0.0040	0	-0.0040
DAr, ppm		0	-0.0934	10	9.9065	0	-0.0934	0	-0.0934
DO2, ppm		0	-2.0945	0	-2.0945	10	7.9054	0	-2.0945
DN2, ppm		0	-7.8080	0	-7.8080	0	-7.8080	10	2.1919

This will lead to the following changes for oxygen, the true and estimated (when N2 is not measured) dO2/N2 ratios and the difference in these dO2/N2 values.

Table A2: Mole fraction to delta conversion for air-like gas compositions according to different scenarios

Change in ppm		DO2 apparent (change + dilution effect)	$dO2_{,norm}/N2_{,norm}$ (per meg) $(dO2_{,norm}/N2_{,norm}/DO2$ in per meg/ppm) (true)	$dO2_{,norm}/N2_{,base}$ (per meg) $(dO2_{,norm}/N2_{,base}/DO2$ in per meg/ppm) (estimated)	Difference in dO2/N2 (true − estimated) in per meg
DCO2 only	10	-2.0945	0 (0)	-10 (4.77)	10
DAr only	10	-2.0945	0 (0)	-10 (4.77)	10
DO2 only	10	7.9054	47.74 (6.04)	37.74 (4.77)	10
DN2 only	10	-2.0946	-12.81 (6.11)	-10 (4.77)	-2.81

$dO_{2,norm}/N_{2,norm}$: calculated (eg Thojima et al., 2000) or measured for instance by mass spectrometry; $dO_{2,norm}/N_{2,base}$: use fixed conversion factor of 4.77 per meg / ppm based on measured O2 mole fraction (ppm) for instance by Picarro 2207.

Incorrectly assumed N2, Ar, CO2 or any additional gas component lead to changes in the estimated $dO2/N2_{,est}$ values as stated in the table A2. For example a 10 ppm increase in CO2 leads to an incorrect value of -10 per meg in $dO_{2,norm}/N_{2,base}$ compared to the true $dO_{2,norm}/N_{2,norm}$ value. This is

simply the dilution effect that the increased CO2 mole fraction has on the correspondingly measured O2 mole fraction (Table A1) (dilution in oxygen corresponds to the percentage-wise assignment of the excess CO2 in ppm to oxygen, i.e. -10 ppm x oxygen mole fraction = 2.0945, if O2 mole fraction corresponds to 0.20945). As you can see from table A1, addition of N2 of 10 ppm leads to a reduced and opposite effect for the difference in dO2/N2 (true – estimated) because the dilution effect on O2 is not able to compensate the change from the increase in nitrogen, therefore it scales with -10 ppm x (oxygen mole fraction/nitrogen mole fraction). This also tells us that the difference in the Delta values (true – est) scales with the O2/N2 ratio present in the sample. Therefore, best results are obtained when the calibration gases for which the gas composition is known equals closely the sample gas composition. In our case this is given – but can certainly be improved – since we are comparing natural air to air standard compositions. Yet, determinations of the standards that have been used in this study have a mole fraction range in N2 of -110 to +110 ppm for the ST-1 to ST-5, whereas ST-6 (+700 ppm) and ST-8 (-6200 ppm) are significantly off compared to our primary standard used for mass spectrometric determination. Therefore, special attention is required for the precise determination of standard gas composition and the control of the air sample composition by means of flask measurements in order to detect potential fractionation effects during air intake.