

Second reply to the Editor's comments

We would like to thank the Editor for his constructive comments which we have addressed below. We keep the editor's comments in red font and our replies in black font.

Dear authors,

Thank you for having addressed all different requests in your revised version of your manuscript.

Please find below a list of minor remarks. I also would like to ask you to include an equation that gives your measurand (O_2/N_2 or $p(O_2)/p$) as a function of measured quantities and calibration gases. This is crucial to evaluate the influence of different parameters on the overall measurement uncertainty and it also avoids misconceptions due to a purely "textual" explication.

Minor comments

L 34 : exponent for year.

Now corrected as yr^{-1}

L 35 : Suggestion : Write "Atmospheric O_2 is commonly expressed in units of per meg due to its small variability with respect to a large background, where ..."

This phrase is now re-written as:

"Atmospheric O_2 is commonly expressed in units of per meg due to its small variability with respect to a large background, where.."

L 42 - 43: I don't think that one can understand the phrase "Note that we convert per meg to parts per million equivalent by multiplying per meg by 0.209500 (the O_2 mole fraction of atmospheric air)." Did you eventually mean "Note that we convert delta (O_2/N_2) values (in per meg) to mole fractions (in ppm) using the conversion factor 0.209500 (the O_2 mole fraction of atmospheric air)." ? This is misleading. If I have delta = 0 per meg using the atmospheric ratio as a standard, I should have a mixing ratio of 0.209500 ppm. If I follow your description and multiply 0 by 0.209500, I get 0. It is preferable that you give an equation that unambiguously converts between the (dry) air mixing ratio and the delta values. The dry air mixing ratio clearly involves noble gases, CO_2 and other minor components, whereas delta (O_2/N_2) does not ... I don't see how one can easily convert by a fixed number.

Regarding the conversion or proportionality between per meg and ppm levels, please have a look at either of the following Webpages.

Regarding zero per meg: This means that the sample corresponds to the standard ratio and since N_2 is constant in the atmosphere (except changes due to seasonal temperature changes of the ocean), that the O_2 of the sample corresponds to the O_2 of the standard. Therefore, no deviation in O_2 which corresponds indeed to zero ppm change.

See https://cdiac.ess-dive.lbl.gov/trends/oxygen/modern_records.html

The units of $\delta(O_2/N_2)$ are per meg; one per meg is one molecule of oxygen out of a million molecules of oxygen. Currently, this is roughly one molecule out of 4.77 million molecules of all gases in the atmosphere, not including water vapor molecules. Thus, 4.8 per meg is roughly one in a million molecules of dry air, or one part per million (ppm).

See <http://scrippsco2.ucsd.edu/faq>

How does one relate ppm and per meg units?

These units refer to different types of quantities, so the question needs to be sharpened before it can be clearly answered. Suppose a tree consumes exactly one molecule of CO₂ for each O₂ molecule produced by photosynthesis. The changes in atmospheric O₂ and CO₂ near the tree will then be inversely proportional. What is the proportionality factor in per meg/ppm?

The answer is $1/0.2095 = 4.8$ per meg/ppm, where 0.2095 is the O₂ mole fraction of air. This can be derived realizing that, because N₂ is constant, the relative change in the O₂/N₂ ratio is the same as the relative change in O₂ and calculating the relative change requires dividing by its abundance.

Therefore, the proportionality factor between per meg/ppm is

4.77 per meg = 1 ppm

1 per meg = $1 / 4.77$ ppm = 0.209500. The latter number corresponds to the O₂ mole fraction of air.

Actually, from eq. 1 you can easily see the proportionality if N₂ is assumed to stay constant (fair assumption see above) and further write O₂ of the sample as O₂ of standard plus DO₂. Resolving to DO₂ yields the mentioned proportionality between per meg and ppm.

Also, please provide a reference for your value of 0.209500.

We have now provided the reference Machta and Hughes, 1970.

L 104: measurement wavelength -> wavelength measurement.

Now corrected accordingly

P 10 : As mentioned previously, the AFGL codes 161 and 162 are used exactly twice in the whole document (apart from the definition). Given that a large part of AMT readership has no spectroscopic background it is preferable to use the more commonly known notation H₂O and HDO (or the IUPAC definition) or the words "normal and deuterated water" at these instances. It has to be admitted that the AFGL notation is very handy for all people used to it.

We have now removed the AFGL codes and used H₂O and HDO

L 151+: Phrase appears twice.

The repeated phrase is now removed

L 257 : I could not find the word "centration" in the dictionary. Do you mean "line centre position", perhaps ?

It is now corrected as “line center position”

L 260 : correct the exponent in wavenumber unit

It is now corrected as cm^{-1}

L 305 : Not clear what is meant by "the correlation may be due in part to the fitting procedure itself". You might need to explain a little bit more, even though a reference is given. I suspect (but I am not sure) that you speak about the choice of variables for the fitting function (rather than the procedure or the algorithm). For example, the width and the line area are necessarily correlated, whereas width and absorption depth are likely less correlated.

The editor’s comments are correct. We meant to say that covariance of the width and area could be part of the explanation for the observed correlation. We now replaced “due in part to the fitting procedure itself” with “due in part to covariance of the fitted amplitude (proportional to line area) and line width”.

L 267 : HITRAN gives a value $\gamma_{\text{H}_2\text{O}} = 0.0514 \text{ cm}^{-1}/\text{atm}$, which seems to come from semi-empirical calculations : <https://arxiv.org/abs/1906.01475> .

Please mention and check origin of that number.

We have now modified the paragraph from 265-272 as follows:

“From the linear fit one obtains a coefficient for collisional broadening of the Q13Q13 line by water vapor of $\gamma_{\text{water}} = 0.0442 \text{ cm}^{-1}/\text{atm}$ at 45 °C. Recently, parameters describing broadening of oxygen lines by water vapor, obtained by empirical modeling of selected experimental data, were added to the Hitran data base (Tan et al., In review). The new Hitran entries predict a value of $0.0486 \text{ cm}^{-1}/\text{atm}$ at 45 °C, which is in agreement with our measurement within the 5-10% uncertainty attributed by Hitran to the broadening parameter.”

L 311 : "because the O2/N2 and water concentration", add "ratio" after "O2/N2" and "the" before "water concentration"

It is now corrected and read as:

“.., because the O2/ N2 ratio and the water concentration affect the line width...”

L 329 : "normalizing absorption amplitudes to line widths does not provide any advantage". It is difficult to understand what is meant here. Could you please clarify further ? Do you mean normalising amplitudes by line widths ?

Yes, we mean normalizing amplitudes by line widths

We now replaced “to” with “by”

L 333 : Perhaps you should remove the word "Consequently" here. (As a reply to your comment on a similar and previous remark, please consider that the reader does not necessarily have Fig 1 at hand and in mind when comparing to the 16O2 absorption. Also, the noise level is not evident from that figure 1,

as residuals usually reflect systematic effects such as bias in the profile, fringes, etc. some of which might scale with the size of the absorption line).

We have now removed the word “Consequently”

L 381 : write "tau is the averaging time" and use the greek symbol instead of the word "Tau"

The sentence in bracket is now modified as follows:

(τ is the averaging time which is the abscissa of the Allan-Werle plot).

1 **High-precision atmospheric oxygen measurement comparisons between a newly built**
2 **CRDS analyzer and existing measurement techniques**

3
4 Tesfaye A. Berhanu^{1,2}, John Hoffnagle², Chris Rella², David Kimhak², Peter Nyfeler¹, Markus
5 Leuenberger¹

6 ¹*Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research,*
7 *University of Bern, Bern, Switzerland*

8 ²*Picarro Inc., 3105 Patrick Henry Drive, Santa Clara, CA, USA*

9

10 **Abstract**

11 Carbon dioxide and oxygen are tightly coupled in land-biospheres CO₂ - O₂ exchange
12 processes, while they are not coupled in oceanic exchange. For this reason, atmospheric
13 oxygen measurements can be used to constrain the global carbon cycle, especially oceanic
14 uptake. However, accurately quantifying the small (~1-100 ppm) variations in O₂ is
15 analytically challenging due to the very large atmospheric background which constitutes
16 about 20.9 % (~209500 ppm) of atmospheric air. Here we present a detailed description of the
17 analyzer and its operating principles as well as comprehensive laboratory and field studies for
18 a newly developed high-precision oxygen mixing ratio and isotopic composition analyzer
19 (Picarro G-2207) that is based on cavity ring-down spectroscopy (CRDS). From the
20 laboratory tests, we have calculated a short-term precision (standard error of one-minute O₂
21 mixing ratio measurements) of < 1 ppm for this analyzer based on measurements of eight
22 standard gases analyzed for two hours consecutively. In contrast to the currently existing
23 techniques, the instrument has an excellent long-term stability and therefore a calibration
24 every 12 hours is sufficient to get an overall uncertainty of < 5 ppm. Measurements of

25 ambient air were also conducted at the High-Altitude Research Station, Jungfraujoch and the
26 Beromünster tall tower in Switzerland. At both sites, we observed opposing and diurnally
27 varying CO₂ and O₂ profiles due to different processes such as combustion, photosynthesis
28 and respiration. Based on the combined measurements at Beromünster tower, we determined
29 height dependent O₂:CO₂ oxidation ratios varying between -0.98 to -1.60 , which increase
30 with the height of the tower inlet, possibly due to different source contribution such as natural
31 gas combustion with high oxidation ratio and biological processes which are at the lower end.

32 1. Introduction

33 Atmospheric oxygen comprises about 20.9 % of the global atmosphere and in the past decade
34 its concentration decreased at a rate of ~ 20 per meg yr⁻¹ (Keeling and Manning, 2014) mainly
35 associated with the increase in fossil fuel combustion. Measurements of atmospheric O₂ are
36 reported as the ratio to the N₂ concentration and expressed as δ(O₂/N₂) because the variations
37 in the concentrations of other atmospheric gases such as CO₂ can influence the O₂ partial
38 pressure while this ratio is insensitive to these changes in other gases. ~~Atmospheric These~~
39 ~~variations in atmospheric~~ O₂ is commonly expressed in units of per meg due to its small
40 ~~variations-variability~~ with respect to a large background, where

$$41 \quad \delta \left(\frac{O_2}{N_2} \right) (\text{per meg}) = \left(\frac{\left(\frac{O_2}{N_2} \right)_{\text{sample}}}{\left(\frac{O_2}{N_2} \right)_{\text{reference}}} - 1 \right) \cdot 10^6 \quad (1)$$

42 Note that we convert per meg to parts per million equivalent by multiplying per meg by
43 0.209500 (the O₂ mole fraction of atmospheric air) (Machta and Hughes, 1970).

44 In contrast to O₂, the global average atmospheric CO₂ mixing ratio increased to 405.0 ppm
45 averaged over 2017 since its preindustrial value of 280 ppm (Le Quéré et al., 2017). As the
46 variability of atmospheric oxygen is directly linked to the carbon cycle, both its short and
47 long-term observations can be used to better constrain the carbon cycle. For example, since

Formatted: Superscript

48 first suggested by Keeling and Shertz (1992) the long-term trends derived from concurrent
49 measurements of atmospheric CO₂ and O₂ have been widely used to quantify the partitioning
50 of atmospheric CO₂ between the land-biosphere and oceanic sinks (Battle et al., 2000; Goto et
51 al., 2017; Manning and Keeling, 2006; Valentino et al., 2008). This method hinges on the
52 linear coupling between CO₂ and O₂ with an oxidation ratio (OR, defined as the
53 stoichiometric ratio of exchange during various process such as photosynthesis and respiration
54 expressed using α) of 1.1 for the terrestrial biosphere photosynthesis-respiration processes
55 (α_b) and 1.4 for fossil fuel combustion (α_f) while they are decoupled for oceanic processes (α_o
56 = 0). Meanwhile, the short-term variability in atmospheric oxygen can be used to estimate
57 marine biological productivity and air-sea gas exchange (Keeling et al., 1998; Nevison et al.,
58 2012). However, the accuracy of these estimates is primarily linked to the accuracy and
59 precision of atmospheric O₂ measurements and the assumed ORs for the different processes
60 which are highly variable in contrast to atmospheric CO₂ that can be well measured within the
61 precision guidelines set by the Global Atmospheric Watch (GAW) (± 0.1 ppm for the
62 northern hemisphere).

63 Currently there are several, mostly custom built techniques that can measure
64 atmospheric O₂ variations as oxygen concentration based on interferometric, paramagnetic,
65 UV absorption and fuel cell technology (Keeling, 1988a; Manning et al., 1999; Stephens et
66 al., 2007) or as O₂/N₂ ratios to account for the large background effect using gas
67 chromatography with thermal conductivity detector (GC-TCD) or gas chromatography
68 coupled to mass spectrometry (GC-MS) (Bender et al., 1994; Tohjima, 2000). Despite the fact
69 that these techniques have been used for more than two decades, accurate quantification of
70 atmospheric oxygen variability remains challenging primarily because the small ppm-level
71 atmospheric oxygen signal rides on a $\sim 210,000$ ppm background, which places stringent

72 requirements on the precision and drift of the analysis methods especially for continuous
73 monitoring(note that the GAW recommendation for the measurement precision of O₂/N₂ is 2
74 per meg). The techniques listed above struggle to routinely achieve the necessary performance
75 for various reasons, including i) instability over time that requires frequent measurement
76 interruption for calibration, ii) measurement bias with ambient and sample temperature and/or
77 pressure, and/or iii) systematic errors in the measurement due to other atmospheric species.
78 Further, some techniques require the use of consumables and rely on high vacuum, which
79 complicates field deployment.

80 In this manuscript we describe a new high precision oxygen concentration and isotopic
81 composition analyzer by Picarro Inc., Santa Clara, USA (G-2207) based on CRDS
82 technology. Here, we will introduce the analyzer design principles in details, describe the
83 unique features of the analyzer and evaluate its performance based on various independent
84 laboratory and field tests by comparing it with currently existing techniques. Then, we will
85 present and interpret our observations based on field measurements. Finally, we will conclude
86 its overall performance and provide recommendations and possible improvements.

87 **2. Analyzer design principles**

88 The analyzer described here is derived from the Picarro G2000 series of CRDS
89 analyzers. The basic elements have been described elsewhere (Crosson, 2008; Martin et al.,
90 2016; Steig et al., 2014): briefly, the instrument is built around a high-finesse, traveling-wave
91 optical cavity, which is coupled to either of two single-frequency Distributed FeedBack-
92 stabilized semiconductor lasers. One cavity mirror is mounted on a piezoelectric translator
93 (PZT) to allow fine tuning of the cavity resonance frequencies. A semiconductor optical
94 amplifier between the laser sources and the cavity boosts the laser power and serves as a fast-
95 optical switch. The cavity body is constructed of invar and enclosed in a temperature

96 stabilized box ($T = 45^\circ \text{C}$, stabilized to approximately 0.01°C) for dimensional and
97 spectroscopic stability. A vacuum pump pulls the gas to be sampled through the cavity and a
98 proportional valve between the cavity and the pump maintains the sample pressure in the
99 cavity at a value of 340 hPa, with variations on the order of 1 Pa. The instrument has a
100 wavelength monitor, based upon measurements of interference fringes from a solid etalon,
101 which is used to control the laser wavelength by adjusting the laser temperature and current.
102 The wavelength monitor is a fiber-coupled device located between the laser and the cavity. A
103 fraction of the beam from the input fiber is collected using a beam splitter for the wavelength
104 measurement ~~wavelength~~ and the remaining power is collected in the output fiber. A high-
105 speed photodiode monitors the optical power emerging from the cavity. The instrument's data
106 acquisition system is used to sweep the laser frequency over the spectral feature to be
107 measured, modulates the laser output to initiate ring-downs, and fits the ring-down signal to
108 an exponential function to generate a spectrogram of optical loss versus laser frequency. For
109 this instrument the empty cavity ring-down time constant is about $39 \mu\text{s}$. Subsequent program
110 modules compare the measured loss spectrum to a spectral model, using non-linear least-
111 squares fitting (Press et al., 1986) to find the best-fit model parameters and thereby obtain a
112 quantitative measure of the absorption due to the target molecule, and finally apply a
113 calibration factor to the optical absorption to deduce the molecular concentration. When
114 operating in its normal gas analysis mode, the instrument acquires about 200-300 ring-downs
115 per second and achieves a noise equivalent absorption of typically about $10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$,
116 with some variation between instruments.

117 The primary goal when designing this analyzer was to measure the molecular oxygen
118 concentration with few-per-meg level precision and stability. In this context operational
119 stability is as important as signal-to-noise. Our experience has been that the most stable

120 operation of the analyzer is achieved when the optical phase length of the cavity is held as
121 nearly constant as possible. In this case the free spectral range (FSR, 0.0206 cm^{-1}) of the
122 temperature stabilized, invar ring-down cavity provides a better optical frequency standard
123 than the etalon-based wavelength monitor, which in turn allows more consistent
124 measurements of absorption line width and integrated absorption line intensity (Steig et al.,
125 2014). For a small, field-deployable instrument, it is not practical to stabilize the absolute
126 frequencies of the cavity modes to an optical frequency standard (Hodges et al., 2004) but the
127 oxygen lines themselves, under conditions of constant temperature and pressure, provide an
128 adequate frequency reference. The oxygen spectrum was also used to calibrate the FSR, by
129 comparing a wide (approximately 10 cm^{-1}) FSR-spaced spectrum with the Hitran database
130 (Rothman et al., 2013).

131 To determine molecular oxygen concentration, the analyzer measures absorption of the
132 Q13Q13 component of the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ band, at $7878.805547 \text{ cm}^{-1}$, according to the latest
133 edition of Hitran (Gordon et al., 2017). This is one of the strongest near-infrared lines of
134 oxygen, well separated from other oxygen lines, and reasonably free of spectral interference
135 from water, carbon dioxide, methane, and other constituents of clean air. The spectral model
136 for this line was developed using reference spectra of clean, dry, synthetic air that were
137 acquired with the same hardware as in the field-deployable analyzer, but with special-purpose
138 software that allows it to operate as a more general spectrometer.

139 Recently, considerable work has been done to advance the understanding of spectral
140 line shapes and to define functional representations that better describe the processes that
141 determine spectral line shapes than does the Voigt model (Hartmann et al., 2008; Tennyson et
142 al., 2014, Tran et al., 2019). Line shape studies have been published for the $1.27 \mu\text{m}$ band of
143 O_2 (Fleisher et al., 2015; Lamouroux et al., 2014), though not to our knowledge for the Q

144 branch. The apparatus used here is not capable of spectroscopic studies of comparable
145 precision; the absolute temperature and pressure monitoring and especially the frequency
146 metrology are far too crude for that purpose. Our goal is merely to define a simple model of
147 the Q13Q13 line that is adequate for least-squares retrievals of the O₂ absorption under the
148 limited range of conditions (stabilized temperature and pressure) that the operational analyzer
149 experiences in the field. The CRDS analyzers use the Galatry function (Varghese and Hanson,
150 1984), which is distinctly better than the Voigt and still easily and quickly evaluated for line
151 shape modeling. Ultimately, the usefulness of the spectral model is to be evaluated by the
152 precision and stability of the O₂ measurements when compared with established techniques.

153 ~~Ultimately, the usefulness of the spectral model is to be evaluated by the precision and~~
154 ~~stability of the O₂ measurements when compared with established techniques.~~For spectral
155 model development, this spectrometer has the drawback that the cavity FSR, is too large to
156 reveal much detail of the absorption line shape, even with the simplifying assumption of a
157 Galatry line shape. We therefore acquired a set of four interleaved spectra, with the PZT-
158 actuated mirror moved to offset the cavity modes of the individual FSR-spaced spectra by
159 one-fourth of an FSR. The precise offsets were determined from fits to the strong and well-
160 isolated O₂ lines in the spectra. From the consistency of the fitted line centers, we estimate
161 that the positioning of the interleaved spectra was accurate to approximately 10 MHz. The
162 spectrum of the Q13Q13 line acquired in this manner is shown in Figure 1, together with the
163 best-fit Galatry function. It stands out that the residuals are largely odd in detuning from the
164 line center: this shows the limitations of the Galatry model in this case, since the Galatry
165 function is purely even about the line center. The shape of the absorption line in this model is
166 specified by two dimensionless parameters: the collisional broadening parameter

167
$$\gamma = \gamma / \sigma_D \quad (2)$$

Formatted: Font: Times New Roman, 12 pt

168 and the collisional narrowing parameter

$$169 \quad z = \beta / \sigma_D \quad (3)$$

170 where γ is the frequency of broadening transitions, β is the velocity change collision rate, and

171 σ_D is the 1/e Doppler half-width of the transition, given by

$$172 \quad \sigma_D = \nu_0(2k_B T/Mc^2)^{1/2} \quad (4)$$

173 where ν_0 is the transition frequency, k_B is Boltzmann's constant ($J \cdot K^{-1}$), T is the sample

174 temperature (K), M is the molecular mass (amu), and c is the speed of light (m/s). Figure 2

175 shows the values of y and z obtained from spectra acquired in the same way as Figure 1, as a

176 function of cavity pressure. The values depend linearly on pressure, as expected from the

177 Galatry model, but the unconstrained linear fits do not go precisely through the origin. It is

178 not clear whether this represents a breakdown of the Galatry model or simply reflects the

179 limited quality of the data set. The slope of y can be converted to an air-broadened collisional

180 width $\gamma_{air} = 0.0442 \text{ cm}^{-1}/\text{atm}$, which agrees with the Hitran value of $0.0460 \text{ cm}^{-1}/\text{atm}$ (Gordon

181 et al., 2016) to within the uncertainty estimate stated by Hitran (uncertainty code 4 for γ_{air}

182 corresponding to 10% --20% relative uncertainty). The slope of z can be interpreted in terms of

183 the optical diffusion coefficient (Fleisher et al., 2015), yielding $D = 0.285 \text{ cm}^2 \text{ s}^{-1}$, compared

184 to the literature value of $0.233 \text{ cm}^2 \text{ s}^{-1}$ for O_2 in air at $45 \text{ }^\circ\text{C}$ (Marrero and Mason, 1972).

185 Although the anticipated use of the analyzer is for ambient air samples having a very small

186 range of O_2 concentrations, we did investigate the variation of the line shape in binary

187 mixtures of O_2 and N_2 shown in Figure 3. The error bars are taken from the output of the

188 Levenberg-Marquardt fitting routine (Press et al., 1992). The dependence of the collisional

189 broadening parameter z on O_2 mole fraction was considered too small to be significant, but

190 the variation in y was used in the subsequent analysis of the air samples. Note that Wójtcwicz

191 et al. (Wójtewicz et al., 2014) also found collisional broadening coefficients for nitrogen to be
192 slightly larger than for oxygen in measurements of one O₂ line in the B-band.

193 The primary goal in designing the analyzer was to achieve high enough precision to
194 make meaningful measurements of O₂ in clean atmospheric samples. Although the current
195 best practice for such high-precision measurements is to work with dried samples, we decided
196 to include high precision measurements of water vapor. There were two reasons for this
197 decision: one is to serve as a monitor for residual water vapor, which is difficult to remove
198 completely from the ring-down cavity and associated sample handling hardware, and the
199 second and more ambitious reason was to see how well the effect of water vapor could be
200 corrected for measurements of undried ambient air. While it was considered unlikely that
201 measurements of undried air could compete in accuracy with those of dried air, it might be
202 possible to correct for water vapor well enough to enable useful measurements in some
203 circumstances without the expense and inconvenience of drying the sample. For this purpose,
204 a second laser was added, which probes the 7_{1,6} → 8_{4,5} component of the 2ν₃ band of water
205 vapor, at of 7816.75210 cm⁻¹ (Gordon et al., 2017). The Galatry model was used to fit spectra
206 of synthetic air humidified to various levels of water vapor concentration. These fits also
207 included two other nearby, very weak water lines, with intensities less than 1% of the strong
208 transition, in order that their absorption should not perturb the line shape of the main
209 transition. Results for the shape of the 7816.75210 cm⁻¹ line are shown in Figure 4. At the
210 level that we can measure, only the y-parameter has a meaningful variation with water
211 concentration. From the linear fit one obtains a pressure broadening coefficient for air, $\gamma_{\text{air}} =$
212 0.0752 cm⁻¹/atm, in reasonable agreement with the Hitran value $\gamma_{\text{air}} = 0.0787$ cm⁻¹/atm
213 (Gordon et al., 2017), and a self-broadening coefficient $\gamma_{\text{self}} = 0.413$ cm⁻¹/atm, to be compared

214 with the Hitran value $\gamma_{\text{self}} = 0.366 \text{ cm}^{-1}/\text{atm}$. Since the uncertainty estimate for the Hitran
215 values is 10 % to 20 %, this level of agreement seems reasonable.

216 We also looked at absorption from water near the Q13Q13 absorption line of O₂.
217 These spectra were measured in a background of pure nitrogen to reveal the very weak lines
218 interfering with the O₂ measurement. Without the strong O₂ lines, it was impossible to
219 interleave FSR-spaced spectra, so in this case the frequency axis comes from the analyzer's
220 wavelength monitor. The upper panel of Figure 5 shows the spectrum of saturated water vapor
221 in nitrogen, together with a fit to a Voigt model of the molecular lines. The measurement was
222 made at a pressure of 340 hPa and temperature of 45° C. The main features are the Q13Q13 line
223 from trace contamination of oxygen in the sample and several lines that arise from normal water
224 (¹H₂¹⁶O, ~~AFGL code 161~~) and deuterated water (¹H²H¹⁶O, ~~AFGL code 162~~, also abbreviated HDO). The
225 lower panel of Figure 5 shows the lines tabulated in Hitran. Immediately after the data in
226 Figure 5 were acquired, measurements were also made at 7816.85210 cm⁻¹, to establish the
227 relationship between the absorption strengths in the two spectral regions. The relative
228 intensities of the ~~+61-H₂O~~ and ~~+62-HDO~~ lines change with variations in the isotopic
229 composition of the water, but fortunately the direct interference with the oxygen Q13Q13
230 lines comes entirely from the ~~+61-H₂O~~ isotopologue, with the strongest ~~+62-HDO~~ line being
231 separated by approximately 8 line widths (FWHM) from the Q13Q13 line. Hitran simulations
232 for molecules other than water that are expected to be present in clean, ambient air indicate
233 that direct interference with the Q13Q13 line should be negligible at the level of precision
234 considered here. In the case of CO₂, the dilution of oxygen due to 400 ppm of CO₂ is
235 significant, and larger than any direct spectral interference.

236 Finally, we investigated the influence of water vapor on the shape of the O₂ Q13Q13
237 line. Switching between the two lasers sources, we acquired FSR-spaced spectra of

Formatted: Subscript

Formatted: Subscript

238 humidified synthetic air, alternately covering the 7817 cm⁻¹ and 7878 cm⁻¹ regions. Individual
239 spectra were acquired in less than 2 s, so changes in water vapor concentration between
240 spectra were small. These spectra, with frequency resolution of 0.0206 cm⁻¹, were analyzed by
241 nonlinear least-squares fitting with the following spectral models: the 7817 cm⁻¹ spectra were
242 modeled as the sum of an empty-cavity baseline having an adjustable offset level and slope
243 and the water spectrum is modeled with three peaks: one strong line and two weak perturbers.
244 The molecular absorption of the main peak was expressed as an adjustable amplitude, A_w ,
245 multiplying a dimensionless, area-normalized Galatry function (Varghese and Hanson, 1984).
246 The weak perturbers were modeled by Voigt profiles with amplitudes and line widths that
247 were constrained to be in fixed proportions to the strong line, and therefore added no new
248 degrees of freedom to the fitting procedure. Since the amplitude A_w multiplies an area-
249 normalized shape function, it is essentially equivalent to the area of the absorption line, to the
250 extent that the Galatry model provides a valid description of the line shape. The Doppler
251 width of the Galatry function was fixed based on the measured cell temperature, the y-
252 parameter was allowed to vary, and the z-parameter was constrained to be proportional to y,
253 based on measurements summarized in Figure 2. In addition, the center frequency of the
254 Galatry function was adjusted to match the data set, giving a total of five free parameters for
255 this fit. The 7878 cm⁻¹ spectra were modeled with an adjustable baseline offset and slope and
256 molecular absorption amplitude, A_{O_2} , describing the Q13Q13 O₂ line. Here, too, the y-
257 parameter and ~~centration-line center position~~ of the O₂ lines were allowed to adjust, and the z-
258 parameter was constrained to be proportional to y. The weak water lines interfering with
259 oxygen absorption were included in the model, but with no additional free parameters; rather
260 the amplitudes were preset based on the measured water absorption at 7817 cm⁻¹ and the
261 previously determined amplitude relationships between the water lines. This procedure does

Formatted: Superscript

262 not account for variations in HDO abundance, which may introduce some systematic error
263 into the water vapor correction for samples of unusual isotopic composition, but it should
264 accurately model the most important lines that interfere with the oxygen measurement.
265 Collisional broadening of the Q13Q13 O₂ line by water vapor is shown in Figure 6. From the
266 linear fit one obtains a coefficient for collisional broadening of the Q13Q13 line by water
267 vapor of $\gamma_{\text{water}} = 0.0442 \text{ cm}^{-1}/\text{atm}$ at 45 °C. ~~We are not aware of previous measurements of~~
268 ~~this quantity. Recently, parameters describing broadening of oxygen lines by water vapor,~~
269 ~~obtained by empirical modeling of selected experimental data, were added to the Hitran data~~
270 ~~base (Tan et al., In review). The new Hitran entries predict a value of 0.0486 cm⁻¹/atm at~~
271 ~~45 °C, which is in agreement with our measurement within the 5-10% uncertainty attributed~~
272 ~~by Hitran to the broadening parameter.~~

273 The alternating measurements at 7817 cm⁻¹ and 7878 cm⁻¹ also calibrated the
274 relationship between water mole fraction and the absorption at 7817 cm⁻¹, using a dilution
275 analysis described by Filges et al. (2018), who showed that the results obtained this way agree
276 well with water vapor fractions measured with a conventional hygrometer. Figure 7 shows the
277 measured amplitudes of the water and oxygen lines for samples of variable humidity. Since
278 the air came from a tank of constant composition, the oxygen concentration changes due to
279 dilution of oxygen when water is added. Assuming that this is the sole cause of the change in
280 measured absorption, since the line shapes were being constantly adjusted to account for
281 changes in collisional broadening, it is straightforward to deduce the relation between the
282 water fraction and the absorption amplitude. This calibration was used to generate the water
283 fraction axes in Figures 4 and 6. We note that we did not take particular care to control or
284 measure the quantity of dissolved gases, especially oxygen and carbon dioxide, in the water
285 used for this experiment. While these gases would not significantly affect the water

286 calibration, they may affect the water vapor correction of the oxygen measurement at the ppm
287 level. More work needs to be done to investigate the water vapor correction of the oxygen
288 measurement.

289 The observations described above were used to design a method to measure oxygen
290 concentration in ambient air. Gas from the inlet to the analyzer is drawn through the cavity at
291 a rate of about 100 sccm (standard cubic centimeter per minute) and the conditions in the
292 cavity are held stable at 340 hPa and 45°C. In its analysis mode the analyzer alternately
293 measures ring-downs in the 7817 cm⁻¹ and 7878 cm⁻¹ regions. At 7878 cm⁻¹ measurements are
294 made at 11 different frequencies, spaced by one FSR of the cavity and centered at the peak of
295 the Q13Q13 line. Multiple ring-down measurements are made to improve the precision of the
296 loss determination, with a total of 305 ring-downs allocated to one spectrum. In the 7817 cm⁻¹
297 region measurements are also made at 11 distinct frequencies at FSR spacings. Only 35 ring-
298 downs are allocated to this spectral region, since the measurement of O₂ is much more
299 important than water vapor. The data sets are analysed using a Levenberg-Marquardt fitting
300 routine, which adjusts five free parameters in each region to find the best agreement to a
301 spectral model based on Galatry line shapes, as described above. One of the outputs of the
302 7878 cm⁻¹ fit is the frequency offset of the FSR grid from the center of the Q13Q13 line. This
303 information is used to adjust the position of the PZT actuated mirror to keep the
304 measurements centered on the line, effectively stabilizing the optical path length of the cavity
305 to the frequency of the O₂ line. The reported water fraction is obtained by multiplying the
306 fitted amplitude of the water line by a calibration constant derived from the dilution
307 experiment as explained above. For the O₂ fraction a slightly more complicated procedure is
308 followed. It was observed that the least-squares fitting of the data gives highly correlated
309 results for the amplitude of the absorption line and the line width parameter γ . The correlation

310 may be due in part to ~~the fitting procedure itself~~covariance of the fitted amplitude
311 (proportional to line area) and line width (Press et al., 1992) and it may also have a
312 contribution from pressure variations that the pressure sensor is unable to detect. The ratio
313 A_{O_2}/y can be determined from the fit much more precisely than A_{O_2} alone and so gives a more
314 sensitive measurement of molecular absorption. It also has the advantage of being
315 independent of sample pressure, to the extent that the Galatry model applies (Figure 2).
316 However, using the ratio A_{O_2}/y as a metric for absorption adds more complications if
317 measurements are to be made over a range of O_2 and water concentrations, because the O_2/N_2
318 ratio and the water concentration affect the line width independently of pressure and O_2
319 concentration alone. To minimize systematic errors due to these broadening effects, we define
320 a nominal y -parameter based on the measured amplitudes of the O_2 and water lines and the
321 line broadening dependences shown in Figures 3 and 4. The measured ratio A_{O_2}/y is
322 normalized by the nominal y to obtain a quantity that is ideally independent of pressure and
323 water concentration, and this is the quantity that is multiplied by a calibration constant to give
324 the reported O_2 fraction. In addition, a dry mole fraction is reported for O_2 , defined as the
325 directly measured mole fraction corrected for water dilution.

326 The main goal in developing this instrument was to make high precision
327 measurements of O_2 mole fraction, based on absorption by the dominant $^{16}O_2$ isotopologue.
328 The absorption lines of the rarer isotopologues are also present nearby, so a mode of operation
329 was included in which one laser is scanned over neighboring lines of $^{16}O_2$ and $^{16}O^{18}O$ and the
330 ratio of amplitudes is used to derive an isotopic ratio, reported in the usual delta notation. In
331 this case the operating pressure was reduced to 160 hPa to improve the resolution of the
332 nearby lines. The lines measured were the Q3Q3 line of $^{16}O_2$, at $7882.18670\text{ cm}^{-1}$, and the
333 Q9Q9 line of $^{16}O^{18}O$, at $7882.050155\text{ cm}^{-1}$. The measurement procedure is very much like

334 that for the O₂ fraction measurement, so it will not be described in detail, only the main
335 differences will be noted. One is that in determining an isotopic ratio, normalizing absorption
336 amplitudes ~~to~~ by line widths does not provide any advantage, instead we simply take the ratio
337 of amplitudes to compute delta. Although the Q9Q9 line and its neighbor Q8Q8 are the
338 strongest ones in this band, absorption by ¹⁶O¹⁸O is still very weak, only about 5x10⁻⁹ cm⁻¹ at
339 the line center under the conditions we used. ~~Consequently,~~ ~~†~~The signal-to-noise that can be
340 achieved with this analyzer is not adequate to determine both the amplitude and the width of
341 the ¹⁶O¹⁸O line with useful precision, so in the fitting step the y-parameter of the ¹⁶O¹⁸O line
342 is constrained to be a constant factor times the fitted y-parameter for the ¹⁶O₂ line.
343 Additionally, because of the weakness of the rare isotopologue absorption, the majority of
344 ring-downs in each spectrum is devoted to measuring ¹⁶O¹⁸O i.e. 232 ring-downs in each
345 spectrum versus only 40 for ¹⁶O₂. This implies that the mole fraction measurement in the
346 isotopic mode is much less precise than when the analyzer measures the Q13Q13 line alone.

347 **3. Results and Discussions**

348 **3.1. Laboratory tests at Picarro, Santa Clara**

349 3.1.1. Temperature and pressure sensitivity

350 One set of tests was done to determine how well the goal was met of minimizing the
351 susceptibility of the concentration measurements to noise or drift of the sample temperature
352 and pressure. For these tests the analyzer sampled dry synthetic air from a tank and the
353 temperature and pressure setpoints of the cavity were adjusted upward and downward from
354 the nominal values, to obtain an estimate of the differential response. We express the
355 sensitivity to experimental conditions in relative form, that is the derivative with respect to
356 temperature or pressure divided by the signal under nominal conditions.

357 From these experiments, we determined a temperature sensitivity of $-2.1 \times 10^{-4} \text{ K}^{-1}$ and
358 a pressure sensitivity of $+9.8 \times 10^{-6} \text{ hPa}^{-1}$. The temperature sensitivity is somewhat larger than
359 expected based on a calculation using Hitran data to estimate the temperature dependences of
360 all the quantities that go into the measured absorption of the Q13Q13 line. The pressure
361 sensitivity is strikingly small, indicating a good cancelation of the pressure dependence of
362 absorption amplitude and line width. Both temperature and pressure sensitivities are small
363 enough to have a negligible effect on short-term precision of measurements made with the
364 stabilized ring-down cavity, though long-term drifts in the sensors are always a matter of
365 concern.

366 3.1.2. Measurement precision and drift

367 Measurement precision was evaluated by analyzing synthetic air containing nominal
368 atmospheric concentrations of CO_2 and CH_4 from an aluminum Luxfer cylinder over a period
369 of several days. The tank, oriented horizontally and thermally insulated (though not
370 controlled), was connected directly to the instrument (S/N TADS2001) with a 2-stage
371 pressure regulator and stainless-steel tubing with an additional orifice to about 55 sccm. For
372 the isotopic mode of operation, the precision of the measurement was also tested by making
373 repeated measurements from a tank of clean, dry synthetic air.

374 Figure 8 shows the time series of the precision test data, displaying the reported
375 oxygen concentration, the height of the oxygen absorption peak, the width of the oxygen
376 absorption peak and the ambient temperature. The residual error of the analyzer, although
377 small, is nevertheless significant given the stringent targets set forth by the WMO-GAW
378 program. Possible sources of error include: temperature drifts due to sensor drift or gradients;
379 pressure errors due to sensor drift; optical artifacts such as parasitic reflections, higher order

380 cavity mode excitation, and/or loss nonlinearity that can distort the reported oxygen spectrum.

381 More work is required to identify and eliminate these small drifts.

382 The Allan standard deviation of the reported O₂ fraction is shown in the Allan-Werle
383 plot in Figure 9. The ordinate on this plot is the square root of the Allan variance of reported
384 mole fraction, so 1 ppm in these units corresponds to about 5 per meg in the ratio of O₂/ N₂.
385 The precision of averaged measurements improves as $\tau^{-1/2}$ for approximately 5000 s and
386 reaches 1 ppm in less than 10 minutes and remains below 1 ppm for time scales on the order
387 of about 1 hour (~~τ_{ave}~~ is the averaging time which is the abscissa of the Allan-Werle plot).

388 Figure 10 shows the precision of $\delta(^{18}\text{O})$ (uncalibrated) derived from the ratio of lines
389 measured at 7882 cm⁻¹. Because of the weak signal from the ¹⁶O¹⁸O line, it is necessary to
390 average for more than 20 seconds or more to achieve 1‰ precision on the isotopic ratio. As
391 for the concentration measurement, averaging improves the measurement precision for time
392 scales up to about 1 hour.

393 3.2. Laboratory measurements at the University of Bern

394 3.2.1. Measurements of standard gases

395 The performance of the instrument was tested by analyzing eight standard gases with
396 precisely known CO₂ and O₂ compositions (Table 1) using the CRDS analyzer and comparing
397 it to parallel measurements with a paramagnetic oxygen sensor (PM1155 oxygen transducer,
398 Servomex Ltd, UK) embedded to a commercially available fuel cell oxygen analyzer
399 (OXZILLA II, Sable Systems International, USA) (Sturm et al., 2006) as well as with an
400 isotope ratio mass spectrometer (IRMS, Finnigan Delta^{Plus}XP). The design of the
401 measurement set-up is shown in Figure 11. Standard gases were directly connected to the
402 pressure controlling unit, and a multi-port valve (V2) was used to select among the standard
403 gases. Flow from each cylinder was adjusted to about 120 sccm which was eventually

404 directed to a selection valve (V1), allowing switching between ambient air and standard gases.
405 Flow towards and out of the fuel cell analyzer was controlled by the pressure controlling unit.
406 The O₂ mixing ratio of this incoming gas was first measured on the Paramagnetic O₂ sensor
407 and then directed towards a non-dispersive infrared analyzer (NDIR) (Li-7000, LICOR, USA)
408 for measuring CO₂ and H₂O. The outflow from this analyzer (100 sccm) returns to the
409 pressure controlling unit and was eventually divided between the CRDS analyzer (which uses
410 about 75-80 sccm) and the IRMS (~ 20 sccm) via a Tee-junction. Each cylinder was measured
411 for two hours in each system controlled by a LabView program.

412 First, we investigated the influence of this Tee-junction, which splits the gas flow
413 between the CRDS and the IRMS, on the measured O₂ values. Manning (2001) showed that
414 the fractionation of O₂ in the presence of a Tee-Junction is strongly dependent on the splitting
415 ratios as well as temperature and pressure gradients. Hence, we measured and compared the
416 O₂ mixing ratios of two standard gases (CA07045 and CA060943) in two cases: i) in the
417 presence of a Tee-junction with different CRDS to IRMS splitting ratios and ii) without a
418 Tee-junction so that all gas flow is directed towards the CRDS analyzer. The splitting ratios in
419 these test experiments vary from 1:1 to 1:100, and reversed to change the major flow direction
420 either to the CRDS or the IRMS. Note that the experimental condition in this manuscript is
421 with a 4:1 splitting ratio (i.e. ~ 80 sccm towards the CRDS analyzer and ~ 20 sccm towards
422 the IRMS).

423 In the cases of the smaller splitting ratios (1:1, 1:4 and 4:1), which are relevant for the
424 results presented in this study, only minor differences in the measured O₂ mixing ratios were
425 observed when compared to case ii (i.e. without a Tee-junction). For these two cylinders
426 measured, the average differences in these cases were about 0.5 ppm, calculated as the mean
427 of the differences in the raw O₂ measurements of the last 60 seconds. The negligible

428 fractionation can indeed be the result of smaller splitting ratios while strong influence is
429 usually expected in case of larger splitting ratios (Stephens et al., 2007). For higher splitting
430 ratios, the result seems inconclusive without any dependence on the ratios due to the strong
431 decline in the cylinder temperature (specifically at the pressure gauge) caused by higher flow
432 to achieve the higher splitting ratios (as high as 1:100). Hence, these tests need to be
433 conducted in a temperature-controlled condition and the results could not be discussed in this
434 manuscript.

435 Figure 12 shows the standard gas measurements for the seven cylinders with known
436 CO₂ and O₂ mixing ratios (Table 1) using both the CRDS and the Paramagnetic analyzers.
437 Standard eight, which has too high O₂, is not shown in the figure as the figure is zoomed-in to
438 better illustrate the change in O₂ for the remaining cylinders. While the first five cylinders
439 contain O₂ and CO₂ mole fractions comparable to ambient air values, standards 6 & 8 had
440 either very low or very high O₂, respectively. In addition, standards 6 and 7 have very low and
441 very high CO₂ mixing ratios. Note that due to its very high CO₂ content (~ 2700 ppm),
442 standard 7 was not measured on the IRMS and hence the O₂ mixing ratio is unknown. The
443 measured mixing ratios for the six standard gases measured with the two systems are in very
444 good agreement while cylinder 7 showed an opposing signal for the two analyzers compared
445 to standard 6 (Figure 12). While the Paramagnetic analyzer showed a higher O₂ mixing ratio,
446 the values from the CRDS analyzer are lower in O₂. This can be associated with the very high
447 CO₂ mixing ratio in standard 7, which leads to a strong dilution effect in the CRDS analyzer
448 as it does not include any correction function for dilution effect from CO₂. However, such
449 high CO₂ mixing ratios may not be that important for most atmospheric research. Yet, it
450 should be considered to include a parallel CO₂ mixing ratios measurement to the instrument

451 as it will further improve the accuracy. This would be especially important for biological or
452 physiological studies where a wide range of CO₂ and O₂ concentrations must be expected.

453 The measurement precision of the CRDS analyzer was calculated as the standard error
454 of the mean i.e. the standard deviation (1- σ) of the last 1-minute raw measurements divided
455 by the square root of the number of measurements (n = 60), and for all these cylinders the
456 values are usually between 0.5 ppm to 0.7 ppm. For parallel measurements of these cylinders
457 using a Paramagnetic analyzer, we obtained a precision of about 1 ppm, calculated exactly the
458 same way.

459 We also made a correlation plot to see which of the two instruments are in better
460 agreement with the assigned values based on IRMS measurements for the individual
461 cylinders. While similar correlation coefficients were observed for both analyzers, different
462 slopes were calculated (Fig. A.1). This is due to the fact that the IRMS measures the O₂ to N₂
463 ratio ($\delta(O_2/N_2)$) in per meg, while the CRDS and the Paramagnetic analyzers provide non-
464 calibrated O₂ mixing ratios in units of ppm and per meg, respectively. If we exclude the two
465 standard gases with the highest and lowest O₂ mixing ratios (standards 7 and 8) that are
466 subjected to strong dilution effects, both the slope and the r^2 values decrease from those
467 shown in Figure A.1. But this decrease is larger in the case of the Paramagnetic
468 measurements, implying a slightly better linearity of the CRDS analyzer.

469 3.2.2. Measurements of ambient air

470 Ambient air measurements were conducted from the roof top of our laboratory at the
471 University of Bern to evaluate the analyzer's performance under atmospheric variability.
472 Ambient air was continuously aspirated from the inlet at the roof of the building at a flow rate
473 of ~ 250 sccm which is then dried using a cooling trap kept at -90 °C towards the switching
474 valve (V1) and measured in similar way to the standard gases as explained above. The

475 measurement values obtained here were compared with the parallel measurements by the
476 Paramagnetic sensor to test the instruments stability and accuracy.

477 Figures 13 panels a & b show the 1-minute average ambient air measurements from the
478 rooftop inlet by the Paramagnetic and the CRDS analyzers at the beginning of the testing
479 period including standard gases measured every 12-hour. While the Paramagnetic analyzer
480 seems to be stable, the CRDS analyzer showed a strong drift for an extended period. This can
481 be due to unstable conditions in the CRDS measurement system as it started operating right
482 after it was unpacked. Hence, we looked into temperature inside the instrument chassis and
483 pressure records, which were stable within the manufacturer's recommended range during this
484 period. As the CRDS analyzer incorporates a water correction function, interference from this
485 species should be well accounted. Even comparing the analyzer's parallel water
486 measurements to water measurements by the NDIR system such a drift was not observed. It
487 should be noted that the two internal standard gases which were less frequently measured
488 (every 12 hours) during this period were also drifting following similar pattern. This implies
489 that the drift is associated with the analyzer. Interestingly, this pattern can be modeled using a
490 polynomial function which can then be used to correct for the observed drift in the ambient air
491 measurements. After applying a polynomial drift correction, we were able to fully accounted
492 for the observed drift. However, the manufacturer decided to further investigate possible
493 causes of this drift. After further improvements, we obtained the first commercial analyzer in
494 September 2017 and repeated the above tests (Figure 13 c & d). No such drift was observed
495 any more in the standard gases or in ambient air measurements.

496 We believe that the optical amplifier has caused the drift in the first system and not anymore
497 included in the design of the product which produced a significant amount of broadband light
498 that could fill the cavity (albeit with a low coupling coefficient), and would ring down with a

499 different (and generally much faster) time constant than the baseline loss of the cavity.
500 However, the ringdown time on the peak of the oxygen line is just 10 microseconds, such that
501 the broadband light might have distorted the single exponential decay of the central laser
502 frequency, leading to the observed drift in the oxygen signal. However, we were not able to
503 confirm this hypothesis.

504 3.2.3. Water correction test

505 Measurements of oxygen are reported as both wet ($O_{2, \text{raw}}$) and dry ($O_{2, \text{dry}}$) mole
506 fractions by the CRDS analyzer as it also measures water vapor in parallel at its water
507 absorption line (7817 cm^{-1}), and corrects for the dilution effect based on an inbuilt numerical
508 function:

$$509 \quad O_{2, \text{dry}} = \frac{O_{2, \text{raw}}}{1 - f_{\text{H}_2\text{O}}} \quad (5)$$

510 where $f_{\text{H}_2\text{O}}$ is the measured water mole fraction.

511 The efficiency of water correction by this function was assessed in two ways: i) by comparing
512 the water vapor content in standard air measured by this analyzer with similar measurements
513 by the NDIR analyzer and ii) by comparing the oxygen mixing ratios between non-dried
514 ambient air measured and corrected for water dilution by the CRDS analyzer with dried air
515 measured using a paramagnetic analyzer.

516 Figure 14 shows the water vapor content for standard gases measured continuously for
517 two days by the CRDS and the NDIR analyzers. Note that the two data sets are manually
518 fitted to each other as the measured water values by the NDIR analyzer are not calibrated.
519 Based on this plot, the two analyzers are in very good agreement although there are small
520 differences during very dry conditions (low water content).

521 Figure 15a shows the dried ambient air water measurements in both analyzers with
522 frequent spikes due to valve switching while measuring standard gases. In the second case,
523 where the water trap was by-passed and non-dried air was allowed to the CRDS analyzer
524 keeping the dried air flow to the NDIR (Figure 15b), a clear increase in the water
525 measurements in the CRDS analyzer can be observed. Here, it should be noted that there are
526 no spikes in the water measurements of the CRDS analyzers as there are no standard gas
527 measurements in between and the inlet is directly connected to the CRDS analyzer (Figure
528 11). Figures 15c & 15d show the difference in oxygen measurements of ambient air measured
529 in both analyzers in the two cases stated above (note that the CRDS uses its built-in water
530 correction function applying Eq. 5). The measurements of the Paramagnetic analyzer were
531 scaled to ppm units by applying the correlation equation obtained from the six standard gas
532 measurements of the two analyzers (Fig. A.1). Note that the CRDS measurements were
533 corrected for the observed drift using the polynomial fit to the two standard gas measurements
534 stated above.

535 In the first period of the measurement when both analyzers measured dried ambient
536 air, the absolute differences between the 1-minute averages measured over two days by the
537 two analyzers were mostly within 15 ppm (Figure 15c) and symmetrically distributed around
538 zero (Figure 15e). However, when wet air was admitted to the CRDS analyzer and the in-built
539 water correction was applied, a stronger variability was observed in the calculated differences
540 (Figure 15d). This implies stronger short term variability in the CRDS analyzer measurement
541 values (as nothing was changed for the Paramagnetic measurement system) when wet samples
542 were analyzed. The more negative values in the differences (Figure 15f) can also be
543 associated with overestimation of the O₂ mixing ratios by the CRDS originating from an

544 overestimated water correction. However, detailed evaluation of the analyzer's water
545 correction function is beyond the scope of this study.

546 **3.3. Field Measurements**

547 After a series of tests at University of Bern, we conducted multiple field measurements
548 at the High Altitude Research Station Jungfraujoch and the Beromünster tall tower sites in
549 Switzerland described below.

550 3.3.1. Tests at the High Altitude Research station Jungfraujoch

551 The High Alpine research station Jungfraujoch is located on the northern ridge of the
552 Swiss Alps (46° 33' N, 7° 59' E) at an elevation of 3580 m a.s.l. It is one of the global
553 atmospheric watch (GAW) stations well-equipped for measurements of numerous species and
554 aerosols. The site is above the planetary boundary layer most of the time due to its high
555 elevation (Henne et al., 2010; Zellweger et al., 2003). However, thermally uplifted air from
556 the surrounding valleys during hot summer days or polluted air from the heavily industrialized
557 northern Italy may reach at this site (Zellweger et al., 2003). The Division of Climate and
558 Environmental Physics at the University of Bern has been monitoring CO₂ and O₂ mixing
559 ratios at this site based on weekly flask sampling and continuous measurements since 2000
560 and 2004, respectively (Schibig et al., 2015). The CO₂ mixing ratio is measured using a
561 commercial NDIR analyzer (S710 UNOR, SICK MAIHAK) while O₂ is measured using the
562 Paramagnetic sensor (PM1155 oxygen transducer, Servomex Ltd, UK) and fuel cells (Max-
563 250, Maxtec, USA) installed inside a home-built controlling unit. Similar to the comparison
564 tests at the University of Bern, we have conducted parallel measurements between the CRDS
565 analyzer and the paramagnetic cell at this high altitude site during 03 – 14 February 2017. The
566 measurement of ambient air at the Jungfraujoch system is composed of sequential switching
567 between low span (LS) and high span (HS) calibration gases followed by a target gas (T)

568 measurement (once a day) to evaluate the overall system performance and finally a working
569 gas (WG) measurement before switching back to ambient air.

570 Figure 16 (top panel) shows the calibrated 1-minute averaged O₂ mixing ratios
571 measured at this high altitude site in comparison with the Paramagnetic oxygen analyzer
572 already available at the site. Despite the strong variability observed during the measurement
573 period of 10-days by both analyzers, a very good agreement was observed between them.

574 Figure 16 (bottom panel) shows the absolute difference of 1-minute averages in
575 atmospheric O₂ measured at Jungfrauoch between the two analyzers which are mostly within
576 ± 5 ppm range (but sometimes going as high as ± 10 ppm) without an offset. However, for
577 generally reported 10-minutes, half-hourly or hourly means these values correspond to < 1.5
578 ppm, < 1 ppm and < 0.65 ppm.

579 3.3.2. Tests at the Beromünster tall tower site

580 The Beromünster tower is located near the southern border of the Swiss Plateau, the
581 comparatively flat part of Switzerland between the Alps in the south and the Jura mountains
582 in the northwest (47° 11' 23" N, 8° 10' 32" E, 797 m a.s.l.), which is characterized by intense
583 agriculture and rather high population density. A detailed description of the tower
584 measurement system as well as a characterization of the site with respect to local
585 meteorological conditions, seasonal and diurnal variations of greenhouse gases, and regional
586 representativeness can be obtained from previous publications (Berhanu et al., 2016; Berhanu
587 et al., 2017; Oney et al., 2015; Satar et al., 2016). The tower is 217.5 m tall with access to five
588 sampling heights (12.5 m, 44.6 m, 71.5 m, 131.6 m, 212.5 m) for measuring CO, CO₂, CH₄
589 and H₂O using Cavity Ring Down Spectroscopy (Picarro Inc., G-2401). By sequentially
590 switching from the highest to the lowest level, mixing ratios of these trace gases were
591 recorded continuously for three minutes per height, but only the last 60 seconds were retained

592 for data analysis. The calibration procedure for ambient air includes measurements of
593 reference gases with high and low mixing ratios traceable to international standards (WMO-
594 X2007 for CO₂ and WMO-X2004 for CO and CH₄), as well as target gas and more frequent
595 working gas determinations to ensure the quality of the measurement system. From two years
596 of data a long-term reproducibility of 2.79 ppb, 0.05 ppm, and 0.29 ppb for CO, CO₂ and
597 CH₄, respectively was determined for this system (Berhanu et al., 2016).

598 Between 15.02.2017 and 02.03.2017, we have connected the new CRDS oxygen
599 analyzer in series with the CO₂ analyzer (Picarro G-2401) and measured the O₂ mixing ratios
600 at the corresponding heights. Similar to the CO₂ measurements, O₂ was also measured for
601 three minutes at each height. During this period, we have evaluated the two features (isotopic
602 mode and concentration mode) of the CRDS analyzer. In the isotopic mode, the CRDS
603 measures the $\delta^{18}\text{O}$ values as well as the O₂ concentration while in concentration mode only
604 the latter was measured.

605 During the tests conducted at this tower site, we first evaluated the two operational
606 modes (concentration vs isotopic modes) of the CRDS analyzer. Ambient air measurements
607 on isotopic mode over a 4-days period showed a strong variability in the measured oxygen
608 mixing ratios and it was not possible to distinguish the variability in the O₂ mixing ratios
609 among the five height levels. The calculated 1-minute standard error for ambient air
610 measurements was as high as 10 ppm while a standard error of less than 1 ppm was
611 determined from similar measurements in the concentration mode. Additionally, comparing
612 the O₂ values between the two modes, frequent short time variation in ambient air O₂ (~ 200
613 ppm) was observed in the isotope mode measurements while the variation in the concentration
614 mode is significantly smaller (~ 30 ppm). This precision degradation is due to the weaker ¹⁶O
615 oxygen line used for the isotopic mode, and the fact that far more ring-downs are collected on

616 the rare isotopologue in isotopic mode Hence, we have conducted the remaining test
617 measurements in concentration mode.

618 As this tower has five sampling height levels, we first followed three minutes of
619 switching per inlet level, which enables four measurements per hour at a given level.
620 However, we noticed hardly any difference among the different levels due to strong short
621 term variability in O₂ mixing ratios between the consecutive heights. Hence, we switched to a
622 longer sampling period of six-minutes per height. Figure 17 shows the diurnal CO₂ and O₂
623 variations at the lowest (12 m) and highest (212.5 m) sampling heights of the tower. These
624 two heights were selected simply to better illustrate the difference in the mixing ratios. The
625 CO₂ mixing ratios on the top panel show higher values at the 12 m inlet than the highest level
626 most of the day due to its closeness to sources except during the afternoon (11:00 - 17:00
627 UTC) when both levels show similar but decreasing CO₂ mixing ratios. This is due to
628 presence of a well-mixed planetary boundary layer (PBL) (Satar et al., 2016). The lag in CO₂
629 peak between the two height levels by about two hours indicates the duration for uniform
630 vertical mixing along the tower during winter 2017. The opposite variability patterns are also
631 clearly visible in the O₂ mixing ratios shown in the lower panel with a clear distinction
632 between the two height levels during early in the morning and in the evening while similar O₂
633 values were observed in the afternoon. These opposing profiles are expected as CO₂ and O₂
634 are linearly coupled with a mean oxidation ratio of -1.1 ± 0.05 (Severinghaus, 1995) for land-
635 biospheric processes (photosynthesis and respiration) and -1.44 ± 0.03 for fossil fuel burning
636 (Keeling, 1988b).

637 Table 2 shows the oxidation ratios derived as the slopes of the linear regression
638 between CO₂ and O₂ mixing ratios at the different height levels measured on 25 February
639 2017. Accordingly, height dependent slopes were observed with a slope of -0.98 ± 0.06 at the

640 lowest level, close to the biological processes induced slope but slightly lower than its mean
641 value. For the highest level, we calculated a slope of -1.60 ± 0.07 a value close to fossil fuel
642 combustion oxidation ratio. Note that depending on fossil fuel type the oxidation ratio can
643 range between -1.17 and -1.95 for coal and natural gas, respectively (Keeling, 1988b). While
644 the slopes derived for the two other levels (44.6 m and 131.6 m) show similar values between
645 the highest and lowest height levels, possibly from mixed sources, the middle level showed a
646 slightly higher slope than these two levels but still in the large range between the lowest and
647 highest inlet heights.

648 3.4. Evaluation of the $\delta^{18}\text{O}$ measurements

649 To further evaluate the analyzer's performance in measuring stable oxygen isotopes,
650 we conducted ambient air isotopic composition measurements as well as analyzed a standard
651 gas without CO_2 which has a known $\delta^{18}\text{O}$ value. The choice of this CO_2 -free air standard gas
652 is twofold: one it has a known $\delta^{18}\text{O}$ value and second as it has no interference from possible
653 CO_2 absorption band overlap. For this test three 0.5 L glass flasks were preconditioned and
654 filled with this standard gas to ambient pressure. These flasks were attached before or after
655 the water trap (Fig. 11) and measured similar to ambient air measurements. These
656 measurements were then compared with $\delta(^{34}\text{O}/^{32}\text{O})$ values obtained by parallel measurements
657 using our IRMS.

658 Figure 18 shows the $\delta^{18}\text{O}$ values of ambient air from the roof top with three
659 consecutive measurements of glass flasks filled with CO_2 -free air in-between followed by a
660 fourth flask filled with breath air. An excellent agreement was observed for measurements
661 from both instruments for the three flasks filled with a standard gas. However, the fourth flask
662 with breath air showed a signal opposite to the measurements by the IRMS. As breath air
663 contains large amount of water and CO_2 in addition to O_2 , which can possibly interfere with

664 the CRDS analyzer measurements, we have removed H₂O and CO₂ by using a cryogenic trap
665 (-130 °C) and in an additional experiment using Schütze reagent to remove both CO and CO₂.
666 However, we have not observed any improvement towards an agreement with the IRMS
667 measurements. Therefore, any other gas component in the breath air must be relevant for the
668 interference. Based on the absorption lines in the spectral range of the instrument (7878 cm⁻¹)
669 retrieved from HITRAN database, we expect interference either from carbon monoxide (now
670 excluded by the tests) or methane or VOCs including acetone, ethanol, methanol or isoprenes,
671 all of which have been measured in breath air (Gao et al., 2017; Gottlieb et al., 2017; McKay
672 et al., 1985; Ryter and Choi, 2013; Wolf et al., 2017). Further investigations have to shed light
673 on these interferences in order to take corresponding action to surpass these shortcomings in
674 the isotope analysis based on cavity ring-down spectroscopy.

675 **4. Conclusions**

676 We have thoroughly evaluated the performance of a new CRDS analyzer which
677 measures O₂ mixing ratios and isotopic composition combining laboratory and field tests.
678 Even if a drift in the analyzer was observed at the beginning of this study, which can be easily
679 corrected by calibration, the recent analyzers built by the manufacturer did not show such
680 instrumental drift. However, prior tests are recommended to see the analyzer's stability.

681 The T-split tests for the current measurement setup based on the measurements of two
682 standard gases showed a difference within the measurement uncertainty. However, this effect
683 may become significant while applying larger splitting ratios and we recommend conducting
684 further experiments to accurately quantify this influence for larger splitting ratios.

685 We have observed a strong influence of dilution in the measured O₂ values during the
686 presence of high CO₂ mixing ratios. Even if such an influence may not be critical for the
687 present study, such an effect might be significant in other studies where higher CO₂ mixing

688 ratios might be present and we recommend following a correction strategy based on parallel
689 CO₂ measurements. This also applies for more accurate analysis.

690 The water correction applied by the instrument's in-built function seems to sufficiently
691 correct for the water vapor influence. However, a larger variability of the difference was
692 observed between the CRDS analyzer and the Paramagnetic cell when dried samples were
693 used in both systems. This can possibly be due to an overcorrection by the water correction
694 function of the CRDS analyzer when dried samples were used. This is particularly true for the
695 very low water vapor range (< 100 ppm). We believe that it is important to further investigate
696 this issue and identify an improved water correction strategy.

697 Based on the analysis of O₂ mixing ratios in the concentration and isotopic modes, we
698 have observed a significant decrease in precision (about ten-fold) in the latter measurement
699 mode. The measured $\delta^{18}\text{O}$ values for the standard air by the CRDS analyzer are in excellent
700 agreement with the IRMS values. However, such measurements for a breath air showed a
701 contrasting signal, possibly due to interference from other gases such as CH₄. Hence, we
702 recommend further investigation on such possible contaminants and how to possibly remove
703 them while conducting ambient air measurements. However, we believe that this analyzer can
704 be used for tracer experiments where artificially enriched isotopes are used to study biological
705 processes such as photosynthesis in plants using isotopically labelled CO₂ and H₂O.

706 **Acknowledgement**

707 We would like to thank ICOS-RI and the Swiss National Science Foundation (SNF) for
708 funding ICOS-CH (20FI21_148994, 20FI21_148992). We are also grateful to the
709 International Foundation High Alpine Research Stations Jungfrauoch and Gornergrat. The
710 measurement system at the Beromünster tower was built and maintained by the CarboCount-
711 CH (CRSII2_136273) and IsoCEP (200020_172550) projects both funded by SNF.

712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727

List of Tables

Table 1. Assigned mixing ratios of standard gases used in this study and their corresponding values measured by the NDIR, CRDS and IRMS at the University of Bern. ¹The assigned values are based on measurements from different institutions (University of Bern (UB), Scripps or NOAA, see column cylinder name). ²Measurements are on the Bern scale for CO₂ and O₂. The Bern scale is shifted by +550 per meg. ³Values on the Scripps scale.

Cylinder name	Assigned CO ₂ (ppm) ¹	Assigned O ₂ (per meg) ¹	CO ₂ -IRMS (ppm) ²	CO ₂ -NDIR (ppm) ²	O ₂ -IRMS (per meg) ²	O ₂ -Paramagnetic (per meg) ²	O ₂ -CRDS (per meg) ²
ST-1 LUX3576- UB	427.47	-1026	427.47	427.59	-1026	-1070	-1057
ST-2 LK922131- UB	368.09	599	368.09	367.82	599	560	590

ST-3 CA07045- Scripps	382.303	-271.6	382.50	381.99	278 (-272.2) ³	302	281
ST-4 CA07043- Scripps	390.528	-476.4	390.69	390.15	71 (-479.5) ³	66	63
ST-5 CA07047- Scripps	374.480	-807.7	374.70	374.17	-253 (-803.3) ³	-212	-233
ST-6 CA04556- NOAA	192.44	-3410	191.21	191.64	-3410	-2905	-3013
ST-7 CA06943- NOAA	2699.45	-		2612.80	-	-2691	-3369
ST-8 LK76852- UB	411.49	37794	411.49	406.25	37794	34513	36017

728

729

730 Table 2. The CO₂ and O₂ correlation coefficients at the different height levels derived using
731 the least square fit and the correlation coefficients (r^2). Uncertainties are calculated as
732 standard error of the slope.

Height	Oxidation Ratios (O ₂ :CO ₂)
12.5 m	-0.98 ± 0.06 (0.48)
44.6 m	-1.29 ± 0.07 (0.50)
71.5 m	-1.49 ± 0.08 (0.47)
131.6 m	-1.23 ± 0.05 (0.55)

212.5 m	-1.60 ± 0.07 (0.61)
---------	---------------------

733

734

735

736

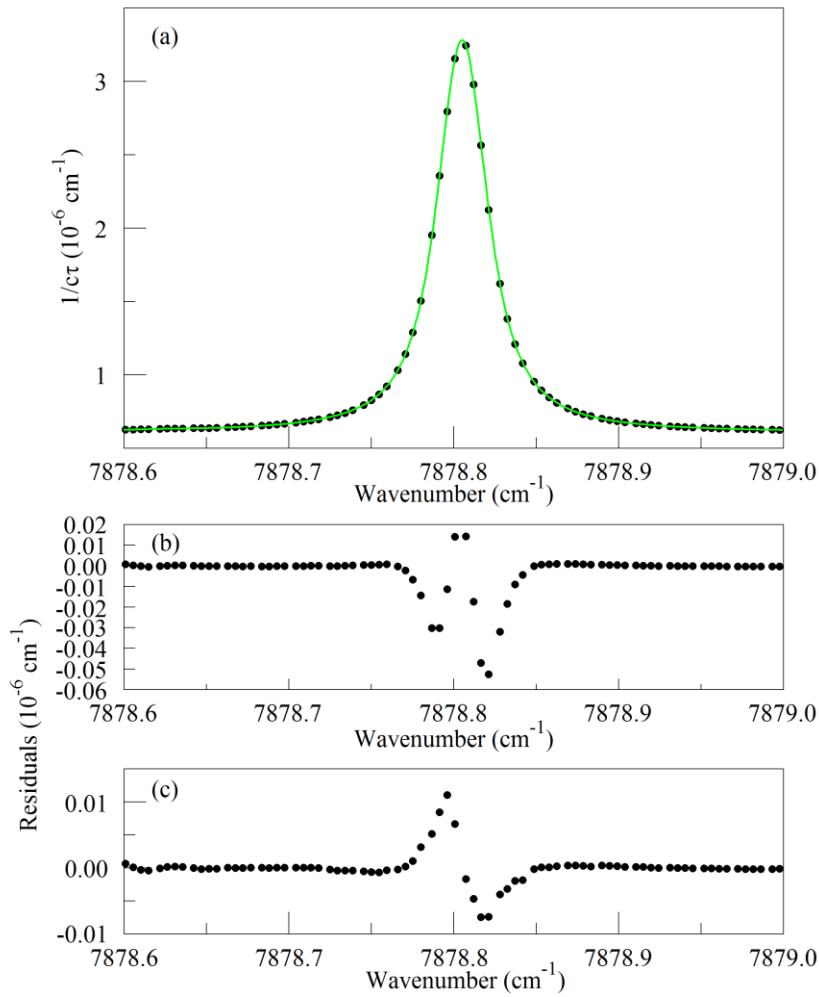
737

738

739

740

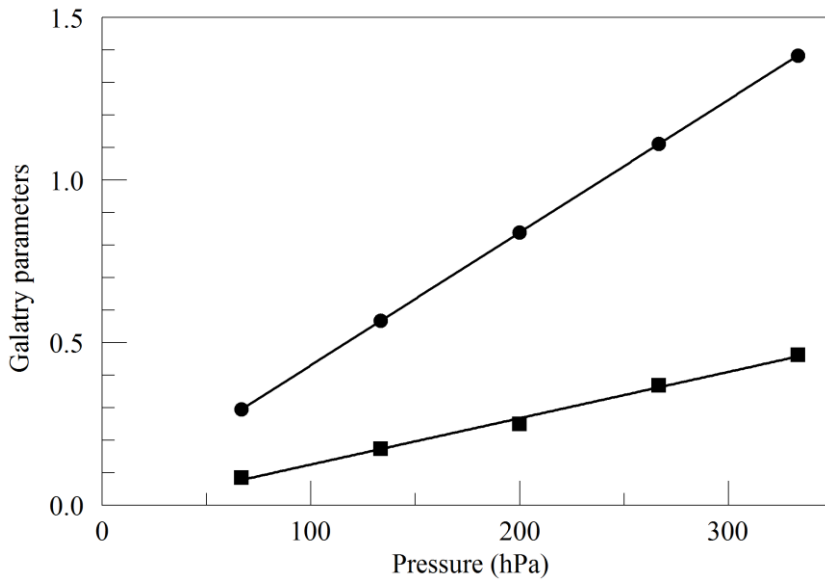
741 List of Figures



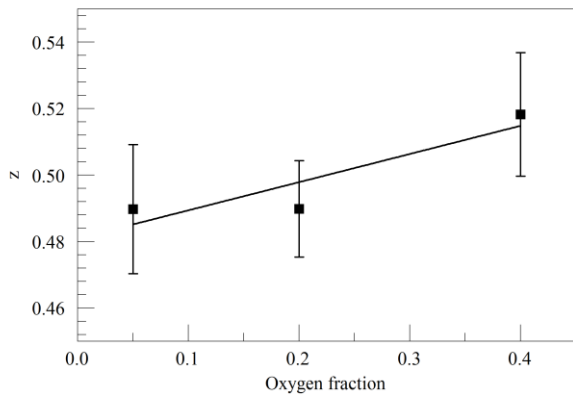
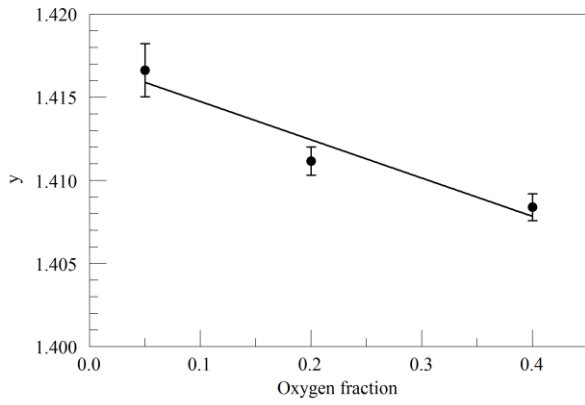
742
 743 Figure 1. The top panel (a) shows the raw data (points) and the best-fit Galatry function (solid
 744 line). Residuals of the Voigt fit are shown in panel (b) and residuals of the Galatry fit are
 745 shown in panel (c).

746

747

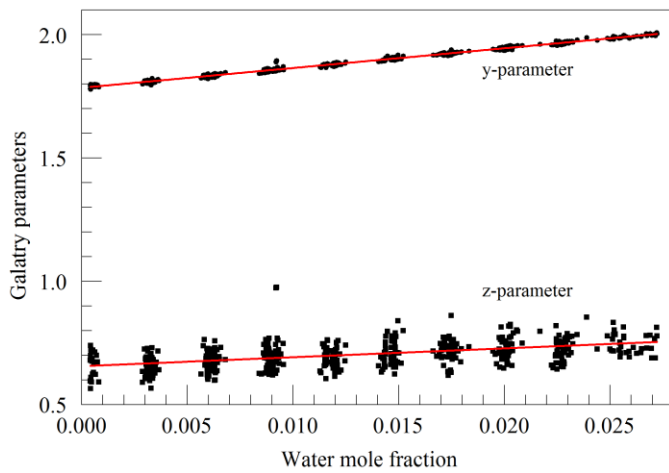


748
 749 Figure 2. Best-fit values for the Galatry parameters of the Q13Q13 line of O₂, as a function of
 750 pressure. The line broadening parameter y is represented by circles and the line narrowing
 751 parameter z by squares. The solid lines are linear fits to the measurements. The best-fit offset
 752 and slope are 0.0227 and 0.004082 hPa⁻¹ for y , and -0.0169 and 0.001424 hPa⁻¹ for z .



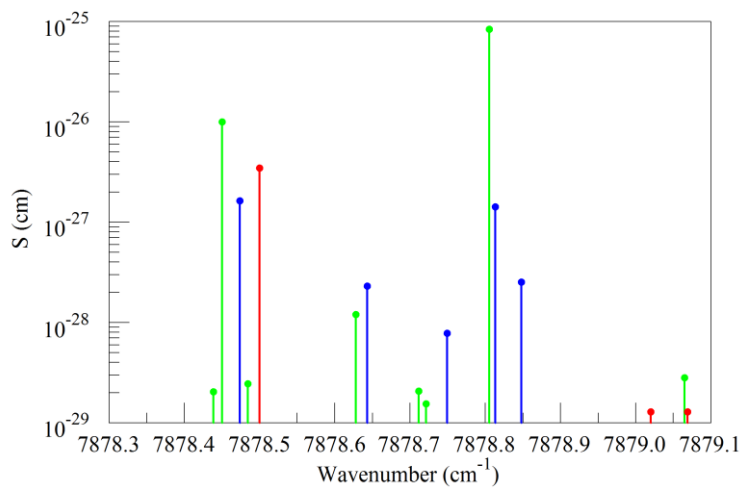
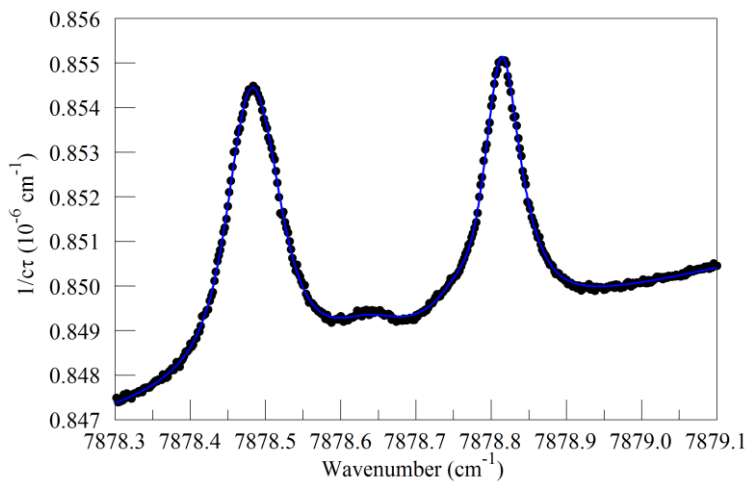
753

754 Figure 3. Galatry parameters of the Q13Q13 line of O₂ at 340 hPa and 45° C as a function of
 755 O₂ mole fraction in binary O₂ - N₂ mixtures. The linear fits to the data are $y = 1.417 - 0.023 x$
 756 f_{O_2} and $z = 0.481 + 0.085 x f_{O_2}$.



757
 758 Figure 4. Galatry parameters of the $7816.75210\text{ cm}^{-1}$ water line in air at 340 hPa and 45° C as
 759 a function of water mole fraction. Black points are from measurements and red lines are
 760 linear fits: $y = 1.7846 + 8.01 \times f_{\text{H}_2\text{O}}$ and $z = 0.656 + 3.60 \times f_{\text{H}_2\text{O}}$.

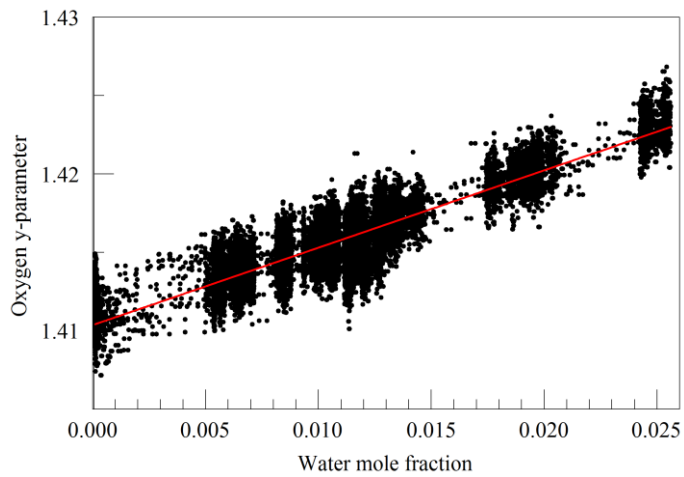
761
 762
 763



764
 765 Figure 5. Upper panel: spectrum of water in nitrogen (points) and fit to Voigt model (blue
 766 curve). Lower panel: Oxygen (green), normal water (blue), and deuterated water (red) lines
 767 in the 2016 Hitran data base.

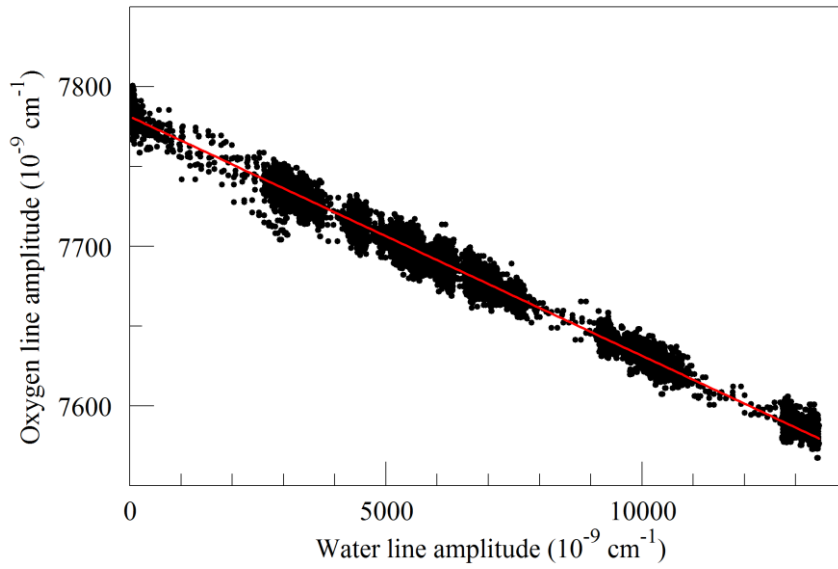
768

769



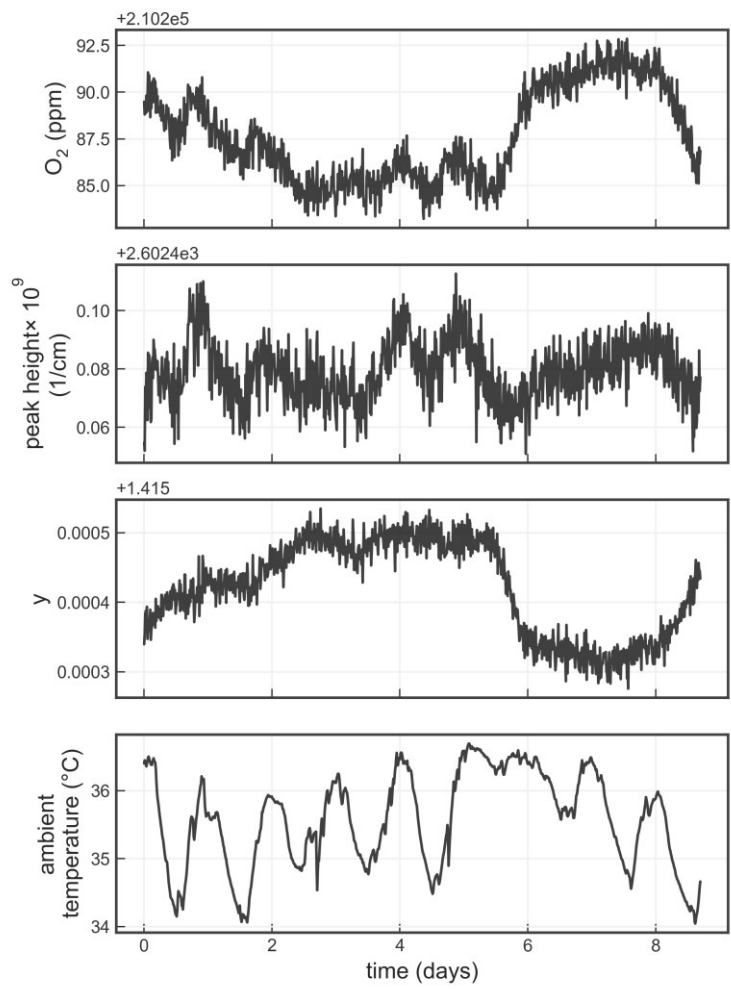
770
771 Figure 6. Galatry collisional broadening parameter of the oxygen Q13Q13 line at 340 hPa
772 and 45° C versus water mole fraction. Black points are from measurements and the red line is
773 a linear fit: $y = 1.4109 + 0.467 f_{\text{H}_2\text{O}}$.

774
775
776

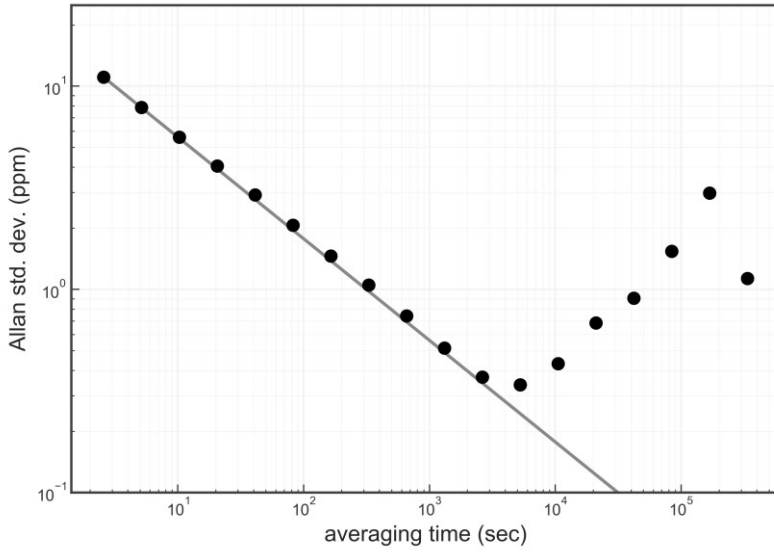


777
 778 Figure 7. Measured absorption line amplitudes for oxygen and water vapor for water vapor
 779 mixing ratios ranging from nearly 0 to 0.025. Black points are from measurements and the
 780 red line is a linear fit: with intercept $7.78001 \times 10^{-6} \text{ cm}^{-1}$ and slope -0.014807 .

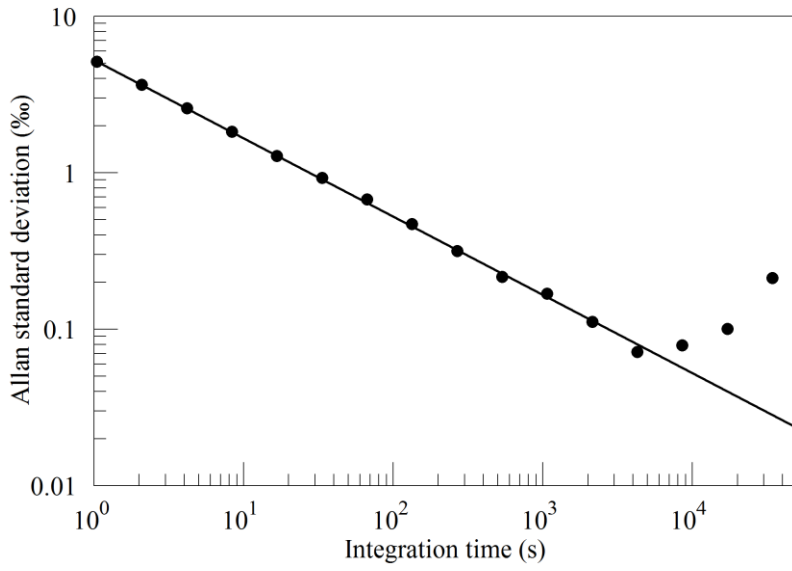
781
 782
 783
 784
 785
 786



787
 788 Figure 8. Time series from a measurement of a single tank over about a week. The four panels
 789 show the water-corrected oxygen concentration, the absorption peak loss minus the baseline
 790 loss, the measured Lorentzian broadening factor, and the ambient temperature (measured in
 791 the instrument housing), respectively. A windowed average of 300 seconds was applied to all
 792 four data sets.

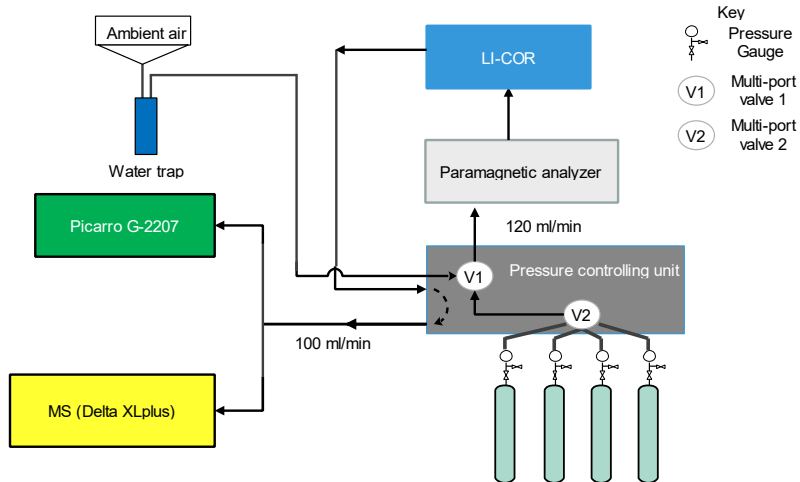


793
794 Figure 9. Precision of O₂ mole fraction measured from a tank of synthetic air. Filled circles
795 are measurements and the line shows the ideal $\tau^{-1/2}$ dependence.
796
797
798
799
800



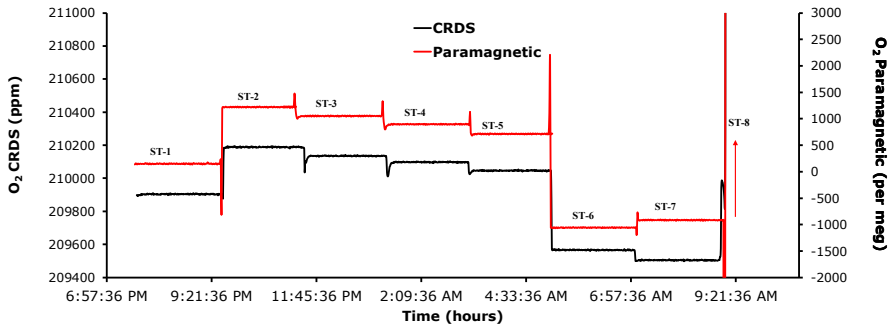
801
 802 Figure 10. Precision of $\delta(^{18}\text{O})$ measured from a tank of synthetic air. Filled circles are
 803 measurements and the line shows the ideal $\tau^{-1/2}$ dependence.

804
 805
 806
 807
 808
 809
 810
 811



812
 813 Figure 11. Schematics of the measurement system used to compare the Picarro analyzer with
 814 the Mass Spectrometer at Bern.

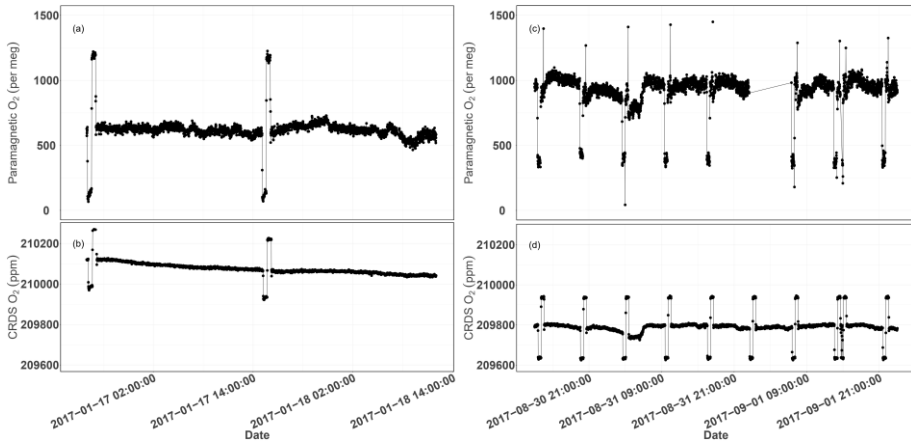
815
 816
 817
 818
 819
 820
 821
 822
 823



824
 825 Figure 12. Comparison of oxygen mixing ratios for the seven standard gases measured using
 826 the CRDS analyzer (black) and the Paramagnetic sensors (red).

827
 828
 829
 830
 831
 832
 833
 834
 835
 836
 837
 838
 839
 840
 841

842



843

844 Figure 13. Parallel ambient air measurements by the Paramagnetic and CRDS analyzers at the
845 beginning of the testing period (Panels a & b, January 2017) and the second phase of testing
846 (Panels c & d, September 2017). The spikes are measurements from the two standard gases
847 bracketing the ambient air values.

848

849

850

851

852

853

854

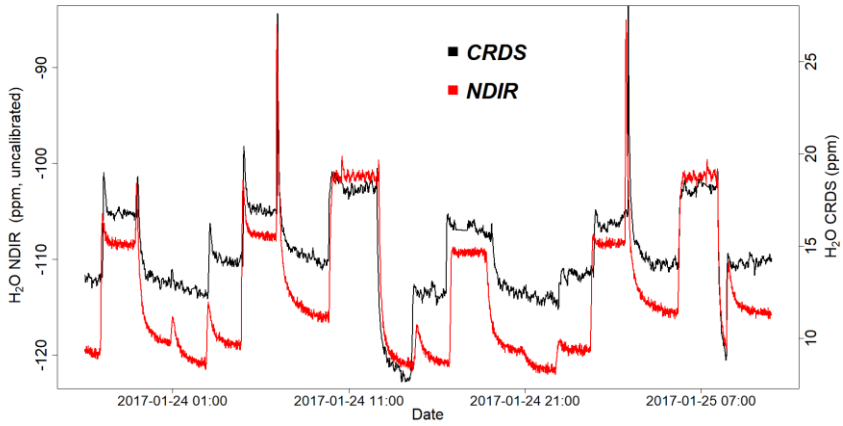
855

856

857

858

859



860

861 Figure 14. Parallel water vapor measurements for a dried ambient air by both the NDIR and

862 CRDS analyzers. Note that the water values from the NDIR analyzer are not calibrated.

863

864

865

866

867

868

869

870

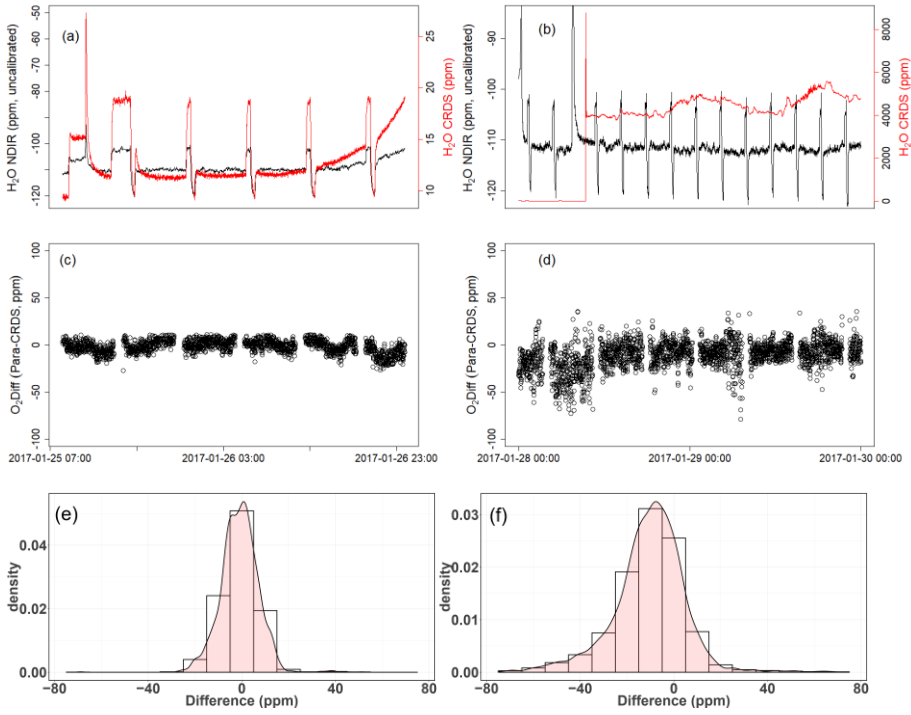
871

872

873

874

875



876

877

878 Figure 15. Results of water correction tests. Water measurements of the NDIR (left scale) for
879 dry conditions (a,b) and the CRDS analyzer (right scale) for dry (a) and wet (b) conditions.
880 The difference in oxygen measurements between the Paramagnetic and the CRDS instrument
881 using the built-in water correction for the CRDS values under dry (c) and wet (d) conditions.
882 Panels (e) and (f) show the population density functions.

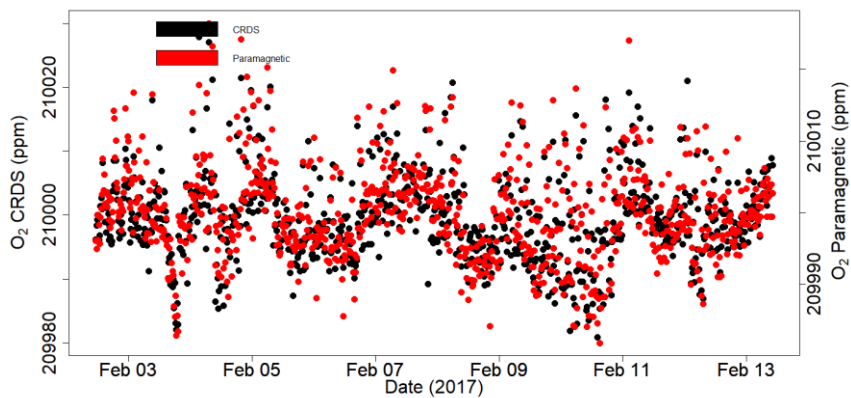
883

884

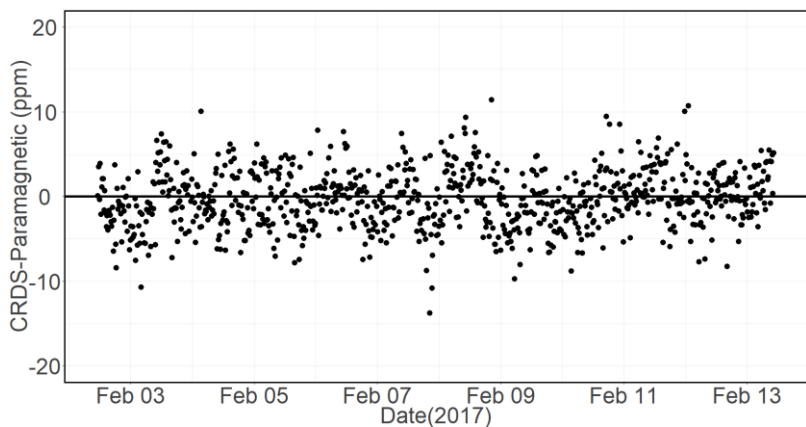
885

886

887



888



889

890 Figure 16. Calibrated ambient air oxygen measurements (1-minute average) at the
 891 Jungfrauoch site using the CRDS and Paramagnetic analyzers both in ppm units (a) and the
 892 absolute difference between the two measurements in ppm (b) by matching time stamps

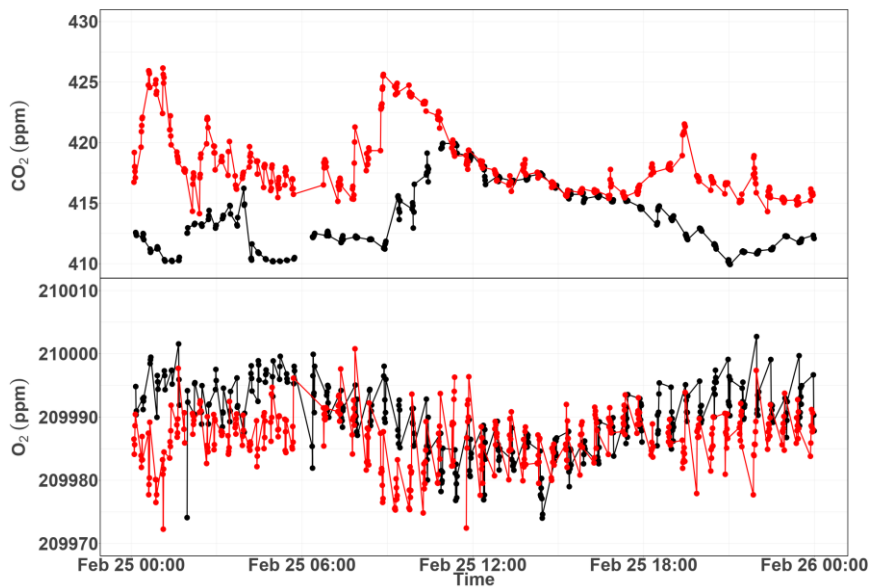
893

894

895

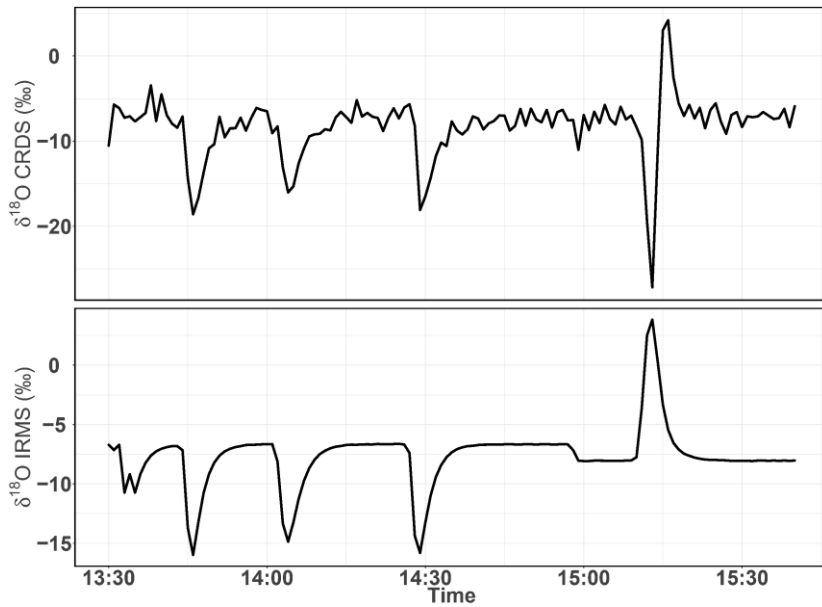
896

897



898
 899 Figure 17. Diurnal variations of CO₂ (top) and O₂ (bottom) measurements from the 12 m (red)
 900 and the 212.5 m (black) height levels at Beromünster tower.

901
 902
 903
 904
 905
 906
 907
 908
 909
 910

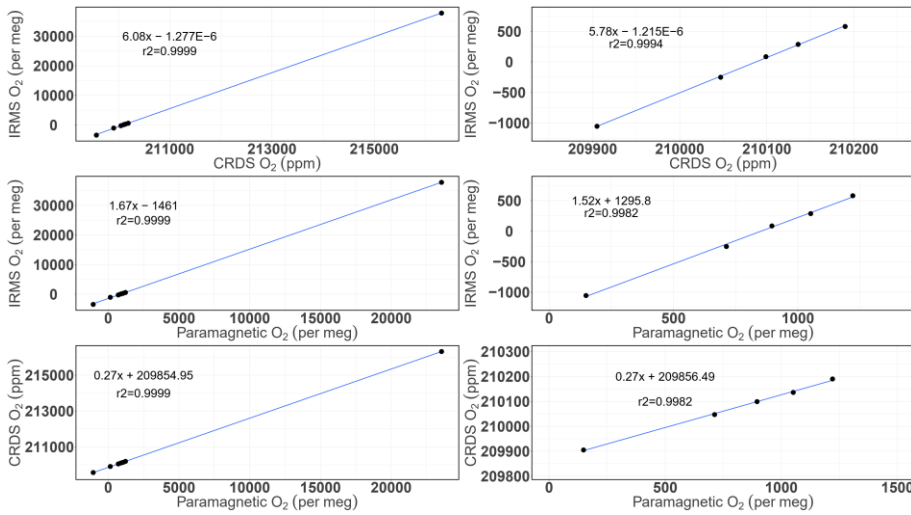


911
 912 Figure 18. Consecutive $\delta^{18}\text{O}$ measurements of a standard gas (CO_2 -free air) filled into three
 913 flasks followed by measurement of breath air using the CRDS analyzer (top) and IRMS
 914 (bottom). These measurements were carried out in the middle of ambient air measurements.

915
 916
 917
 918
 919
 920
 921
 922
 923
 924

925 **Appendix A.**

926



927

928 Figure A.1. Correlations between the O₂ mixing ratios measured by the CRDS and
929 Paramagnetic analyzers with the mass spectrometric measurements (uncalibrated values). The
930 left panels are for all the cylinders measured (standards 1 to 8) while the right ones are after
931 selecting standards 1-5.

932

933

934

935

936

937

938

939

940 **References**

- 941 Battle, M., Bender, M. L., Tans, P. P., White, J. W. C., Ellis, J. T., Conway, T., and Francey, R. J.: Global
942 carbon sinks and their variability inferred from atmospheric O-2 and delta C-13, *Science*, 287, 2467-
943 2470, 2000.
- 944 Bender, M. L., Tans, P. P., Ellis, J. T., Orchardo, J., and Habfast, K.: A High-Precision Isotope Ratio
945 Mass-Spectrometry Method for Measuring the O-2 N-2 Ratio of Air, *Geochim Cosmochim Ac*, 58,
946 4751-4758, 1994.
- 947 Berhanu, T. A., Satar, E., Schanda, R., Nyfeler, P., Moret, H., Brunner, D., Oney, B., and Leuenberger,
948 M.: Measurements of greenhouse gases at Beromünster tall tower station in Switzerland, *Atmos.*
949 *Meas. Tech.* , 9, 2016.
- 950 Berhanu, T. A., Szidat, S., Brunner, D., Satar, E., Schanda, R., Nyfeler, P., Battaglia, M., Steinbacher,
951 M., Hammer, S., and Leuenberger, M.: Estimation of the fossil-fuel component in atmospheric CO2
952 based on radiocarbon measurements at the Beromünster tall tower, Switzerland, *Atmos. Chem.*
953 *Phys. Discuss.*, 2017, 1-33, 2017.
- 954 Crosson, E. R. J. A. P. B.: A cavity ring-down analyzer for measuring atmospheric levels of methane,
955 carbon dioxide, and water vapor, 92, 403-408, 2008.
- 956 Filges, A., Gerbig, C., Rella, C. W., Hoffnagle, J., Smit, H., KrÄxmer, M., Spelten, N., Rolf, C., BozÄ³ki, Z.,
957 Buchholz, B., and Ebert, V.: Evaluation of the IAGOS-Core GHG Package H2O measurements during
958 the DENCHAR airborne inter-comparison campaign in 2011, *Atmos. Meas. Tech.*, 11, 5279–5297,
959 2018, <https://doi.org/10.5194/amt-11-5279-2018>. Gao, F., Zhang, X., Zhang, X., Wang, M., and Wang,
960 P.: Virtual electronic nose with diagnosis model for the detection of hydrogen and methane in breath
961 from gastrointestinal bacteria, 28-31 May 2017 2017, 1-3.
- 962 Gordon, E., Rothman, S., Hill, C., Kochanov, V., Tan, Y., Bernath, P., Birk, M., Boudon, V., Campargue,
963 A., Chance, K., Drouin, J., Flaud, J., Gamache, R. R., Hodges, J., Jacquemart, D., Perevalov, I., Perrin, A.,
964 Shine, P., Smith, M., Tennyson, J., Toon, G., Tran, H., Tyuterev, G., Barbe, A., Császár, G., Devi, M.,

965 Furtenbacher, T., Harrison, J., Hartmann, J., Jolly, A., Johnson, J., Karman, T., Kleiner, I., Kyuberis, A.
966 A., Loos, J., Lyulin, M., Massie, S., Mikhailenko, S., Moazzen-Ahmadi, N., Muller, S., Naumenko, O. V.,
967 Nikitin, A. V., Polyansky, O. L., Rey, M., Rotger, M., Sharpe, S., Sung, K., Starikova, E., Tashkun, S.,
968 Auwera, J., Wagner, G., Wilzewski, J., Wcisło, P., Yu, S., and Zak, E. J.: The HITRAN2016 molecular
969 spectroscopic database, 203, 3 - 69, 2017.

970 Goto, D., Morimoto, S., Ishidoya, S., Aoki, S., and Nakazawa, T.: Terrestrial biospheric and oceanic
971 CO₂ uptake estimated from long-term measurements of atmospheric CO₂ mole fraction, $\delta^{13}\text{C}$ and
972 $\delta(\text{O}_2/\text{N}_2)$ at Ny-Ålesund, Svalbard, *Journal of Geophysical Research: Biogeosciences*, doi:
973 10.1002/2017JG003845, 2017. n/a-n/a, 2017.

974 Gottlieb, K., Le, C. X., Wacher, V., Sliman, J., Cruz, C., Porter, T., and Carter, S.: Selection of a cut-off
975 for high- and low-methane producers using a spot-methane breath test: results from a large north
976 American dataset of hydrogen, methane and carbon dioxide measurements in breath, *Gastroenterol*
977 *Rep*, 5, 193-199, 2017.

978 Hartmann, J.-M., Boulet, C., and Robert, D.: *Collisional Effects on Molecular Spectra*, Elsevier Science,
979 2008.

980 Henne, S., Brunner, D., Folini, D., Solberg, S., Klausen, J., and Buchmann, B.: Assessment of
981 parameters describing representativeness of air quality in-situ measurement sites, *Atmos. Chem.*
982 *Phys.*, 10, 3561-3581, 2010.

983 Hodges, J. T., Layer, H. P., Miller, W. W., and Scace, G. E.: Frequency-stabilized single-mode cavity
984 ring-down apparatus for high-resolution absorption spectroscopy, 75, 849-863, 2004.

985 Keeling, R. F.: *Development of an Interferometric Oxygen Analyzer for Precise Measurement of the*
986 *Atmospheric O₂ Mole Fraction*, UMI, 1988a.

987 Keeling, R. F.: Measuring correlations between atmospheric oxygen and carbon dioxide mole
988 fractions: A preliminary study in urban air, *J Atmos Chem*, 7, 153-176, 1988b.

989 Keeling, R. F. and Manning, A. C.: 5.15 - Studies of Recent Changes in Atmospheric O₂ Content A2 -
990 Holland, Heinrich D. In: Treatise on Geochemistry (Second Edition), Turekian, K. K. (Ed.), Elsevier,
991 Oxford, 2014.

992 Keeling, R. F. and Shertz, S. R.: Seasonal and Interannual Variations in Atmospheric Oxygen and
993 Implications for the Global Carbon-Cycle, *Nature*, 358, 723-727, 1992.

994 Keeling, R. F., Stephens, B. B., Najjar, R. G., Doney, S. C., Archer, D., and Heimann, M.: Seasonal
995 variations in the atmospheric O₂/N₂ ratio in relation to the kinetics of air-sea gas exchange, *Global*
996 *Biogeochem Cy*, 12, 141-163, 1998.

997 Lamouroux, J., Sironneau, V., Hodges, J. T., and Hartmann, J. M.: Isolated line shapes of molecular
998 oxygen: Requantized classical molecular dynamics calculations versus measurements, *Physical*
999 *Review A*, 89, 042504, 2014.

1000 Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., Korsbakken, J. I.,
1001 Peters, G. P., Canadell, J. G., Jackson, R. B., Boden, T. A., Tans, P. P., Andrews, O. D., Arora, V. K.,
1002 Bakker, D. C. E., Barbero, L., Becker, M., Betts, R. A., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P.,
1003 Cosca, C. E., Cross, J., Currie, K., Gasser, T., Harris, I., Hauck, J., Haverd, V., Houghton, R. A., Hunt, C.
1004 W., Hurtt, G., Ilyina, T., Jain, A. K., Kato, E., Kautz, M., Keeling, R. F., Klein Goldewijk, K., Körtzinger, A.,
1005 Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lima, I., Lombardozzi, D., Metzl, N., Millero, F.,
1006 Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S. I., Nojiri, Y., Padín, X. A., Pregon, A.,
1007 Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Reimer, J., Rödenbeck, C., Schwinger, J., Séférian, R.,
1008 Skjelvan, I., Stocker, B. D., Tian, H., Tilbrook, B., van der Laan-Luijckx, I. T., van der Werf, G. R., van
1009 Heuven, S., Viovy, N., Vuichard, N., Walker, A. P., Watson, A. J., Wiltshire, A. J., Zaehle, S., and Zhu,
1010 D.: Global Carbon Budget 2017, *Earth Syst. Sci. Data Discuss.*, 2017, 1-79, 2017.

1011 [Machta, L. Hughes, E. Atmospheric Oxygen in 1967 to 1970, *Science*, 168, 3939, 1582-1584, 1970.](#)

1012 Manning, A.: Temporal variability of atmospheric oxygen from both continuous and measurements
1013 and a flask sampling network: tools for studying the global carbon cycle, Ph.D. Ph.D., University of
1014 California, San Diego, San Diego, California, USA, 2001.

1015 Manning, A. C. and Keeling, R. F.: Global oceanic and land biotic carbon sinks from the Scripps
1016 atmospheric oxygen flask sampling network, *Tellus B*, 58, 95-116, 2006.

1017 Manning, A. C., Keeling, R. F., and Severinghaus, J. P.: Precise atmospheric oxygen measurements
1018 with a paramagnetic oxygen analyzer, *Global Biogeochem Cy*, 13, 1107-1115, 1999.

1019 Marrero, T. R. and Mason, E. A.: Gaseous Diffusion Coefficients, *Journal of Physical and Chemical*
1020 *Reference Data* 1, 3, 1972.

1021 Martin, N. A., Ferracci, V., Cassidy, N., and Hoffnagle, J. A. J. A. P. B.: The application of a cavity ring-
1022 down spectrometer to measurements of ambient ammonia using traceable primary standard gas
1023 mixtures, 122, 219, 2016.

1024 McKay, L. F., Eastwood, M. A., and Brydon, W. G.: Methane Excretion in Man - a Study of Breath,
1025 Flatus, and Feces, *Gut*, 26, 69-74, 1985.

1026 Nevison, C. D., Keeling, R. F., Kahru, M., Manizza, M., Mitchell, B. G., and Cassar, N.: Estimating net
1027 community production in the Southern Ocean based on atmospheric potential oxygen and satellite
1028 ocean color data, *Global Biogeochem Cy*, 26, 2012.

1029 Oney, B., Henne, S., Gruber, N., Leuenberger, M., Bamberger, I., Eugster, W., and Brunner, D.: The
1030 CarboCount CH sites: characterization of a dense greenhouse gas observation network, *Atmos.*
1031 *Chem. Phys.*, 15, 11147-11164, 2015.

1032 Press, W. H., Teukolsky, S. A., Vetterling, W. T., and Flannery, B. P.: *Numerical Recipes 3rd Edition:*
1033 *The Art of Scientific Computing*, Cambridge Printing Press, Cambridge, England, 1986.

1034 Press, W. H., Teukolsky, S. A., Vetterling, W. T., and Flannery, B. P.: *Numerical recipes in C: the art of*
1035 *scientific computing*, Cambridge University Press, London, 1992.

1036 Ryter, S. W. and Choi, A. M. K.: Carbon monoxide in exhaled breath testing and therapeutics, *J Breath*
1037 *Res*, 7, 2013.

1038 Satar, E., Berhanu, T. A., Brunner, D., Henne, S., and Leuenberger, M.: Continuous CO₂/CH₄/CO
1039 measurements (2012–2014) at Beromünster tall tower station in Switzerland, *Biogeosciences*, 13,
1040 2623-2635, 2016.

1041 Schibig, M. F., Steinbacher, M., Buchmann, B., van der Laan-Luijkx, I. T., van der Laan, S., Ranjan, S.
1042 and Leuenberger, M. C.: Comparison of continuous in situ CO₂ observations at Jungfraujoeh using
1043 two different measurement techniques, *Atmospheric Measurement Techniques*
1044 , 8, 57-68, 10.5194/amt-8-57-2015, 2015.

1045 Severinghaus, J. P.: Studies of the terrestrial O₂ and carbon cycles in sand dune gases and in
1046 Biosphere Doctoral Ph.D., Columbia University, New York, USA, 1995.

1047 Steig, E. J., Gkinis, V., Schauer, A. J., Schoenemann, S. W., Samek, K., Hoffnagle, J., Dennis, K. J., and
1048 Tan, S. M.: Calibrated high-precision ¹⁷O-excess measurements using cavity ring-down
1049 spectroscopy with laser-current-tuned cavity resonance, *Atmos. Meas. Tech.*, 7, 2014.

1050 Stephens, B. B., Bakwin, P. S., Tans, P. P., Teclaw, R. M., and Baumann, D. D.: Application of a
1051 differential fuel-cell analyzer for measuring atmospheric oxygen variations, *J Atmos Ocean Tech*, 24,
1052 82-94, 2007.

1053 Sturm, P., ~~M. Leuenberger, M. F. L. Valentino, F. L. B. Lehmann, B.~~ and B. Ihlly: Measurements of
1054 CO₂, its stable isotopes, O₂/N₂, and ²²²Rn at Bern, Switzerland, *Atmospheric Chemistry and Physics*, 6,
1055 1991-2004, 2006.

1056 [Tan, Y., Kochanov, R.V., Rothman, L., and Gordon, I.E.: Introduction of water-vapor broadening](#)
1057 [coefficients and their temperature dependence exponents into the HITRAN database, Part 1: CO₂,](#)
1058 [N₂O, CO, CH₄, O₂, NH₃, and H₂S, Submitted to Journal of Geophysical Research Atmospheres, 2019,](#)
1059 [arXiv:1906.01475 .](#)

Field Code Changed

1060 Tennyson, J., Bernath, P. F., Campargue, A., Császár, A. G., Daumont, L., Gamache, R. R., Hodges, J. T.,
1061 Lisak, D., Naumenko, O. V., Rothman, L. S., Tran, H., Zobov, N. F., Buldyreva, J., Boone, C. D., De Vizia,
1062 M. D., Gianfrani, L., Hartmann, J.-M., McPheat, R., Weidmann, D., Murray, J., Ngo, N. H., and
1063 Polyansky, O. L.: Recommended isolated-line profile for representing high-resolution spectroscopic
1064 transitions (IUPAC Technical Report), 86, 1931–1943, 2014.

1065 Tohjima, Y.: Method for measuring changes in the atmospheric O-2/N-2 ratio by a gas
1066 chromatograph equipped with a thermal conductivity detector, *J Geophys Res-Atmos*, 105, 14575-
1067 14584, 2000.

1068 Tran, H., Turbet, M., Hanoufa, S., Landsheere, X., Chelin, P., Ma, Q., Hartmann, J.: The CO₂-
1069 broadened H₂O continuum in the 100–1500 cm⁻¹ region: Measurements, predictions and empirical
1070 model, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 230, 75-80, 2019.

1071 Valentino, F. L., Leuenberger, M., Uglietti, C., and Sturm, P.: Measurements and trend analysis of O₂,
1072 CO₂ and $\delta^{13}\text{C}$ of CO₂ from the high altitude research station Jungfraujoch, Switzerland — A
1073 comparison with the observations from the remote site Puy de Dôme, France, *Sci Total Environ*, 391,
1074 203-210, 2008.

1075 Varghese, P. L. and Hanson, R. K.: Collisional narrowing effects on spectral line shapes measured at
1076 high resolution, *Appl. Opt.*, 23, 2376-2385, 1984.

1077 Wójtewicz, S., Cygan, A., Masłowski, P., Domysławska, J., Wcisło, P., Zaborowski, M., Lisak, D.,
1078 Trawiński, R. S., and Ciuryło, R.: Spectral line-shapes of oxygen B-band transitions measured with
1079 cavity ring-down spectroscopy, *Journal of Physics: Conference Series*, 548, 012028, 2014.

1080 Wolf, P. G., Parthasarathy, G., Chen, J., O'Connor, H. M., Chia, N., Bharucha, A. E., and Gaskins, H. R.:
1081 Assessing the colonic microbiome, hydrogenogenic and hydrogenotrophic genes, transit and breath
1082 methane in constipation, *Neurogastroent Motil*, 29, 2017.

1083 Zellweger, C., Forrer, J., Hofer, P., Nyeki, S., Schwarzenbach, B., Weingartner, E., Ammann, M., and
1084 Baltensperger, U.: Partitioning of reactive nitrogen (NO_x) and dependence on
1085 meteorological conditions in the lower free troposphere, *Atmos. Chem. Phys.*, 3, 779-796, 2003.

1086