

## Fifth reply to the Editor's comments

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

Dear authors,

Associate Editor Decision: Publish subject to minor revisions (review by editor) (24 Sep 2019) by Christof Janssen

Comments to the Author:

Dear authors,

Thank you for your corrections.

I think the quantitative difference between O<sub>2</sub> mole fractions and the O<sub>2</sub>/N<sub>2</sub> ratio is clear for the general reader and there is no need for the proposed appendix. What is less clear and what yet seems to be an inconsistency in the article is the following:

The abstract characterises the instrument performance in terms of O<sub>2</sub> mole fraction and the uncertainty is expressed correspondingly. However, the article implies that it is rather the O<sub>2</sub>/N<sub>2</sub> ratio that needs to be measured. This can be done easily when the composition of air is known. But if the composition of air is not known exactly, the relative uncertainty of O<sub>2</sub>/N<sub>2</sub> is likely different from that of the O<sub>2</sub> mole fraction alone and the uncertainty cannot be determined as easily. Please include a discussion/quantification of the additional factors/contribution to the uncertainty of O<sub>2</sub>/N<sub>2</sub> such that the article can be published.

With best regards,

In order to clarify the above comment, we have now added the following paragraph at the end of section 3.2.1.

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Furthermore, the slope between the IRMS and CRDS O<sub>2</sub> values in Figure A1 corresponds to 5.78 per meg ppm<sup>-1</sup>, significantly larger than the conversion factor of 4.78 per meg ppm<sup>-1</sup> as derived from equation 1 assuming constant N<sub>2</sub> content. This higher slope is due to dilution effect originating from any gas component change (Delta, given in ppm) on all air components of air samples, which has not been corrected for the CRDS values. When accounting for this dilution effect - which scales with  $1/(1+\Delta)$ , the factor approaches 4.78 per meg ppm<sup>-1</sup>. The scaling of dilution effects is independent on which air component is changing and it affects all air components relative to their molecular fractions similarly. O<sub>2</sub> values on a CRDS or paramagnetic cell instrument is affected even if there is no change in O<sub>2</sub> or N<sub>2</sub> but only in CO<sub>2</sub> or water vapor or any other component which is present. This is in contrast to measurements of O<sub>2</sub>/N<sub>2</sub> ratios for the same case where equal ratio would be measured. Major dilution influences are expected from O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O changes due to natural exchange processes on air samples or when using artificial air-like compositions.

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

3

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9

10 **Abstract**

11 Carbon dioxide and oxygen are tightly coupled in land-biospheres CO<sub>2</sub> - O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub>  
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, Jungfrauoch and the  
 26 Beromünster tall tower in Switzerland. At both sites, we observed opposing and diurnally  
 27 varying CO<sub>2</sub> and O<sub>2</sub> 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 O<sub>2</sub>:CO<sub>2</sub> 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<sup>-1</sup> (Keeling and Manning, 2014) mainly  
 35 associated with the increase in fossil fuel combustion. Measurements of atmospheric O<sub>2</sub> are  
 36 reported as the ratio to the N<sub>2</sub> concentration and expressed as δ(O<sub>2</sub>/N<sub>2</sub>) because the variations  
 37 in the concentrations of other atmospheric gases such as CO<sub>2</sub> can influence the O<sub>2</sub> partial  
 38 pressure while this ratio is insensitive to these changes in other gases. Atmospheric O<sub>2</sub> is  
 39 commonly expressed in units of per meg due to its small variability with respect to a large  
 40 background, where

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

42 Note that under the assumption the atmospheric N<sub>2</sub> content is constant (i.e. N<sub>2sample</sub> equals  
 43 N<sub>2reference</sub>), we convert relative changes in oxygen given in per meg following equation 1 to  
 44 oxygen changes in parts per million (equivalent to micromol/mol) by multiplying by the O<sub>2</sub>  
 45 mole fraction (O<sub>2reference</sub>) expressed as 209500 ppm. (the O<sub>2</sub> mole fraction of atmospheric air)  
 46 (Machta and Hughes, 1970). Hence 1 ppm corresponds approximately to 4.8 per meg, or 1 per  
 47 meg to 1/4.8 (209500/10<sup>6</sup>) ppm.

48 In contrast to O<sub>2</sub>, the global average atmospheric CO<sub>2</sub> mixing ratio increased to 405.0 ppm  
49 averaged over 2017 since its preindustrial value of 280 ppm (Le Quéré et al., 2017). As the  
50 variability of atmospheric oxygen is directly linked to the carbon cycle, both its short and  
51 long-term observations can be used to better constrain the carbon cycle. For example, since  
52 first suggested by Keeling and Shertz (1992) the long-term trends derived from concurrent  
53 measurements of atmospheric CO<sub>2</sub> and O<sub>2</sub> have been widely used to quantify the partitioning  
54 of atmospheric CO<sub>2</sub> between the land-biosphere and oceanic sinks (Battle et al., 2000; Goto et  
55 al., 2017; Manning and Keeling, 2006; Valentino et al., 2008). This method hinges on the  
56 linear coupling between CO<sub>2</sub> and O<sub>2</sub> with an oxidation ratio (OR, defined as the  
57 stoichiometric ratio of exchange during various process such as photosynthesis and respiration  
58 expressed using  $\alpha$ ) of 1.1 for the terrestrial biosphere photosynthesis-respiration processes  
59 ( $\alpha_b$ ) and 1.4 for fossil fuel combustion ( $\alpha_f$ ) while they are decoupled for oceanic processes ( $\alpha_o$   
60 = 0). Meanwhile, the short-term variability in atmospheric oxygen can be used to estimate  
61 marine biological productivity and air-sea gas exchange (Keeling et al., 1998; Nevison et al.,  
62 2012). However, the accuracy of these estimates is primarily linked to the accuracy and  
63 precision of atmospheric O<sub>2</sub> measurements and the assumed ORs for the different processes  
64 which are highly variable in contrast to atmospheric CO<sub>2</sub> that can be well measured within the  
65 precision guidelines set by the Global Atmospheric Watch (GAW) ( $\pm 0.1$  ppm for the  
66 northern hemisphere).

67 Currently there are several, mostly custom built techniques that can measure  
68 atmospheric O<sub>2</sub> variations as oxygen concentration based on interferometric, paramagnetic,  
69 UV absorption and fuel cell technology (Keeling, 1988a; Manning et al., 1999; Stephens et  
70 al., 2007) or as O<sub>2</sub>/N<sub>2</sub> ratios to account for the large background effect using gas  
71 chromatography with thermal conductivity detector (GC-TCD) or gas chromatography

72 coupled to mass spectrometry (GC-MS) (Bender et al., 1994; Tohjima, 2000). Despite the fact  
73 that these techniques have been used for more than two decades, accurate quantification of  
74 atmospheric oxygen variability remains challenging primarily because the small ppm-level  
75 atmospheric oxygen signal rides on a  $\sim 210,000$  ppm background, which places stringent  
76 requirements on the precision and drift of the analysis methods especially for continuous  
77 monitoring (note that the GAW recommendation for the measurement precision of  $O_2/N_2$  is 2  
78 per meg). The techniques listed above struggle to routinely achieve the necessary performance  
79 for various reasons, including i) instability over time that requires frequent measurement  
80 interruption for calibration, ii) measurement bias with ambient and sample temperature and/or  
81 pressure, and/or iii) systematic errors in the measurement due to other atmospheric species.  
82 Further, some techniques require the use of consumables and rely on high vacuum, which  
83 complicates field deployment.

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

## 91 **2. Analyzer design principles**

92 The analyzer described here is derived from the Picarro G2000 series of CRDS  
93 analyzers. The basic elements have been described elsewhere (Crosson, 2008; Martin et al.,  
94 2016; Steig et al., 2014): briefly, the instrument is built around a high-finesse, traveling-wave  
95 optical cavity, which is coupled to either of two single-frequency Distributed FeedBack-

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

119 per second and achieves a noise equivalent absorption of typically about  $10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ ,  
120 with some variation between instruments.

121 The primary goal when designing this analyzer was to measure the molecular oxygen  
122 concentration with few-per-meg level precision and stability. In this context operational  
123 stability is as important as signal-to-noise. Our experience has been that the most stable  
124 operation of the analyzer is achieved when the optical phase length of the cavity is held as  
125 nearly constant as possible. In this case the free spectral range (FSR,  $0.0206 \text{ cm}^{-1}$ ) of the  
126 temperature stabilized, invar ring-down cavity provides a better optical frequency standard  
127 than the etalon-based wavelength monitor, which in turn allows more consistent  
128 measurements of absorption line width and integrated absorption line intensity (Steig et al.,  
129 2014). For a small, field-deployable instrument, it is not practical to stabilize the absolute  
130 frequencies of the cavity modes to an optical frequency standard (Hodges et al., 2004) but the  
131 oxygen lines themselves, under conditions of constant temperature and pressure, provide an  
132 adequate frequency reference. The oxygen spectrum was also used to calibrate the FSR, by  
133 comparing a wide (approximately  $10 \text{ cm}^{-1}$ ) FSR-spaced spectrum with the Hitran database  
134 (Rothman et al., 2013).

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

143           Recently, considerable work has been done to advance the understanding of spectral  
144 line shapes and to define functional representations that better describe the processes that  
145 determine spectral line shapes than does the Voigt model (Hartmann et al., 2008; Tennyson et  
146 al., 2014, Tran et al., 2019). Line shape studies have been published for the 1.27  $\mu\text{m}$  band of  
147  $\text{O}_2$  (Fleisher et al., 2015; Lamouroux et al., 2014), though not to our knowledge for the Q  
148 branch. The apparatus used here is not capable of spectroscopic studies of comparable  
149 precision; the absolute temperature and pressure monitoring and especially the frequency  
150 metrology are far too crude for that purpose. Our goal is merely to define a simple model of  
151 the Q13Q13 line that is adequate for least-squares retrievals of the  $\text{O}_2$  absorption under the  
152 limited range of conditions (stabilized temperature and pressure) that the operational analyzer  
153 experiences in the field. The CRDS analyzers use the Galatry function (Varghese and Hanson,  
154 1984), which is distinctly better than the Voigt and still easily and quickly evaluated for line  
155 shape modeling. Ultimately, the usefulness of the spectral model is to be evaluated by the  
156 precision and stability of the  $\text{O}_2$  measurements when compared with established techniques.  
157 For spectral model development, this spectrometer has the drawback that the cavity FSR, is  
158 too large to reveal much detail of the absorption line shape, even with the simplifying  
159 assumption of a Galatry line shape. We therefore acquired a set of four interleaved spectra,  
160 with the PZT-actuated mirror moved to offset the cavity modes of the individual FSR-spaced  
161 spectra by one-fourth of an FSR. The precise offsets were determined from fits to the strong  
162 and well-isolated  $\text{O}_2$  lines in the spectra. From the consistency of the fitted line centers, we  
163 estimate that the positioning of the interleaved spectra was accurate to approximately 10  
164 MHz. The spectrum of the Q13Q13 line acquired in this manner is shown in Figure 1,  
165 together with the best-fit Galatry function. It stands out that the residuals are largely odd in  
166 detuning from the line center: this shows the limitations of the Galatry model in this case,



167 since the Galatry function is purely even about the line center. The shape of the absorption  
168 line in this model is specified by two dimensionless parameters: the collisional broadening  
169 parameter

$$170 \quad \gamma = \gamma / \sigma_D \quad (2)$$

171 and the collisional narrowing parameter

$$172 \quad z = \beta / \sigma_D \quad (3)$$

173 where  $\gamma$  is the frequency of broadening transitions,  $\beta$  is the velocity change collision rate, and  
174  $\sigma_D$  is the 1/e Doppler half-width of the transition, given by

$$175 \quad \sigma_D = \nu_0 (2k_B T / M c^2)^{1/2} \quad (4)$$

176 where  $\nu_0$  is the transition frequency,  $k_B$  is Boltzmann's constant ( $J \cdot K^{-1}$ ),  $T$  is the sample  
177 temperature (K),  $M$  is the molecular mass (amu), and  $c$  is the speed of light (m/s). Figure 2  
178 shows the values of  $\gamma$  and  $z$  obtained from spectra acquired in the same way as Figure 1, as a  
179 function of cavity pressure. The values depend linearly on pressure, as expected from the  
180 Galatry model, but the unconstrained linear fits do not go precisely through the origin. It is  
181 not clear whether this represents a breakdown of the Galatry model or simply reflects the  
182 limited quality of the data set. The slope of  $\gamma$  can be converted to an air-broadened collisional  
183 width  $\gamma_{\text{air}} = 0.0442 \text{ cm}^{-1}/\text{atm}$ , which agrees with the Hitran value of  $0.0460 \text{ cm}^{-1}/\text{atm}$  (Gordon  
184 et al., 2016) to within the uncertainty estimate stated by Hitran (uncertainty code 4 for  $\gamma_{\text{air}}$   
185 corresponding to 10% --20% relative uncertainty). The slope of  $z$  can be interpreted in terms of  
186 the optical diffusion coefficient (Fleisher et al., 2015), yielding  $D = 0.285 \text{ cm}^2 \text{ s}^{-1}$ , compared  
187 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).  
188 Although the anticipated use of the analyzer is for ambient air samples having a very small  
189 range of  $O_2$  concentrations, we did investigate the variation of the line shape in binary  
190 mixtures of  $O_2$  and  $N_2$  shown in Figure 3. The error bars are taken from the output of the

191 Levenberg-Marquardt fitting routine (Press et al., 1992). The dependence of the collisional  
192 broadening parameter  $z$  on  $O_2$  mole fraction was considered too small to be significant, but  
193 the variation in  $y$  was used in the subsequent analysis of the air samples. Note that Wójtewicz  
194 et al. (Wójtewicz et al., 2014) also found collisional broadening coefficients for nitrogen to be  
195 slightly larger than for oxygen in measurements of one  $O_2$  line in the B-band.

196 The primary goal in designing the analyzer was to achieve high enough precision to  
197 make meaningful measurements of  $O_2$  in clean atmospheric samples. Although the current  
198 best practice for such high-precision measurements is to work with dried samples, we decided  
199 to include high precision measurements of water vapor. There were two reasons for this  
200 decision: one is to serve as a monitor for residual water vapor, which is difficult to remove  
201 completely from the ring-down cavity and associated sample handling hardware, and the  
202 second and more ambitious reason was to see how well the effect of water vapor could be  
203 corrected for measurements of undried ambient air. While it was considered unlikely that  
204 measurements of undried air could compete in accuracy with those of dried air, it might be  
205 possible to correct for water vapor well enough to enable useful measurements in some  
206 circumstances without the expense and inconvenience of drying the sample. For this purpose,  
207 a second laser was added, which probes the  $7_{1,6} \rightarrow 8_{4,5}$  component of the  $2\nu_3$  band of water  
208 vapor, at of  $7816.75210 \text{ cm}^{-1}$  (Gordon et al., 2017). The Galatry model was used to fit spectra  
209 of synthetic air humidified to various levels of water vapor concentration. These fits also  
210 included two other nearby, very weak water lines, with intensities less than 1% of the strong  
211 transition, in order that their absorption should not perturb the line shape of the main  
212 transition. Results for the shape of the  $7816.75210 \text{ cm}^{-1}$  line are shown in Figure 4. At the  
213 level that we can measure, only the  $y$ -parameter has a meaningful variation with water  
214 concentration. From the linear fit one obtains a pressure broadening coefficient for air,  $\gamma_{\text{air}} =$

215 0.0752 cm<sup>-1</sup>/atm, in reasonable agreement with the Hitran value  $\gamma_{\text{air}} = 0.0787$  cm<sup>-1</sup>/atm  
216 (Gordon et al., 2017), and a self-broadening coefficient  $\gamma_{\text{self}} = 0.413$  cm<sup>-1</sup>/atm, to be compared  
217 with the Hitran value  $\gamma_{\text{self}} = 0.366$  cm<sup>-1</sup>/atm. Since the uncertainty estimate for the Hitran  
218 values is 10 % to 20 %, this level of agreement seems reasonable.

219 We also looked at absorption from water near the Q13Q13 absorption line of O<sub>2</sub>.  
220 These spectra were measured in a background of pure nitrogen to reveal the very weak lines  
221 interfering with the O<sub>2</sub> measurement. Without the strong O<sub>2</sub> lines, it was impossible to  
222 interleave FSR-spaced spectra, so in this case the frequency axis comes from the analyzer's  
223 wavelength monitor. The upper panel of Figure 5 shows the spectrum of saturated water vapor  
224 in nitrogen, together with a fit to a Voigt model of the molecular lines. The measurement was  
225 made at a pressure of 340 hPa and temperature of 45° C. The main features are the Q13Q13 line  
226 from trace contamination of oxygen in the sample and several lines that arise from normal water  
227 (<sup>1</sup>H<sub>2</sub><sup>16</sup>O) and deuterated water (<sup>1</sup>H<sup>2</sup>H<sup>16</sup>O also abbreviated HDO). The lower panel of Figure 5 shows  
228 the lines tabulated in Hitran. Immediately after the data in Figure 5 were acquired,  
229 measurements were also made at 7816.85210 cm<sup>-1</sup>, to establish the relationship between the  
230 absorption strengths in the two spectral regions. The relative intensities of the H<sub>2</sub>O and HDO  
231 lines change with variations in the isotopic composition of the water, but fortunately the direct  
232 interference with the oxygen Q13Q13 lines comes entirely from the H<sub>2</sub>O isotopologue, with  
233 the strongest HDO line being separated by approximately 8 line widths (FWHM) from the  
234 Q13Q13 line. Hitran simulations for molecules other than water that are expected to be  
235 present in clean, ambient air indicate that direct interference with the Q13Q13 line should be  
236 negligible at the level of precision considered here. In the case of CO<sub>2</sub>, the dilution of oxygen  
237 due to 400 ppm of CO<sub>2</sub> is significant, and larger than any direct spectral interference.

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

262 amplitudes were preset based on the measured water absorption at  $7817\text{ cm}^{-1}$  and the  
263 previously determined amplitude relationships between the water lines. This procedure does  
264 not account for variations in HDO abundance, which may introduce some systematic error  
265 into the water vapor correction for samples of unusual isotopic composition, but it should  
266 accurately model the most important lines that interfere with the oxygen measurement.  
267 Collisional broadening of the Q13Q13  $\text{O}_2$  line by water vapor is shown in Figure 6. From the  
268 linear fit one obtains a coefficient for collisional broadening of the Q13Q13 line by water  
269 vapor of  $\gamma_{\text{water}} = 0.0442\text{ cm}^{-1}/\text{atm}$  at  $45\text{ }^\circ\text{C}$ . Recently, parameters describing broadening of  
270 oxygen lines by water vapor, obtained by empirical modeling of selected experimental  
271 data, were added to the Hitran data base (Tan et al., In review). The new Hitran entries predict  
272 a value of  $0.0486\text{ cm}^{-1}/\text{atm}$  at  $45\text{ }^\circ\text{C}$ , which is in agreement with our measurement within the  
273 5-10% uncertainty attributed by Hitran to the broadening parameter. The alternating  
274 measurements at  $7817\text{ cm}^{-1}$  and  $7878\text{ cm}^{-1}$  also calibrated the relationship between water mole  
275 fraction and the absorption at  $7817\text{ cm}^{-1}$ , using a dilution analysis described by Filges et al.  
276 (2018), who showed that the results obtained this way agree well with water vapor fractions  
277 measured with a conventional hygrometer. Figure 7 shows the measured amplitudes of the  
278 water and oxygen lines for samples of variable humidity. Since the air came from a tank of  
279 constant composition, the oxygen concentration changes due to dilution of oxygen when  
280 water is added. Assuming that this is the sole cause of the change in measured absorption,  
281 since the line shapes were being constantly adjusted to account for changes in collisional  
282 broadening, it is straightforward to deduce the relation between the water fraction and the  
283 absorption amplitude. This calibration was used to generate the water fraction axes in Figures  
284 4 and 6. We note that we did not take particular care to control or measure the quantity of  
285 dissolved gases, especially oxygen and carbon dioxide, in the water used for this experiment.

286 While these gases would not significantly affect the water calibration, they may affect the  
287 water vapor correction of the oxygen measurement at the ppm level. More work needs to be  
288 done to investigate the water vapor correction of the oxygen 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  $\text{cm}^{-1}$  and 7878  $\text{cm}^{-1}$  regions. At 7878  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$   
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  $\text{O}_2$  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  $\text{cm}^{-1}$  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  $\text{O}_2$  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  $\text{O}_2$  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  $\gamma$ . The correlation

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

325         The main goal in developing this instrument was to make high precision  
326 measurements of  $O_2$  mole fraction, based on absorption by the dominant  $^{16}O_2$  isotopologue.  
327 The absorption lines of the rarer isotopologues are also present nearby, so a mode of operation  
328 was included in which one laser is scanned over neighboring lines of  $^{16}O_2$  and  $^{16}O^{18}O$  and the  
329 ratio of amplitudes is used to derive an isotopic ratio, reported in the usual delta notation. In  
330 this case the operating pressure was reduced to 160 hPa to improve the resolution of the  
331 nearby lines. The lines measured were the Q3Q3 line of  $^{16}O_2$ , at  $7882.18670\text{ cm}^{-1}$ , and the  
332 Q9Q9 line of  $^{16}O^{18}O$ , at  $7882.050155\text{ cm}^{-1}$ . The measurement procedure is very much like  
333 that for the  $O_2$  fraction measurement, so it will not be described in detail, only the main

334 differences will be noted. One is that in determining an isotopic ratio, normalizing absorption  
335 amplitudes by line widths does not provide any advantage, instead we simply take the ratio of  
336 amplitudes to compute delta. Although the Q9Q9 line and its neighbor Q8Q8 are the strongest  
337 ones in this band, absorption by  $^{16}\text{O}^{18}\text{O}$  is still very weak, only about  $5 \times 10^{-9} \text{ cm}^{-1}$  at the line  
338 center under the conditions we used. The signal-to-noise that can be achieved with this  
339 analyzer is not adequate to determine both the amplitude and the width of the  $^{16}\text{O}^{18}\text{O}$  line with  
340 useful precision, so in the fitting step the y-parameter of the  $^{16}\text{O}^{18}\text{O}$  line is constrained to be a  
341 constant factor times the fitted y-parameter for the  $^{16}\text{O}_2$  line. Additionally, because of the  
342 weakness of the rare isotopologue absorption, the majority of ring-downs in each spectrum is  
343 devoted to measuring  $^{16}\text{O}^{18}\text{O}$  i.e. 232 ring-downs in each spectrum versus only 40 for  $^{16}\text{O}_2$ .  
344 This implies that the mole fraction measurement in the isotopic mode is much less precise  
345 than when the analyzer measures the Q13Q13 line alone.

### 346 **3. Results and Discussions**

#### 347 **3.1. Laboratory tests at Picarro, Santa Clara**

##### 348 3.1.1. Temperature and pressure sensitivity

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

356 From these experiments, we determined a temperature sensitivity of  $-2.1 \times 10^{-4} \text{ K}^{-1}$  and  
357 a pressure sensitivity of  $+9.8 \times 10^{-6} \text{ hPa}^{-1}$ . The temperature sensitivity is somewhat larger than



358 expected based on a calculation using Hitran data to estimate the temperature dependences of  
359 all the quantities that go into the measured absorption of the Q13Q13 line. The pressure  
360 sensitivity is strikingly small, indicating a good cancelation of the pressure dependence of  
361 absorption amplitude and line width. Both temperature and pressure sensitivities are small  
362 enough to have a negligible effect on short-term precision of measurements made with the  
363 stabilized ring-down cavity, though long-term drifts in the sensors are always a matter of  
364 concern.

### 365 3.1.2. Measurement precision and drift

366 Measurement precision was evaluated by analyzing synthetic air containing nominal  
367 atmospheric concentrations of CO<sub>2</sub> and CH<sub>4</sub> from an aluminum Luxfer cylinder over a period  
368 of several days. The tank, oriented horizontally and thermally insulated (though not  
369 controlled), was connected directly to the instrument (S/N TADS2001) with a 2-stage  
370 pressure regulator and stainless-steel tubing with an additional orifice to about 55 sccm. For  
371 the isotopic mode of operation, the precision of the measurement was also tested by making  
372 repeated measurements from a tank of clean, dry synthetic air.

373 Figure 8 shows the time series of the precision test data, displaying the reported  
374 oxygen concentration, the height of the oxygen absorption peak, the width of the oxygen  
375 absorption peak and the ambient temperature. The residual error of the analyzer, although  
376 small, is nevertheless significant given the stringent targets set forth by the WMO-GAW  
377 program. Possible sources of error include: temperature drifts due to sensor drift or gradients;  
378 pressure errors due to sensor drift; optical artifacts such as parasitic reflections, higher order  
379 cavity mode excitation, and/or loss nonlinearity that can distort the reported oxygen spectrum.  
380 More work is required to identify and eliminate these small drifts.

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

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

## 392 **3.2. Laboratory measurements at the University of Bern**

### 393 3.2.1. Measurements of standard gases

394 The performance of the instrument was tested by analyzing eight standard gases with  
395 precisely known CO<sub>2</sub> and O<sub>2</sub> compositions (Table 1) using the CRDS analyzer and comparing  
396 it to parallel measurements with a paramagnetic oxygen sensor (PM1155 oxygen transducer,  
397 Servomex Ltd, UK) embedded to a commercially available fuel cell oxygen analyzer  
398 (OXZILLA II, Sable Systems International, USA) (Sturm et al., 2006) as well as with an  
399 isotope ratio mass spectrometer (IRMS, Finnigan Delta<sup>Plus</sup>XP). The design of the  
400 measurement set-up is shown in Figure 11. Standard gases were directly connected to the  
401 pressure controlling unit, and a multi-port valve (V2) was used to select among the standard  
402 gases. Flow from each cylinder was adjusted to about 120 sccm which was eventually  
403 directed to a selection valve (V1), allowing switching between ambient air and standard gases.  
404 Flow towards and out of the fuel cell analyzer was controlled by the pressure controlling unit.

405 The O<sub>2</sub> mixing ratio of this incoming gas was first measured on the Paramagnetic O<sub>2</sub> sensor  
406 and then directed towards a non-dispersive infrared analyzer (NDIR) (Li-7000, LICOR, USA)  
407 for measuring CO<sub>2</sub> and H<sub>2</sub>O. The outflow from this analyzer (100 sccm) returns to the  
408 pressure controlling unit and was eventually divided between the CRDS analyzer (which uses  
409 about 75-80 sccm) and the IRMS (~ 20 sccm) via a Tee-junction. Each cylinder was measured  
410 for two hours in each system controlled by a LabView program.

411 First, we investigated the influence of this Tee-junction, which splits the gas flow  
412 between the CRDS and the IRMS, on the measured O<sub>2</sub> values. Manning (2001) showed that  
413 the fractionation of O<sub>2</sub> in the presence of a Tee-Junction is strongly dependent on the splitting  
414 ratios as well as temperature and pressure gradients. Hence, we measured and compared the  
415 O<sub>2</sub> mixing ratios of two standard gases (CA07045 and CA060943) in two cases: i) in the  
416 presence of a Tee-junction with different CRDS to IRMS splitting ratios and ii) without a  
417 Tee-junction so that all gas flow is directed towards the CRDS analyzer. The splitting ratios in  
418 these test experiments vary from 1:1 to 1:100, and reversed to change the major flow direction  
419 either to the CRDS or the IRMS. Note that the experimental condition in this manuscript is  
420 with a 4:1 splitting ratio (i.e. ~ 80 sccm towards the CRDS analyzer and ~ 20 sccm towards  
421 the IRMS).

422 In the cases of the smaller splitting ratios (1:1, 1:4 and 4:1), which are relevant for the  
423 results presented in this study, only minor differences in the measured O<sub>2</sub> mixing ratios were  
424 observed when compared to case ii (i.e. without a Tee-junction). For these two cylinders  
425 measured, the average differences in these cases were about 0.5 ppm, calculated as the mean  
426 of the differences in the raw O<sub>2</sub> measurements of the last 60 seconds. The negligible  
427 fractionation can indeed be the result of smaller splitting ratios while strong influence is  
428 usually expected in case of larger splitting ratios (Stephens et al., 2007). For higher splitting

429 ratios, the result seems inconclusive without any dependence on the ratios due to the strong  
430 decline in the cylinder temperature (specifically at the pressure gauge) caused by higher flow  
431 to achieve the higher splitting ratios (as high as 1:100). Hence, these tests need to be  
432 conducted in a temperature-controlled condition and the results could not be discussed in this  
433 manuscript.

434 Figure 12 shows the standard gas measurements for the seven cylinders with known  
435 CO<sub>2</sub> and O<sub>2</sub> mixing ratios (Table 1) using both the CRDS and the Paramagnetic analyzers.  
436 Standard eight, which has too high O<sub>2</sub>, is not shown in the figure as the figure is zoomed-in to  
437 better illustrate the change in O<sub>2</sub> for the remaining cylinders. While the first five cylinders  
438 contain O<sub>2</sub> and CO<sub>2</sub> mole fractions comparable to ambient air values, standards 6 & 8 had  
439 either very low or very high O<sub>2</sub>, respectively. In addition, standards 6 and 7 have very low and  
440 very high CO<sub>2</sub> mixing ratios. Note that due to its very high CO<sub>2</sub> content (~ 2700 ppm),  
441 standard 7 was not measured on the IRMS and hence the O<sub>2</sub> mixing ratio is unknown. The  
442 measured mixing ratios for the six standard gases measured with the two systems are in very  
443 good agreement while cylinder 7 showed an opposing signal for the two analyzers compared  
444 to standard 6 (Figure 12). While the Paramagnetic analyzer showed a higher O<sub>2</sub> mixing ratio,  
445 the values from the CRDS analyzer are lower in O<sub>2</sub>. This can be associated with the very high  
446 CO<sub>2</sub> mixing ratio in standard 7, which leads to a strong dilution effect in the CRDS analyzer  
447 as it does not include any correction function for dilution effect from CO<sub>2</sub>. However, such  
448 high CO<sub>2</sub> mixing ratios may not be that important for most atmospheric research. Yet, it  
449 should be considered to include a parallel CO<sub>2</sub> mixing ratios measurement to the instrument  
450 as it will further improve the accuracy. This would be especially important for biological or  
451 physiological studies where a wide range of CO<sub>2</sub> and O<sub>2</sub> concentrations must be expected.

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

458 We also made a correlation plot to see which of the two instruments are in better  
459 agreement with the assigned values based on IRMS measurements for the individual  
460 cylinders. While similar correlation coefficients were observed for both analyzers, different  
461 slopes were calculated (Fig. A.1). This is due to the fact that the IRMS measures the O<sub>2</sub> to N<sub>2</sub>  
462 ratio ( $\delta(\text{O}_2/\text{N}_2)$ ) in per meg, while the CRDS and the Paramagnetic analyzers provide non-  
463 calibrated O<sub>2</sub> mixing ratios in units of ppm and per meg, respectively. If we exclude the two  
464 standard gases with the highest and lowest O<sub>2</sub> mixing ratios (standards 7 and 8) that are  
465 subjected to strong dilution effects, both the slope and the  $r^2$  values decrease from those  
466 shown in Figure A.1. But this decrease is larger in the case of the Paramagnetic  
467 measurements, implying a slightly better linearity of the CRDS analyzer.

468 Furthermore, the slope between the IRMS and CRDS O<sub>2</sub> values in Figure A1  
469 corresponds to 5.78 per meg ppm<sup>-1</sup>, significantly larger than the conversion factor of 4.78 per  
470 meg ppm<sup>-1</sup> as derived from equation 1 assuming constant N<sub>2</sub> content. This higher slope is due  
471 to dilution effect originating from any gas component change (Delta, given in ppm) on all air  
472 components of air samples, which has not been corrected for the CRDS values. When  
473 accounting for this dilution effect - which scales with  $1/(1+\text{Delta})$ , the factor approaches 4.78  
474 per meg ppm<sup>-1</sup>. The scaling of dilution effects is independent on which air component is  
475 changing and it affects all air components relative to their molecular fractions similarly. O<sub>2</sub>

476 values on a CRDS or paramagnetic cell instrument is affected even if there is no change in O<sub>2</sub>  
477 or N<sub>2</sub> but only in CO<sub>2</sub> or water vapor or any other component which is present. This is in  
478 contrast to measurements of O<sub>2</sub>/N<sub>2</sub> ratios for the same case where equal ratio would be  
479 measured. Major dilution influences are expected from O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O changes due to  
480 natural exchange processes on air samples or when using artificial air-like compositions.

### 481 3.2.2. Measurements of ambient air

482 Ambient air measurements were conducted from the roof top of our laboratory at the  
483 University of Bern to evaluate the analyzer's performance under atmospheric variability.  
484 Ambient air was continuously aspirated from the inlet at the roof of the building at a flow rate  
485 of ~ 250 sccm which is then dried using a cooling trap kept at -90 °C towards the switching  
486 valve (V1) and measured in similar way to the standard gases as explained above. The  
487 measurement values obtained here were compared with the parallel measurements by the  
488 Paramagnetic sensor to test the instruments stability and accuracy.

489 Figures 13 panels a &b show the 1-minute average ambient air measurements from the  
490 rooftop inlet by the Paramagnetic and the CRDS analyzers at the beginning of the testing  
491 period including standard gases measured every 12-hour. While the Paramagnetic analyzer  
492 seems to be stable, the CRDS analyzer showed a strong drift for an extended period. This can  
493 be due to unstable conditions in the CRDS measurement system as it started operating right  
494 after it was unpacked. Hence, we looked into temperature inside the instrument chassis and  
495 pressure records, which were stable within the manufacturer's recommended range during this  
496 period. As the CRDS analyzer incorporates a water correction function, interference from this  
497 species should be well accounted. Even comparing the analyzer's parallel water  
498 measurements to water measurements by the NDIR system such a drift was not observed. It  
499 should be noted that the two internal standard gases which were less frequently measured

500 (every 12 hours) during this period were also drifting following similar pattern. This implies  
501 that the drift is associated with the analyzer. Interestingly, this pattern can be modeled using a  
502 polynomial function which can then be used to correct for the observed drift in the ambient air  
503 measurements. After applying a polynomial drift correction, we were able to fully accounted  
504 for the observed drift. However, the manufacturer decided to further investigate possible  
505 causes of this drift. After further improvements, we obtained the first commercial analyzer in  
506 September 2017 and repeated the above tests (Figure 13 c &d). No such drift was observed  
507 any more in the standard gases or in ambient air measurements.

508 We believe that the optical amplifier has caused the drift in the first system and not anymore  
509 included in the design of the product which produced a significant amount of broadband light  
510 that could fill the cavity (albeit with a low coupling coefficient), and would ring down with a  
511 different (and generally much faster) time constant than the baseline loss of the cavity.  
512 However, the ringdown time on the peak of the oxygen line is just 10 microseconds, such that  
513 the broadband light might have distorted the single exponential decay of the central laser  
514 frequency, leading to the observed drift in the oxygen signal. However, we were not able to  
515 confirm this hypothesis.

### 516 3.2.3. Water correction test

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

$$521 \quad O_{2,dry} = \frac{O_{2,raw}}{1-H_2O} \quad (5)$$

522 where  $H_2O$  is the measured water mole fraction.

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

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

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



547 In the first period of the measurement when both analyzers measured dried ambient  
548 air, the absolute differences between the 1-minute averages measured over two days by the  
549 two analyzers were mostly within 15 ppm (Figure 15c) and symmetrically distributed around  
550 zero (Figure 15e). However, when wet air was admitted to the CRDS analyzer and the in-built  
551 water correction was applied, a stronger variability was observed in the calculated differences  
552 (Figure 15d). This implies stronger short term variability in the CRDS analyzer measurement  
553 values (as nothing was changed for the Paramagnetic measurement system) when wet samples  
554 were analyzed. The more negative values in the differences (Figure 15f) can also be  
555 associated with overestimation of the O<sub>2</sub> mixing ratios by the CRDS originating from an  
556 overestimated water correction. However, detailed evaluation of the analyzer's water  
557 correction function is beyond the scope of this study.

### 558 **3.3. Field Measurements**

559 After a series of tests at University of Bern, we conducted multiple field measurements  
560 at the High Altitude Research Station Jungfrauoch and the Beromünster tall tower sites in  
561 Switzerland described below.

#### 562 **3.3.1. Tests at the High Altitude Research station Jungfrauoch**

563 The High Alpine research station Jungfrauoch is located on the northern ridge of the  
564 Swiss Alps (46° 33' N, 7° 59' E) at an elevation of 3580 m a.s.l. It is one of the global  
565 atmospheric watch (GAW) stations well-equipped for measurements of numerous species and  
566 aerosols. The site is above the planetary boundary layer most of the time due to its high  
567 elevation (Henne et al., 2010; Zellweger et al., 2003). However, thermally uplifted air from  
568 the surrounding valleys during hot summer days or polluted air from the heavily industrialized  
569 northern Italy may reach at this site (Zellweger et al., 2003). The Division of Climate and  
570 Environmental Physics at the University of Bern has been monitoring CO<sub>2</sub> and O<sub>2</sub> mixing

571 ratios at this site based on weekly flask sampling and continuous measurements since 2000  
572 and 2004, respectively (Schibig et al., 2015). The CO<sub>2</sub> mixing ratio is measured using a  
573 commercial NDIR analyzer (S710 UNOR, SICK MAIHAK) while O<sub>2</sub> is measured using the  
574 Paramagnetic sensor (PM1155 oxygen transducer, Servomex Ltd, UK) and fuel cells (Max-  
575 250, Maxtec, USA) installed inside a home-built controlling unit. Similar to the comparison  
576 tests at the University of Bern, we have conducted parallel measurements between the CRDS  
577 analyzer and the paramagnetic cell at this high altitude site during 03 – 14 February 2017. The  
578 measurement of ambient air at the Jungfrauoch system is composed of sequential switching  
579 between low span (LS) and high span (HS) calibration gases followed by a target gas (T)  
580 measurement (once a day) to evaluate the overall system performance and finally a working  
581 gas (WG) measurement before switching back to ambient air.

582         Figure 16 (top panel) shows the calibrated 1-minute averaged O<sub>2</sub> mixing ratios  
583 measured at this high altitude site in comparison with the Paramagnetic oxygen analyzer  
584 already available at the site. Despite the strong variability observed during the measurement  
585 period of 10-days by both analyzers, a very good agreement was observed between them.

586         Figure 16 (bottom panel) shows the absolute difference of 1-minute averages in  
587 atmospheric O<sub>2</sub> measured at Jungfrauoch between the two analyzers which are mostly within  
588 ±5 ppm range (but sometimes going as high as ±10 ppm) without an offset. However, for  
589 generally reported 10-minutes, half-hourly or hourly means these values correspond to < 1.5  
590 ppm, < 1 ppm and < 0.65 ppm.

### 591 3.3.2. Tests at the Beromünster tall tower site

592         The Beromünster tower is located near the southern border of the Swiss Plateau, the  
593 comparatively flat part of Switzerland between the Alps in the south and the Jura mountains  
594 in the northwest (47° 11' 23" N, 8° 10' 32" E, 797 m a.s.l.), which is characterized by intense

595 agriculture and rather high population density. A detailed description of the tower  
596 measurement system as well as a characterization of the site with respect to local  
597 meteorological conditions, seasonal and diurnal variations of greenhouse gases, and regional  
598 representativeness can be obtained from previous publications (Berhanu et al., 2016; Berhanu  
599 et al., 2017; Oney et al., 2015; Satar et al., 2016). The tower is 217.5 m tall with access to five  
600 sampling heights (12.5 m, 44.6 m, 71.5 m, 131.6 m, 212.5 m) for measuring CO, CO<sub>2</sub>, CH<sub>4</sub>  
601 and H<sub>2</sub>O using Cavity Ring Down Spectroscopy (Picarro Inc., G-2401). By sequentially  
602 switching from the highest to the lowest level, mixing ratios of these trace gases were  
603 recorded continuously for three minutes per height, but only the last 60 seconds were retained  
604 for data analysis. The calibration procedure for ambient air includes measurements of  
605 reference gases with high and low mixing ratios traceable to international standards (WMO-  
606 X2007 for CO<sub>2</sub> and WMO-X2004 for CO and CH<sub>4</sub>), as well as target gas and more frequent  
607 working gas determinations to ensure the quality of the measurement system. From two years  
608 of data a long-term reproducibility of 2.79 ppb, 0.05 ppm, and 0.29 ppb for CO, CO<sub>2</sub> and  
609 CH<sub>4</sub>, respectively was determined for this system (Berhanu et al., 2016).

610         Between 15.02.2017 and 02.03.2017, we have connected the new CRDS oxygen  
611 analyzer in series with the CO<sub>2</sub> analyzer (Picarro G-2401) and measured the O<sub>2</sub> mixing ratios  
612 at the corresponding heights. Similar to the CO<sub>2</sub> measurements, O<sub>2</sub> was also measured for  
613 three minutes at each height. During this period, we have evaluated the two features (isotopic  
614 mode and concentration mode) of the CRDS analyzer. In the isotopic mode, the CRDS  
615 measures the  $\delta^{18}\text{O}$  values as well as the O<sub>2</sub> concentration while in concentration mode only  
616 the latter was measured.

617         During the tests conducted at this tower site, we first evaluated the two operational  
618 modes (concentration vs isotopic modes) of the CRDS analyzer. Ambient air measurements

619 on isotopic mode over a 4-days period showed a strong variability in the measured oxygen  
620 mixing ratios and it was not possible to distinguish the variability in the O<sub>2</sub> mixing ratios  
621 among the five height levels. The calculated 1-minute standard error for ambient air  
622 measurements was as high as 10 ppm while a standard error of less than 1 ppm was  
623 determined from similar measurements in the concentration mode. Additionally, comparing  
624 the O<sub>2</sub> values between the two modes, frequent short time variation in ambient air O<sub>2</sub> (~ 200  
625 ppm) was observed in the isotope mode measurements while the variation in the concentration  
626 mode is significantly smaller (~ 30 ppm). This precision degradation is due to the weaker <sup>16</sup>O  
627 oxygen line used for the isotopic mode, and the fact that far more ring-downs are collected on  
628 the rare isotopologue in isotopic mode. Hence, we have conducted the remaining test  
629 measurements in concentration mode.

630 As this tower has five sampling height levels, we first followed three minutes of  
631 switching per inlet level, which enables four measurements per hour at a given level.  
632 However, we noticed hardly any difference among the different levels due to strong short  
633 term variability in O<sub>2</sub> mixing ratios between the consecutive heights. Hence, we switched to a  
634 longer sampling period of six-minutes per height. Figure 17 shows the diurnal CO<sub>2</sub> and O<sub>2</sub>  
635 variations at the lowest (12 m) and highest (212.5 m) sampling heights of the tower. These  
636 two heights were selected simply to better illustrate the difference in the mixing ratios. The  
637 CO<sub>2</sub> mixing ratios on the top panel show higher values at the 12 m inlet than the highest level  
638 most of the day due to its closeness to sources except during the afternoon (11:00 - 17:00  
639 UTC) when both levels show similar but decreasing CO<sub>2</sub> mixing ratios. This is due to  
640 presence of a well-mixed planetary boundary layer (PBL) (Satar et al., 2016). The lag in CO<sub>2</sub>  
641 peak between the two height levels by about two hours indicates the duration for uniform  
642 vertical mixing along the tower during winter 2017. The opposite variability patterns are also

643 clearly visible in the O<sub>2</sub> mixing ratios shown in the lower panel with a clear distinction  
644 between the two height levels during early in the morning and in the evening while similar O<sub>2</sub>  
645 values were observed in the afternoon. These opposing profiles are expected as CO<sub>2</sub> and O<sub>2</sub>  
646 are linearly coupled with a mean oxidation ratio of  $-1.1 \pm 0.05$  (Severinghaus, 1995) for land-  
647 biospheric processes (photosynthesis and respiration) and  $-1.44 \pm 0.03$  for fossil fuel burning  
648 (Keeling, 1988b).

649 Table 2 shows the oxidation ratios derived as the slopes of the linear regression  
650 between CO<sub>2</sub> and O<sub>2</sub> mixing ratios at the different height levels measured on 25 February  
651 2017. Accordingly, height dependent slopes were observed with a slope of  $-0.98 \pm 0.06$  at the  
652 lowest level, close to the biological processes induced slope but slightly lower than its mean  
653 value. For the highest level, we calculated a slope of  $-1.60 \pm 0.07$  a value close to fossil fuel  
654 combustion oxidation ratio. Note that depending on fossil fuel type the oxidation ratio can  
655 range between  $-1.17$  and  $-1.95$  for coal and natural gas, respectively (Keeling, 1988b). While  
656 the slopes derived for the two other levels (44.6 m and 131.6 m) show similar values between  
657 the highest and lowest height levels, possibly from mixed sources, the middle level showed a  
658 slightly higher slope than these two levels but still in the large range between the lowest and  
659 highest inlet heights.

#### 660 3.4. Evaluation of the $\delta^{18}\text{O}$ measurements

661 To further evaluate the analyzer's performance in measuring stable oxygen isotopes,  
662 we conducted ambient air isotopic composition measurements as well as analyzed a standard  
663 gas without CO<sub>2</sub> which has a known  $\delta^{18}\text{O}$  value. The choice of this CO<sub>2</sub>-free air standard gas  
664 is twofold: one it has a known  $\delta^{18}\text{O}$  value and second as it has no interference from possible  
665 CO<sub>2</sub> absorption band overlap. For this test three 0.5 L glass flasks were preconditioned and  
666 filled with this standard gas to ambient pressure. These flasks were attached before or after

667 the water trap (Fig. 11) and measured similar to ambient air measurements. These  
668 measurements were then compared with  $\delta(^{34}\text{O}/^{32}\text{O})$  values obtained by parallel measurements  
669 using our IRMS.

670 Figure 18 shows the  $\delta^{18}\text{O}$  values of ambient air from the roof top with three  
671 consecutive measurements of glass flasks filled with  $\text{CO}_2$ -free air in-between followed by a  
672 fourth flask filled with breath air. An excellent agreement was observed for measurements  
673 from both instruments for the three flasks filled with a standard gas. However, the fourth flask  
674 with breath air showed a signal opposite to the measurements by the IRMS. As breath air  
675 contains large amount of water and  $\text{CO}_2$  in addition to  $\text{O}_2$ , which can possibly interfere with  
676 the CRDS analyzer measurements, we have removed  $\text{H}_2\text{O}$  and  $\text{CO}_2$  by using a cryogenic trap  
677 ( $-130\text{ }^\circ\text{C}$ ) and in an additional experiment using Schütze reagent to remove both  $\text{CO}$  and  $\text{CO}_2$ .  
678 However, we have not observed any improvement towards an agreement with the IRMS  
679 measurements. Therefore, any other gas component in the breath air must be relevant for the  
680 interference. Based on the absorption lines in the spectral range of the instrument ( $7878\text{ cm}^{-1}$ )  
681 retrieved from HITRAN database, we expect interference either from carbon monoxide (now  
682 excluded by the tests) or methane or VOCs including acetone, ethanol, methanol or isoprenes,  
683 all of which have been measured in breath air (Gao et al., 2017; Gottlieb et al., 2017; McKay  
684 et al., 1985; Ryter and Choi, 2013; Wolf et al., 2017). Further investigations have to shed light  
685 on these interferences in order to take corresponding action to surpass these shortcomings in  
686 the isotope analysis based on cavity ring-down spectroscopy.

#### 687 **4. Conclusions**

688 We have thoroughly evaluated the performance of a new CRDS analyzer which  
689 measures  $\text{O}_2$  mixing ratios and isotopic composition combining laboratory and field tests.  
690 Even if a drift in the analyzer was observed at the beginning of this study, which can be easily

691 corrected by calibration, the recent analyzers built by the manufacturer did not show such  
692 instrumental drift. However, prior tests are recommended to see the analyzer's stability.

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

697 We have observed a strong influence of dilution in the measured O<sub>2</sub> values during the  
698 presence of high CO<sub>2</sub> mixing ratios. Even if such an influence may not be critical for the  
699 present study, such an effect might be significant in other studies where higher CO<sub>2</sub> mixing  
700 ratios might be present and we recommend following a correction strategy based on parallel  
701 CO<sub>2</sub> measurements. This also applies for more accurate analysis.

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

709 Based on the analysis of O<sub>2</sub> mixing ratios in the concentration and isotopic modes, we  
710 have observed a significant decrease in precision (about ten-fold) in the latter measurement  
711 mode. The measured  $\delta^{18}\text{O}$  values for the standard air by the CRDS analyzer are in excellent  
712 agreement with the IRMS values. However, such measurements for a breath air showed a  
713 contrasting signal, possibly due to interference from other gases such as CH<sub>4</sub>. Hence, we  
714 recommend further investigation on such possible contaminants and how to possibly remove

715 them while conducting ambient air measurements. However, we believe that this analyzer can  
716 be used for tracer experiments where artificially enriched isotopes are used to study biological  
717 processes such as photosynthesis in plants using isotopically labelled CO<sub>2</sub> and H<sub>2</sub>O.

## 718 **Acknowledgement**

719 We would like to thank ICOS-RI and the Swiss National Science Foundation (SNF) for  
720 funding ICOS-CH (20FI21\_148994, 20FI21\_148992). We are also grateful to the  
721 International Foundation High Alpine Research Stations Jungfraujoch and Gornergrat. The  
722 measurement system at the Beromünster tower was built and maintained by the CarboCount-  
723 CH (CRSII2\_136273) and IsoCEP (200020\_172550) projects both funded by SNF.

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## 733 List of Tables

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



Cylinder name	Assigned CO <sub>2</sub> (ppm) <sup>1</sup>	Assigned O <sub>2</sub> (per meg) <sup>1</sup>	CO <sub>2</sub> -IRMS (ppm) <sup>2</sup>	CO <sub>2</sub> -NDIR (ppm) <sup>2</sup>	O <sub>2</sub> -IRMS (per meg) <sup>2</sup>	O <sub>2</sub> -Paramagnetic (per meg) <sup>2</sup>	O <sub>2</sub> -CRDS (per meg) <sup>2</sup>
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) <sup>3</sup>	302	281
ST-4 CA07043-Scripps	390.528	-476.4	390.69	390.15	71 (-479.5) <sup>3</sup>	66	63
ST-5 CA07047-Scripps	374.480	-807.7	374.70	374.17	-253 (-803.3) <sup>3</sup>	-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

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741

742 Table 2. The CO<sub>2</sub> and O<sub>2</sub> correlation coefficients at the different height levels derived using  
743 the least square fit and the correlation coefficients ( $r^2$ ). Uncertainties are calculated as  
744 standard error of the slope.

Height	Oxidation Ratios (O <sub>2</sub> :CO <sub>2</sub> )
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)

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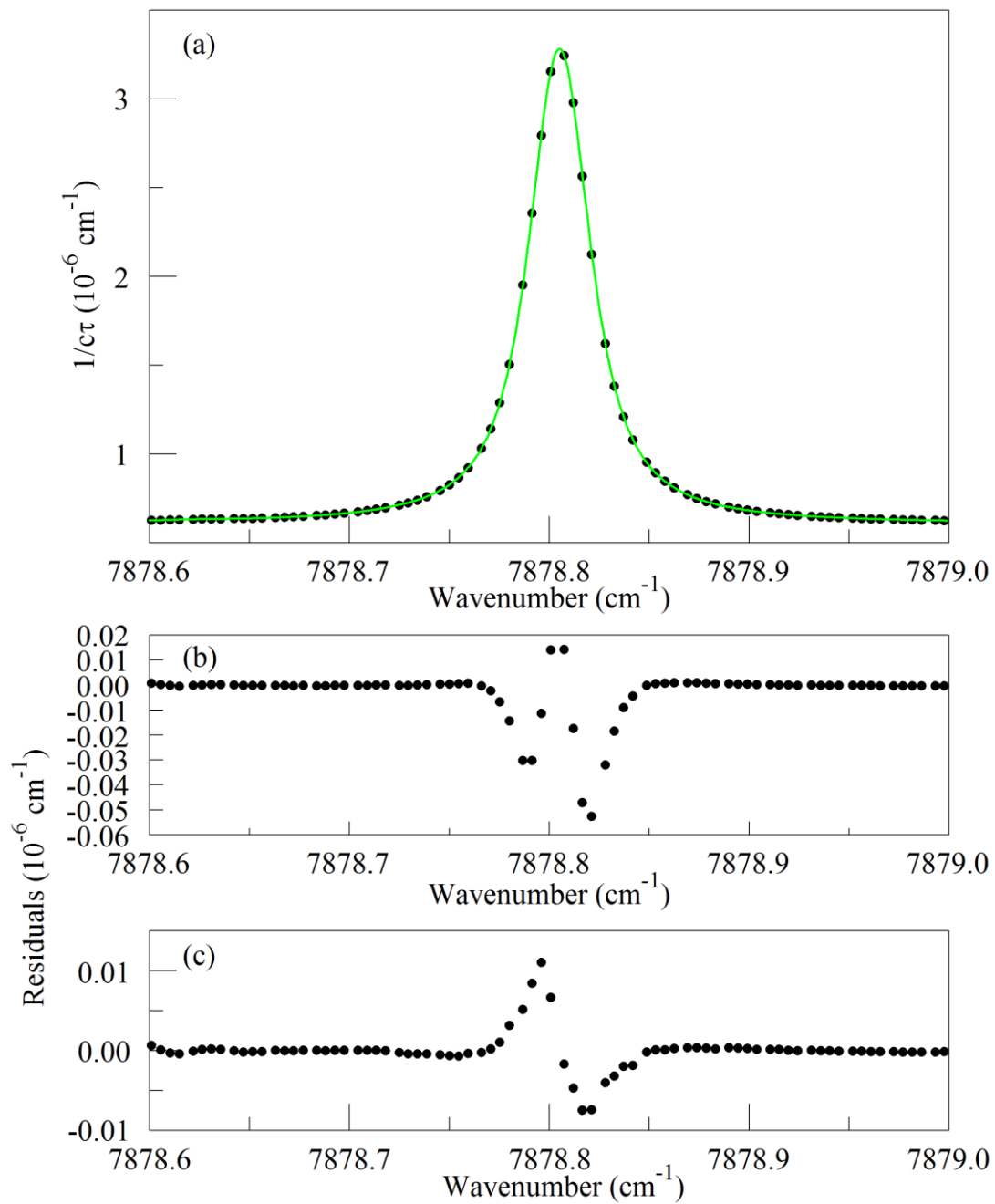
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753 List of Figures



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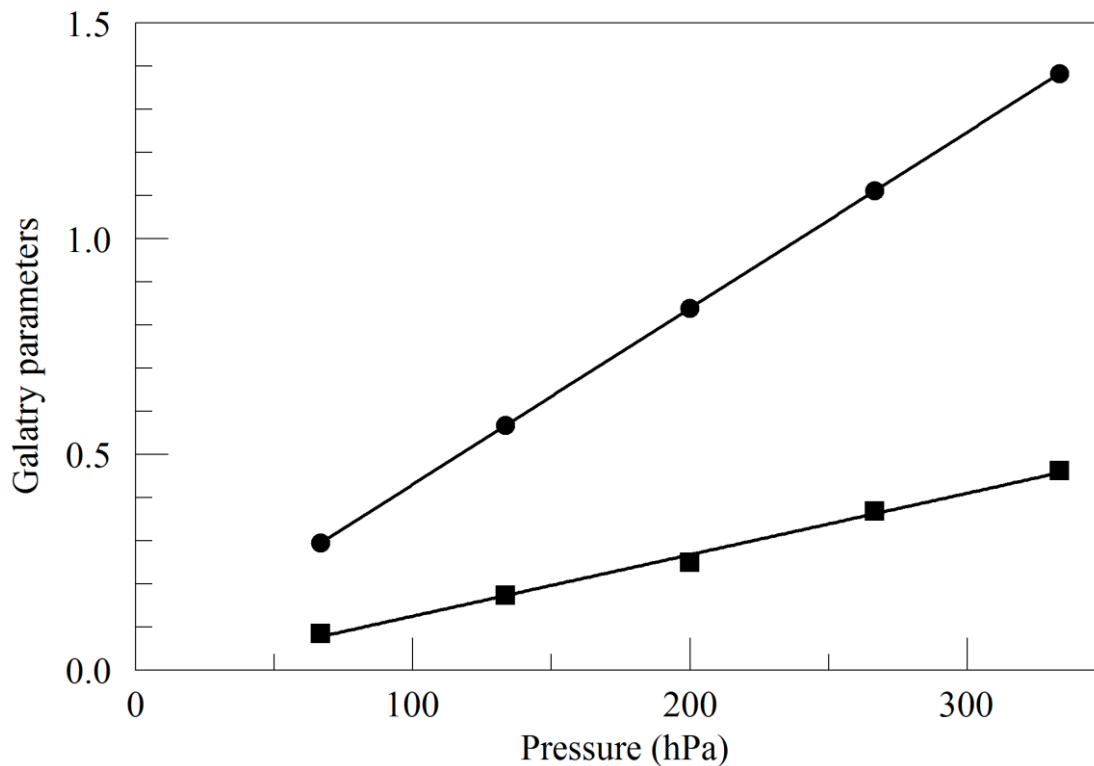
755 Figure 1. The top panel (a) shows the raw data (points) and the best-fit Galatry function (solid

756 line). Residuals of the Voigt fit are shown in panel (b) and residuals of the Galatry fit are

757 shown in panel (c).

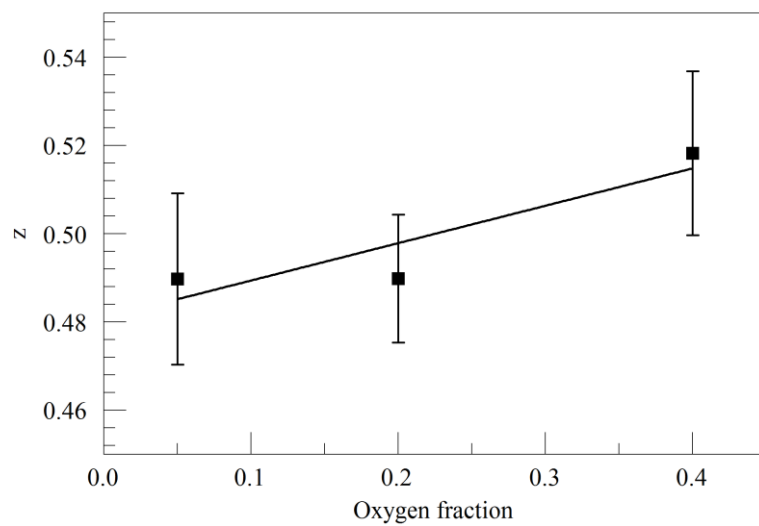
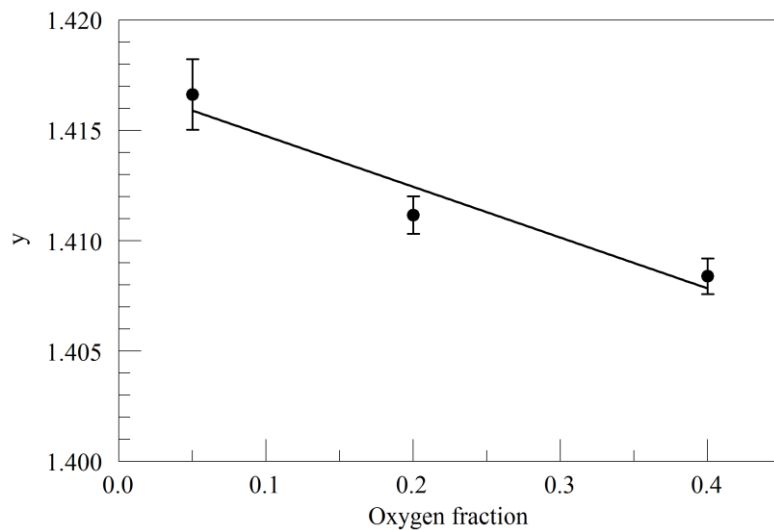
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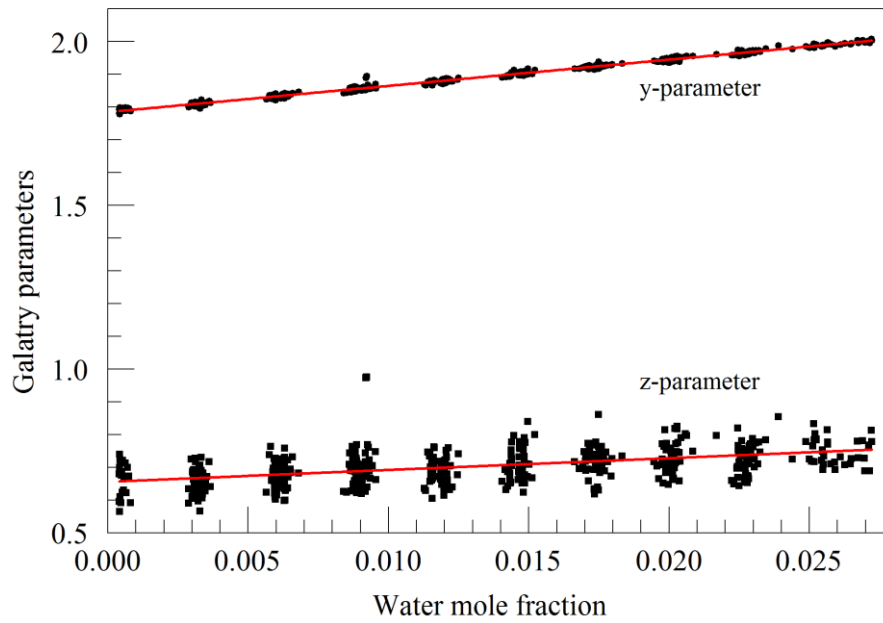
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761 Figure 2. Best-fit values for the Galatry parameters of the Q13Q13 line of O<sub>2</sub>, as a function of  
 762 pressure. The line broadening parameter  $y$  is represented by circles and the line narrowing  
 763 parameter  $z$  by squares. The solid lines are linear fits to the measurements. The best-fit offset  
 764 and slope are 0.0227 and 0.004082 hPa<sup>-1</sup> for  $y$ , and -0.0169 and 0.001424 hPa<sup>-1</sup> for  $z$ .



765

766 Figure 3. Galatry parameters of the Q13Q13 line of O<sub>2</sub> at 340 hPa and 45° C as a function of  
 767 O<sub>2</sub> mole fraction in binary O<sub>2</sub> - N<sub>2</sub> mixtures. The linear fits to the data are  $y = 1.417 - 0.023 x$   
 768  $f_{O_2}$  and  $z = 0.481 + 0.085 x f_{O_2}$ .



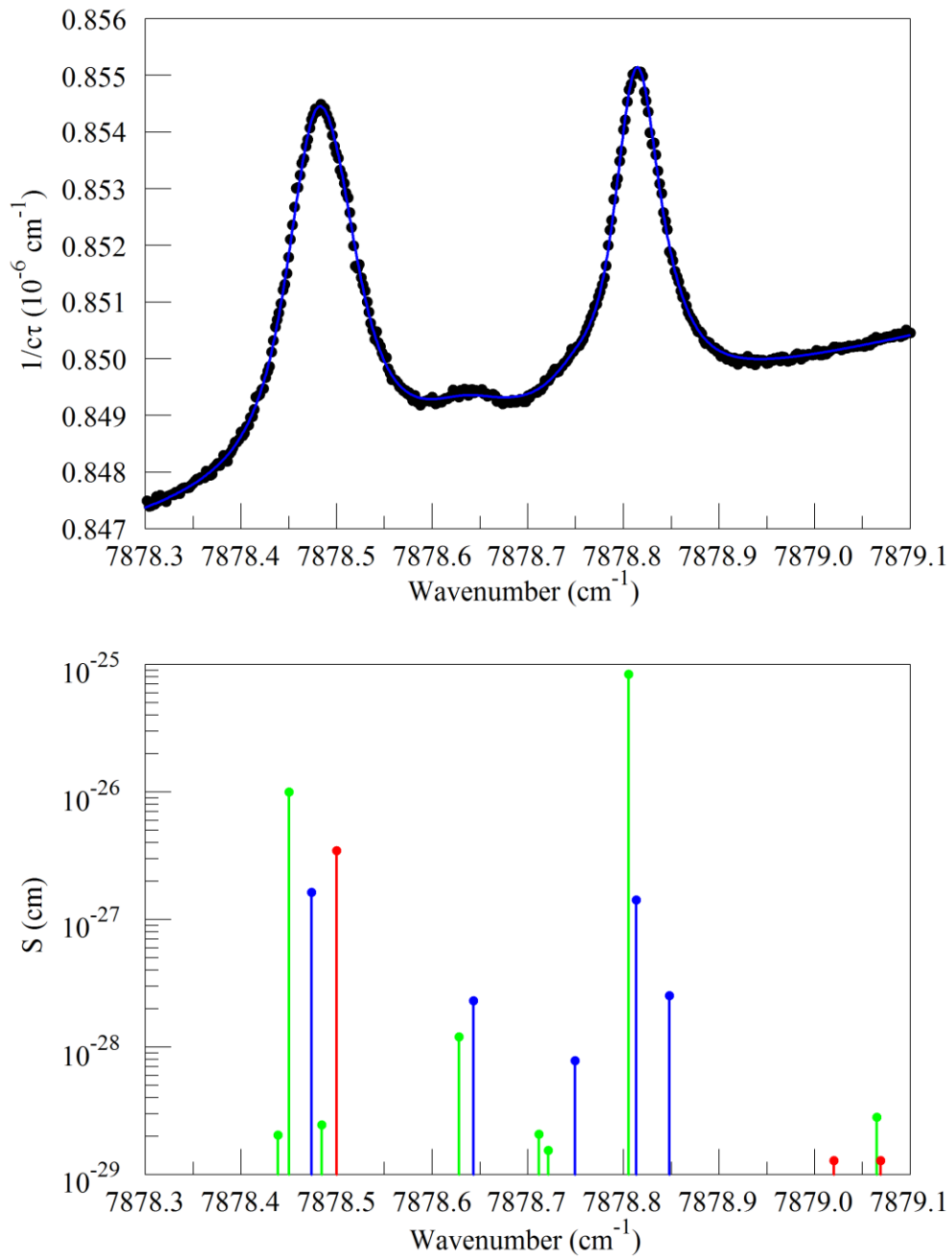
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770 Figure 4. Galatry parameters of the  $7816.75210 \text{ cm}^{-1}$  water line in air at 340 hPa and  $45^\circ \text{ C}$  as  
 771 a function of water mole fraction. Black points are from measurements and red lines are  
 772 linear fits:  $y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

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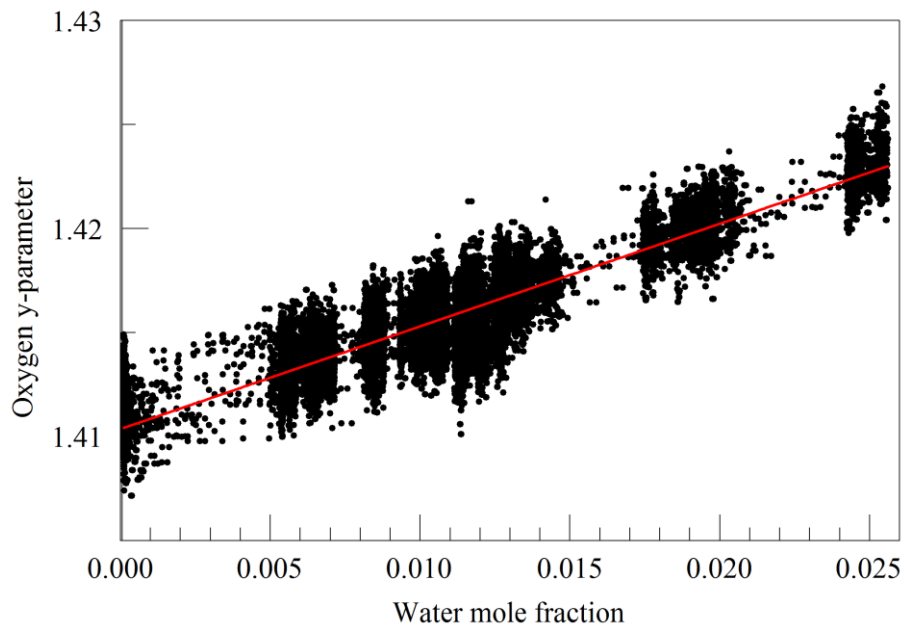
777 Figure 5. Upper panel: spectrum of water in nitrogen (points) and fit to Voigt model (blue

778 curve). Lower panel: Oxygen (green), normal water (blue), and deuterated water (red) lines

779 in the 2016 Hitran data base.

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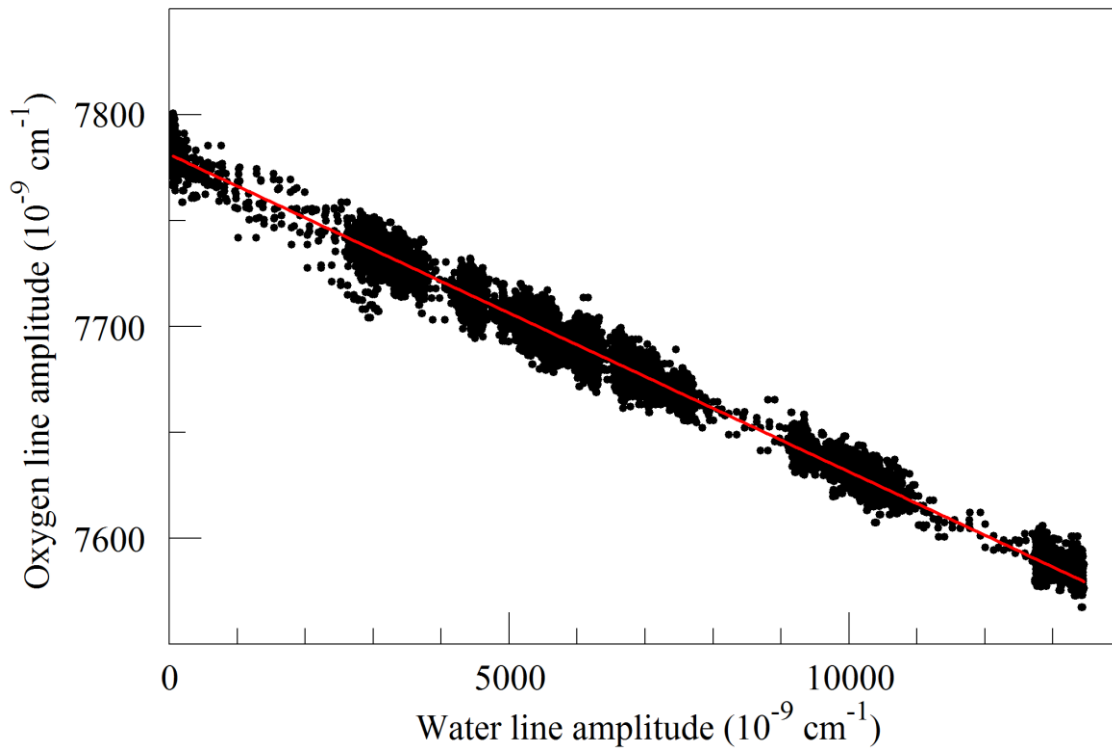
783 Figure 6. Galatry collisional broadening parameter of the oxygen Q13Q13 line at 340 hPa  
784 and 45° C versus water mole fraction. Black points are from measurements and the red line is  
785 a linear fit:  $y = 1.4109 + 0.467 f_{\text{H}_2\text{O}}$ .

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

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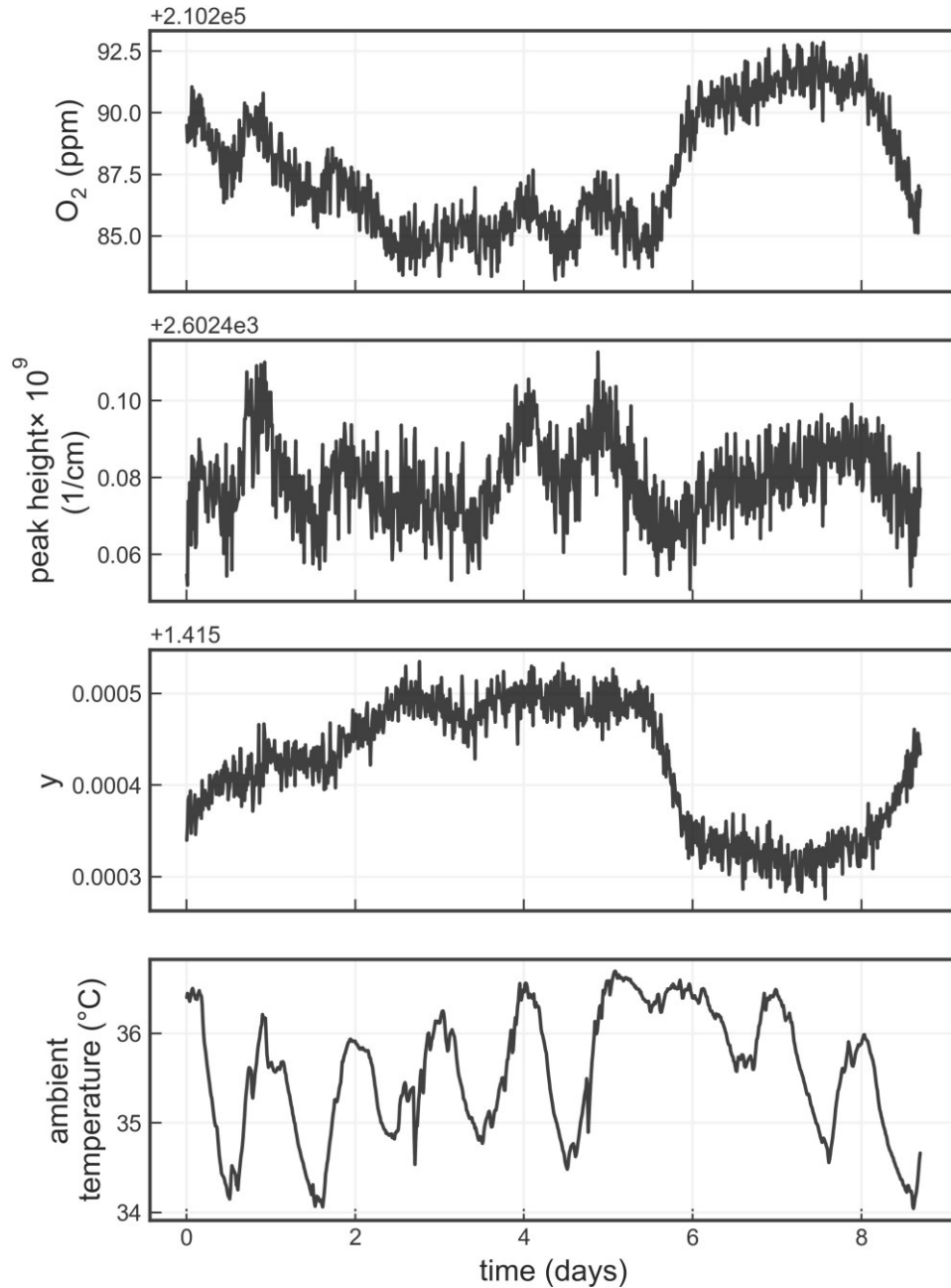
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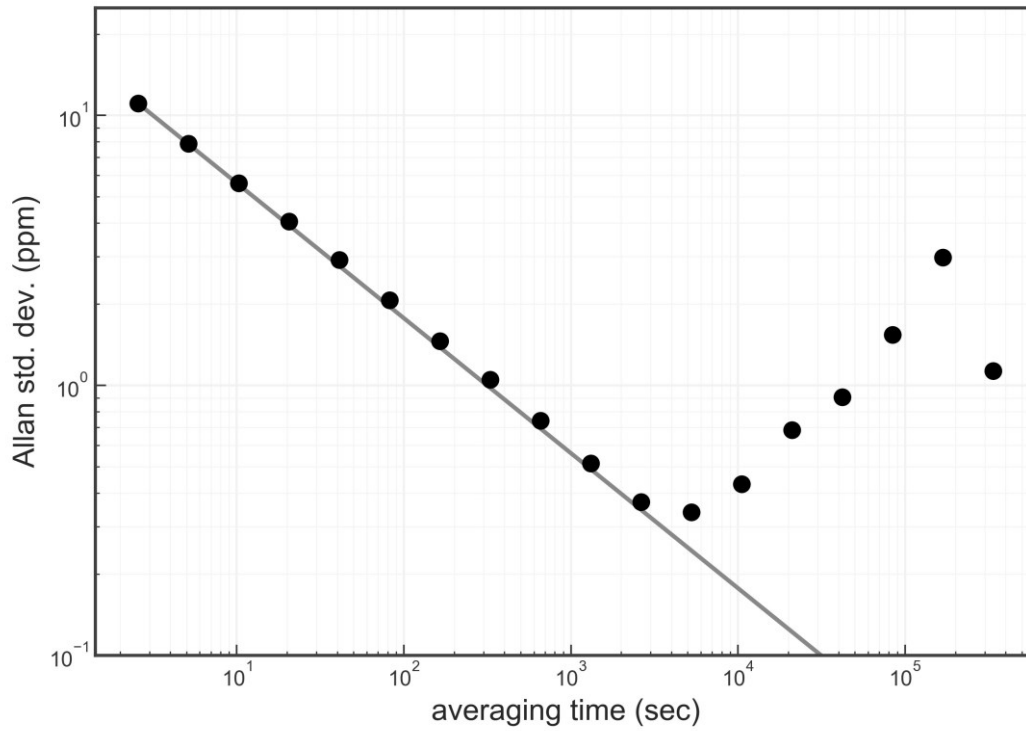
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800 Figure 8. Time series from a measurement of a single tank over about a week. The four panels  
 801 show the water-corrected oxygen concentration, the absorption peak loss minus the baseline  
 802 loss, the measured Lorentzian broadening factor,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



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806 Figure 9. Precision of O<sub>2</sub> mole fraction measured from a tank of synthetic air. Filled circles

807 are measurements and the line shows the ideal  $\tau^{-1/2}$  dependence.

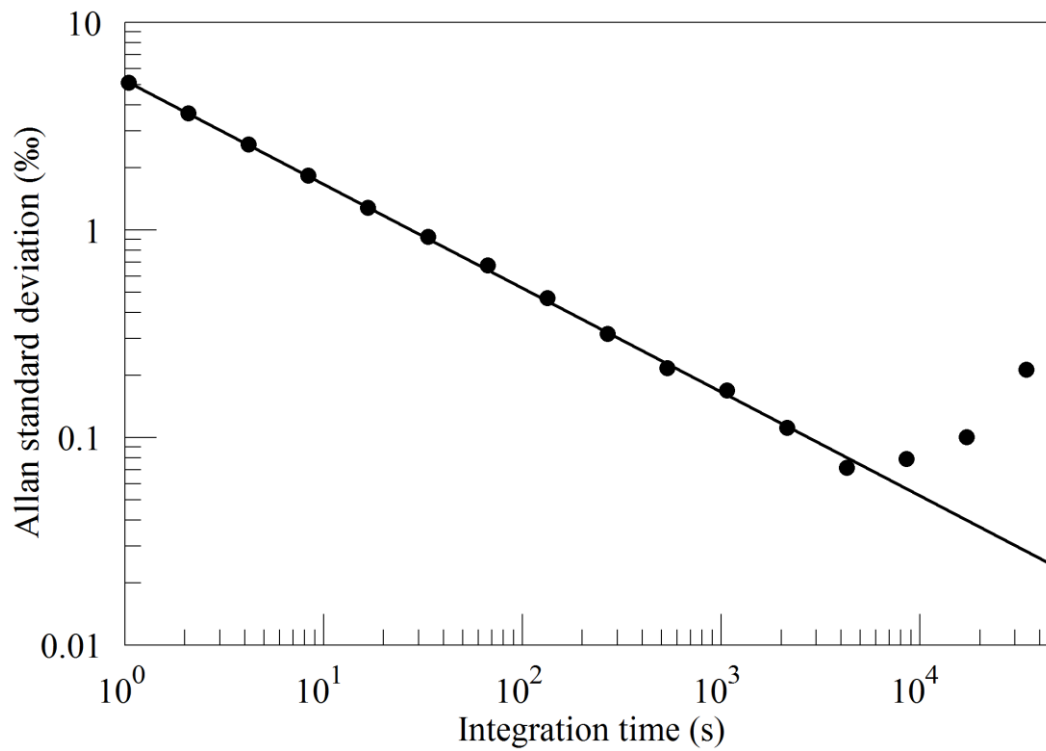
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814 Figure 10. Precision of  $\delta(^{18}\text{O})$  measured from a tank of synthetic air. Filled circles are

815 measurements and the line shows the ideal  $\tau^{-1/2}$  dependence.

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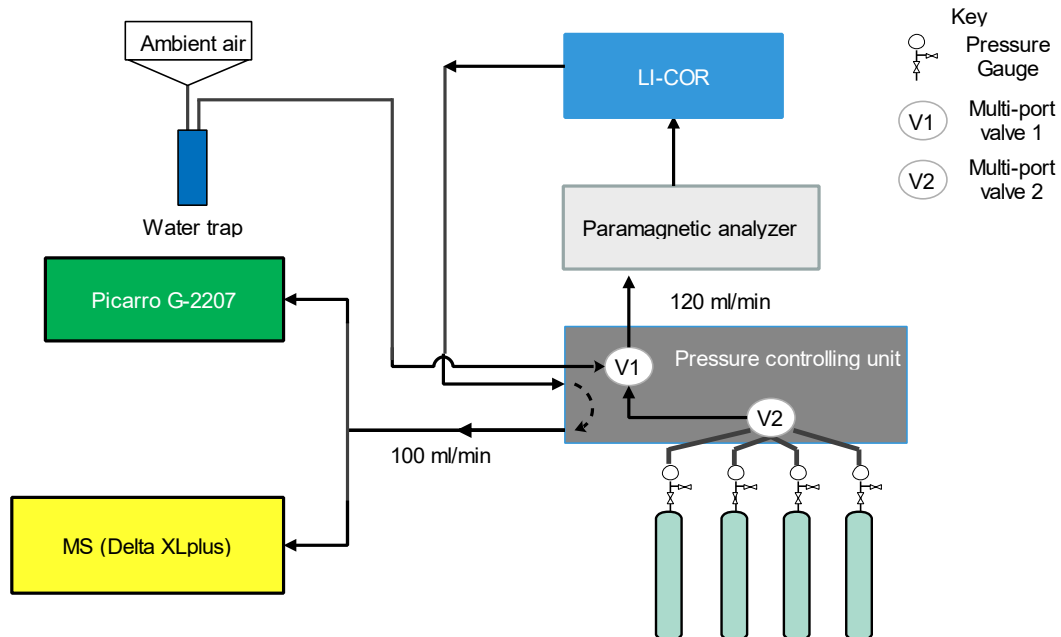
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825 Figure 11. Schematics of the measurement system used to compare the Picarro analyzer with  
 826 the Mass Spectrometer at Bern.

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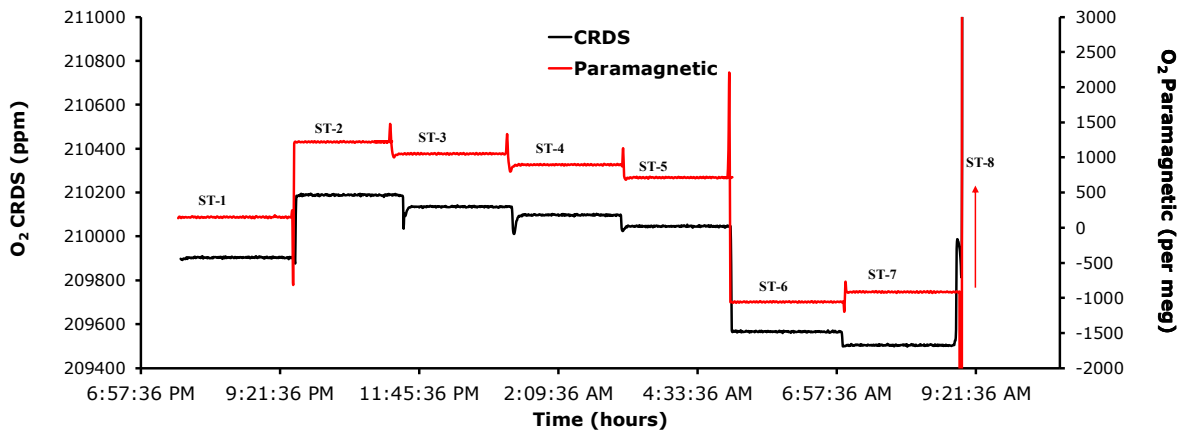
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837 Figure 12. Comparison of oxygen mixing ratios for the seven standard gases measured using  
 838 the CRDS analyzer (black) and the Paramagnetic sensors (red).

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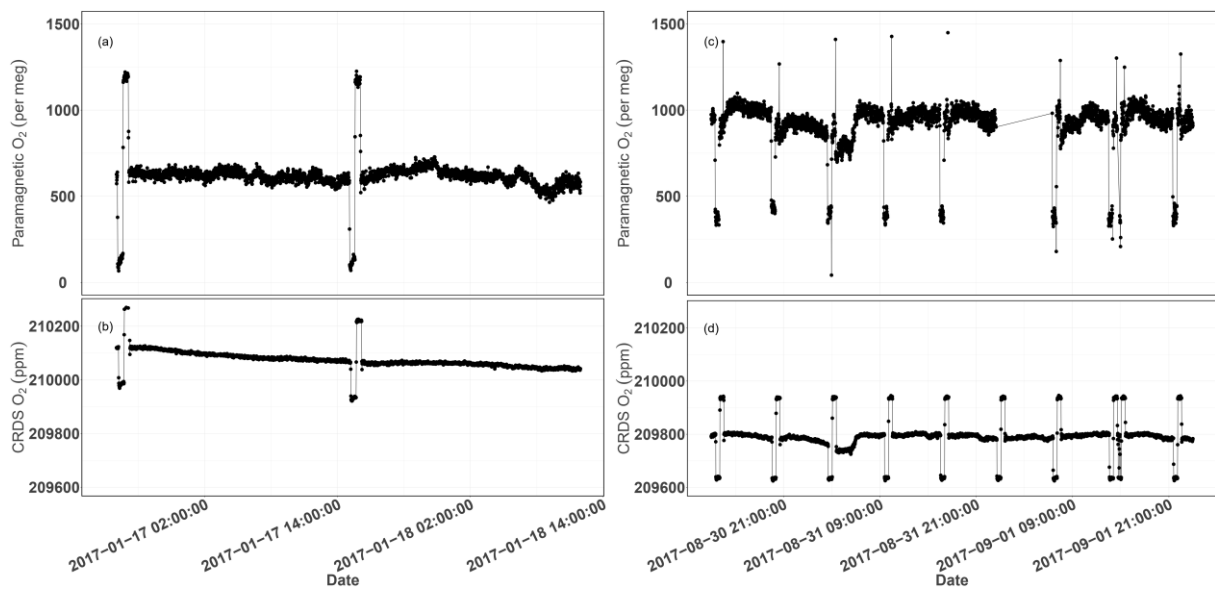
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856 Figure 13. Parallel ambient air measurements by the Paramagnetic and CRDS analyzers at the  
857 beginning of the testing period (Panels a & b, January 2017) and the second phase of testing  
858 (Panels c & d, September 2017). The spikes are measurements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

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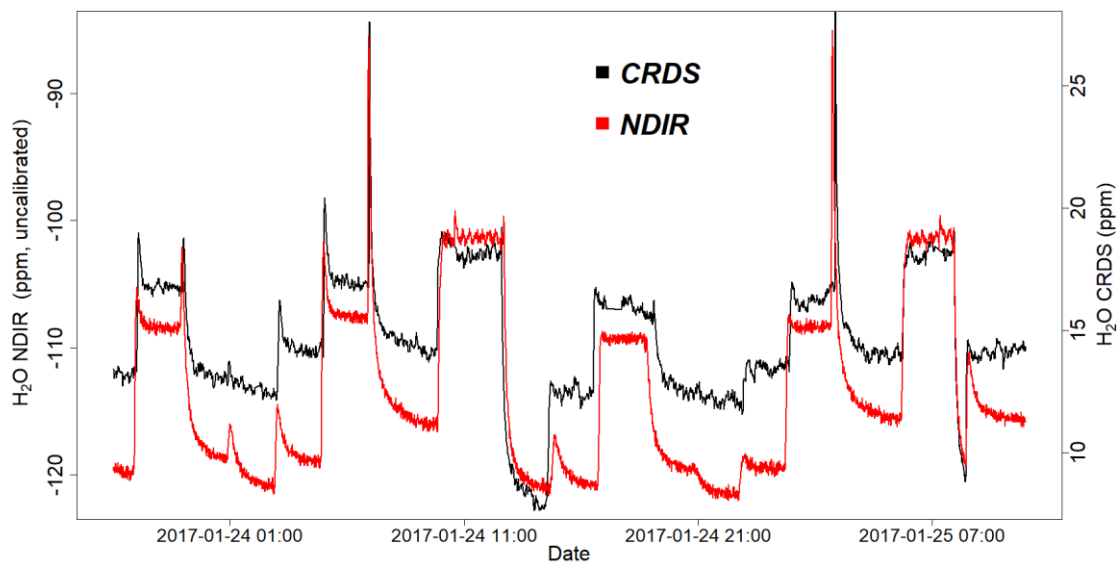
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873 Figure 14. Parallel water vapor measurements for a dried ambient air by both the NDIR and  
874 CRDS analyzers. Note that the water values from the NDIR analyzer are not calibrated.

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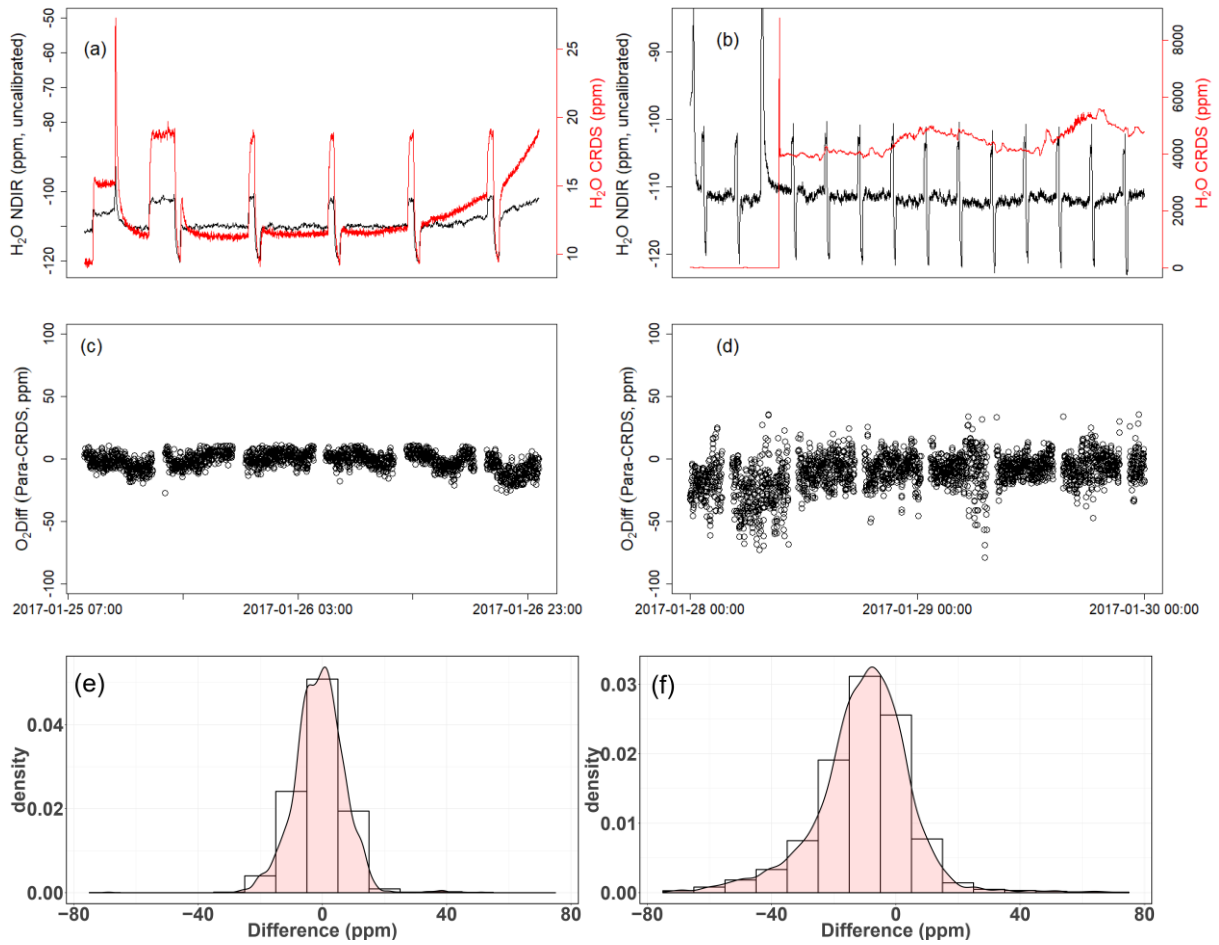
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890 Figure 15. Results of water correction tests. Water measurements of the NDIR (left scale) for  
891 dry conditions (a,b) and the CRDS analyzer (right scale) for dry (a) and wet (b) conditions.  
892 The difference in oxygen measurements between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

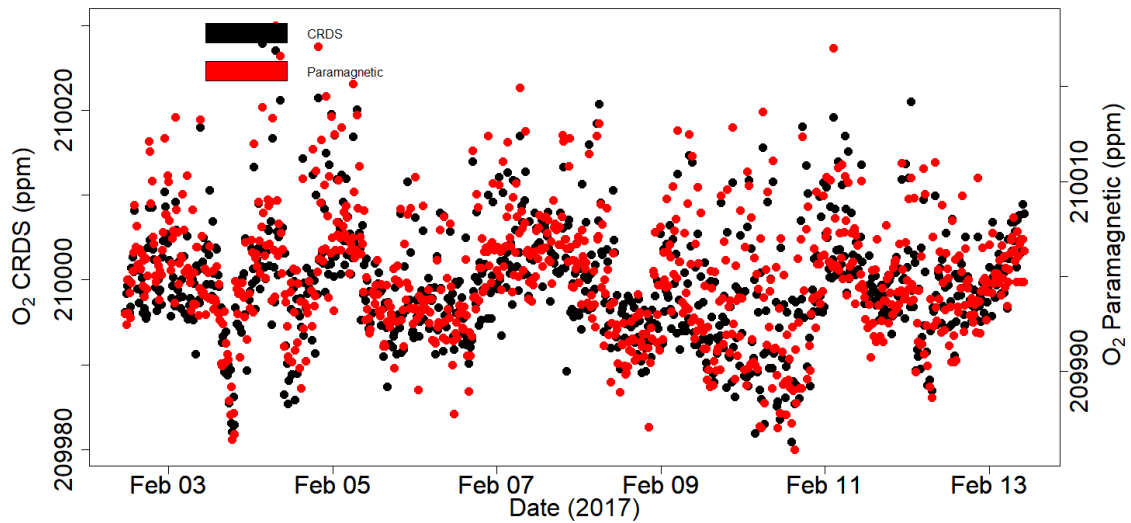
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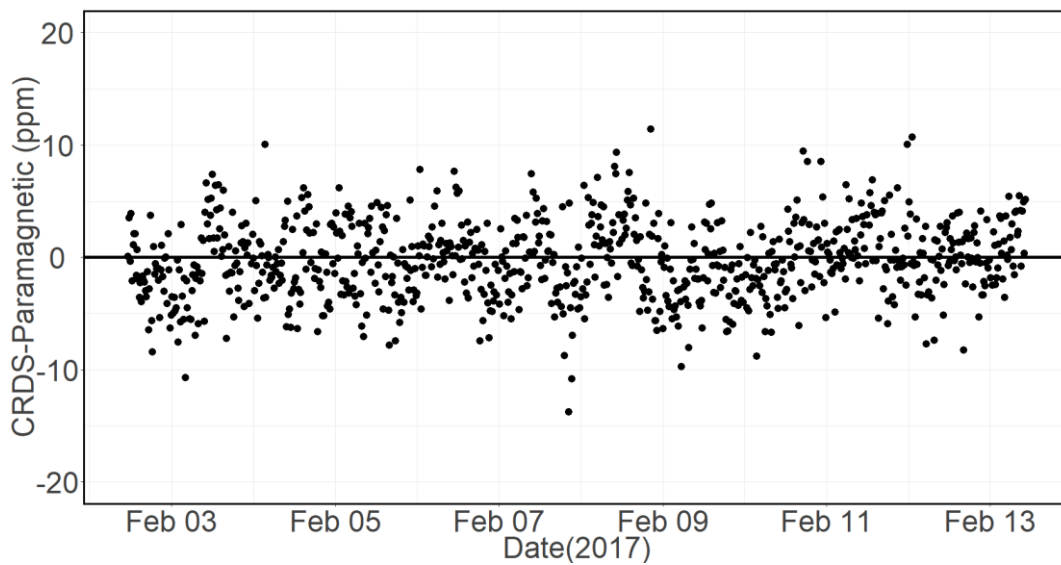
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902 Figure 16. Calibrated ambient air oxygen measurements (1-minute average) at the  
 903 Jungfrauoch site using the CRDS and Paramagnetic analyzers both in ppm units (a) and the  
 904 absolute difference between the two measurements in ppm (b) by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

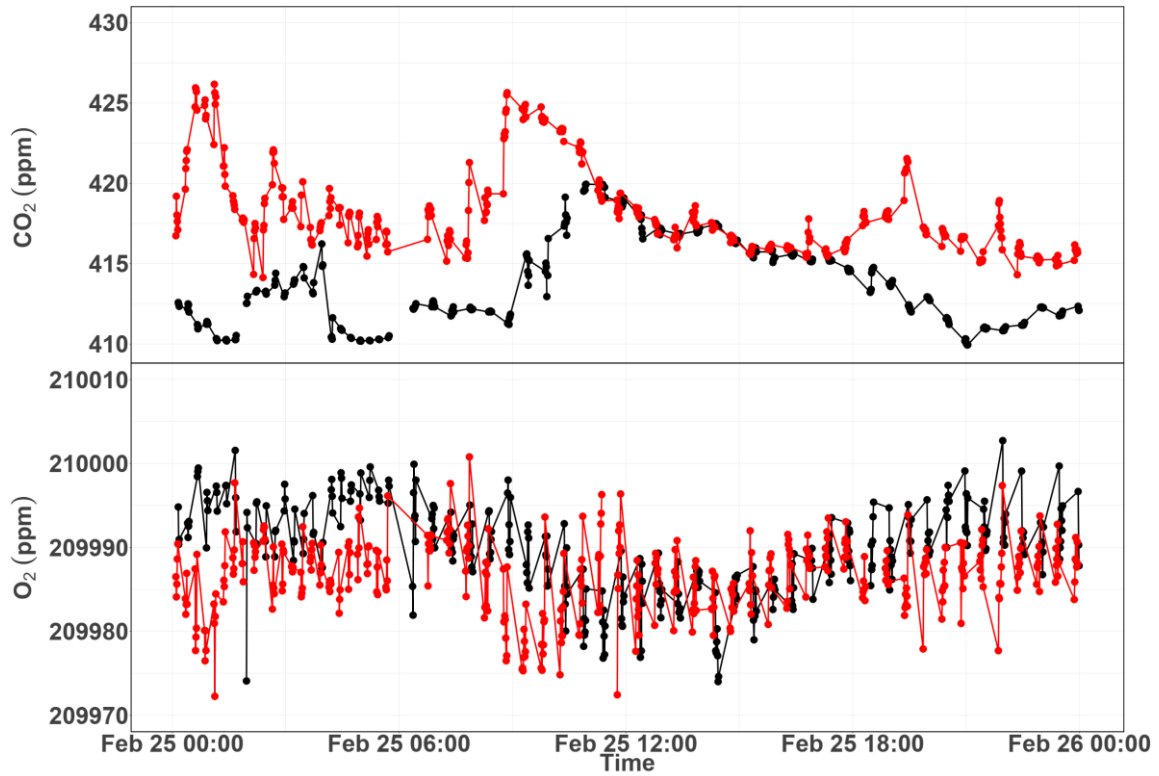
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911 Figure 17. Diurnal variations of CO<sub>2</sub> (top) and O<sub>2</sub> (bottom) measurements from the 12 m (red)  
 912 and the 212.5 m (black) height levels at Beromünster tower.

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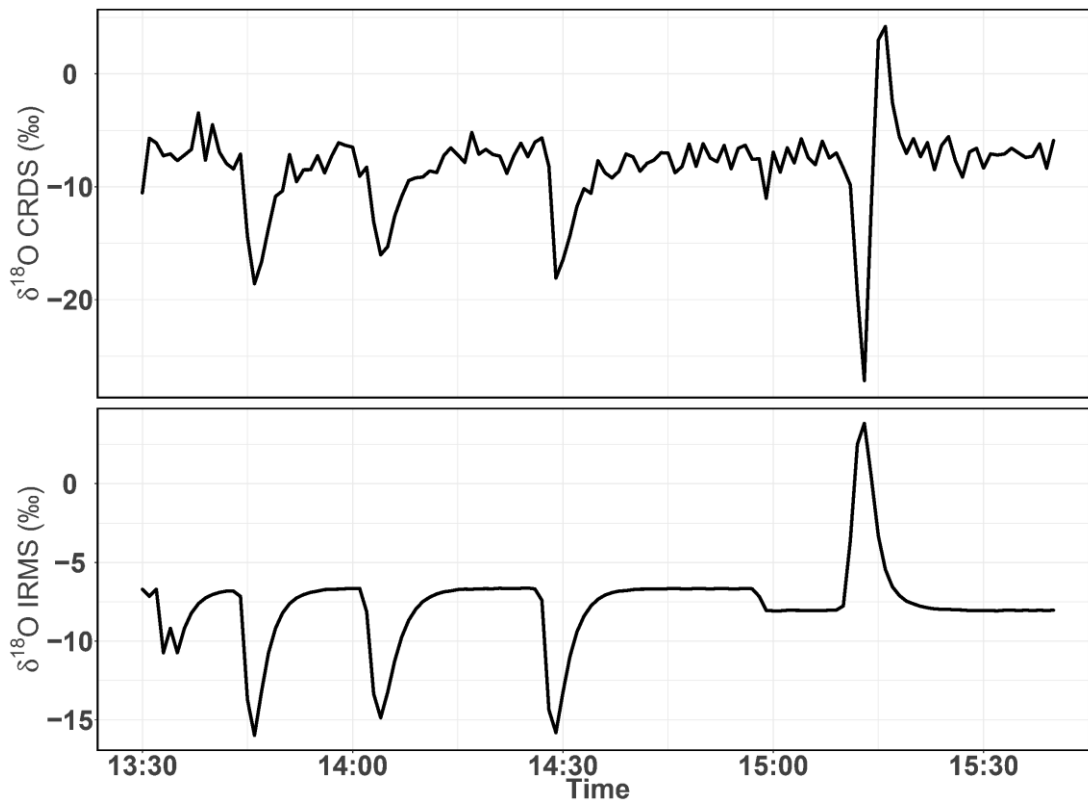
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924 Figure 18. Consecutive  $\delta^{18}\text{O}$  measurements of a standard gas ( $\text{CO}_2$ -free air) filled into three  
 925 flasks followed by measurement of breath air using the CRDS analyzer (top) and IRMS  
 926 (bottom). These measurements were carried out in the middle of ambient air measurements.

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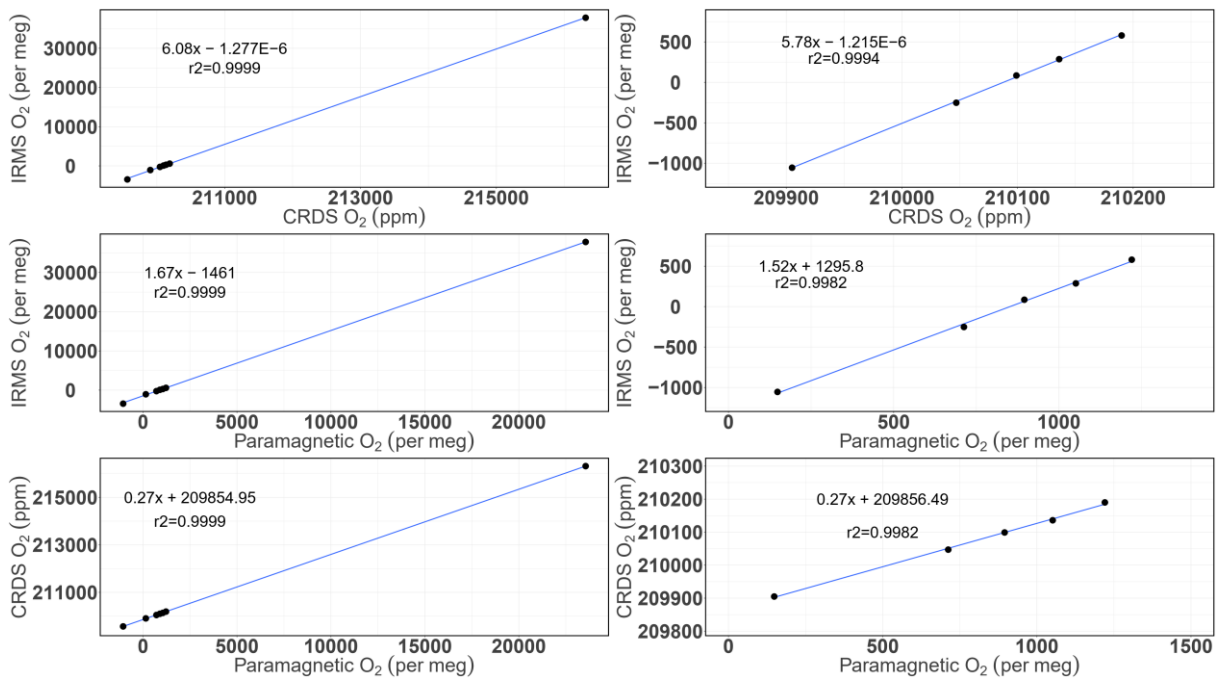
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937 **Appendix A.**

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940 Figure A.1. Correlations between the O<sub>2</sub> mixing ratios measured by the CRDS and  
 941 Paramagnetic analyzers with the mass spectrometric measurements (uncalibrated values). The  
 942 left panels are for all the cylinders measured (standards 1 to 8) while the right ones are after  
 943 selecting standards 1-5.

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