

Continuous Measurements of Dissolved Ne, Ar, Kr, and Xe Ratios with a Field-deployable Gas Equilibration Mass Spectrometer

Cara C. Manning,^{*,†,‡} Rachel H. R. Stanley,[¶] and Dempsey E. Lott III[‡]

Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography, Woods Hole, MA, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, and Department of Chemistry, Wellesley College, Wellesley, MA

E-mail: cmanning@whoi.edu

Abstract

Noble gases dissolved in natural waters are useful tracers for quantifying physical processes. Here, we describe a field-deployable gas equilibration mass spectrometer (GEMS) that provides continuous, real-time measurements of Ne, Ar, Kr, and Xe mole ratios in natural waters. Gas is equilibrated with a membrane contactor cartridge and measured with a quadrupole mass spectrometer, after in-line purification with reactive metal alloy getters. We use an electron energy of 35 V for Ne to eliminate isobaric interferences, and a higher electron energy for the other gases to improve sensitivity. The precision is 0.7 % or better and 1.0 % or better for all mole ratios when the instrument is installed in a temperature-controlled environment and a variable-temperature environment, respectively. In the lab, the accuracy is 0.9 % or better for

*To whom correspondence should be addressed

[†]MIT/WHOI Joint Program

[‡]Woods Hole Oceanographic Institution

[¶]Wellesley College

Cite as:

Manning, CC, RHR Stanley, DE Lott (2016) Continuous measurements of dissolved Ne, Ar, Kr, and Xe ratios with a field-deployable gas equilibration mass spectrometer. *Anal.*

Chem., 2016, 88 (6), 3040–3048.

DOI: 10.1021/acs.analchem.5b03102

12 all gas ratios using air as the only calibration standard. In the field (and/or at greater levels of
13 disequilibrium), the accuracy is 0.7 % or better for Ne/Kr, Ne/Ar, and Ar/Kr, and 2.5 % or bet-
14 ter for Ne/Xe, Ar/Xe, and Kr/Xe using air as the only calibration standard. The field accuracy
15 improves to 0.6 % or better for Ne/Xe, Ar/Xe, and Kr/Xe when the data is calibrated using
16 discrete water samples run on a laboratory-based mass spectrometer. The e-folding response
17 time is 90–410 s. This instrument enables the collection of a large number of continuous,
18 high-precision and accuracy noble gas measurements at substantially reduced cost and labor
19 compared to laboratory-based methods.

20 **Introduction**

21 Noble gases are biologically and chemically inert, making them useful tracers of physical processes
22 in the environment.¹ In water, measurements of dissolved noble gases in tandem with bioactive
23 gases such as O₂ can be used to separate the effects of biological versus physical processes on
24 the equilibrium state of gases, enabling accurate estimates of biological productivity.^{2–4} Dissolved
25 noble gas measurements can also be used to quantify oceanic processes such as gas ventilation in
26 deep-water formation regions, diapycnal mixing, and sea ice melting and formation.^{3,5–7} On land,
27 measurements of noble gases in groundwater can be used to generate paleotemperature records
28 and for studies of groundwater-aquifer and groundwater-ocean interactions.^{8–10}

29 Traditional methods for measuring multiple noble gases in natural waters via mass spectrom-
30 etry involve the collection of discrete samples and laboratory-based analysis. Sample processing
31 and analysis is time-consuming (often multiple hours per sample) and requires specialized and
32 expensive equipment. Currently, very few labs in the world are capable of high-precision and
33 high-accuracy (1 % or better) measurements of Ne, Kr, and Xe in natural waters, and oceanic
34 measurements of dissolved noble gases are sparse, particularly for Xe.^{3,5,7,11,12}

35 Recently, the development of mass spectrometric methods for measurement of dissolved gases
36 in the field^{13–16} has led to high-resolution datasets of gases including O₂, Ar, N₂O and dimethyl
37 sulfide.^{2,17,18} These instruments can analyze water in the field, in some cases eliminating the need

38 to transport discrete samples back to the laboratory for subsequent analysis. In this paper we
39 describe the gas equilibration mass spectrometer (GEMS), a new method for on-site measurement
40 of Ne, Ar, Kr, and Xe gas mole ratios in natural waters. We evaluate the precision and accuracy
41 of the GEMS through comparison with a published laboratory-based method.¹⁹ Our relatively low
42 cost (~50 000 USD for the entire system in 2013) and low labor method will allow much higher
43 throughput of noble gas measurement and will increase the number of scientists who are able to
44 measure a suite of noble gases and use them as tracers for quantifying physical processes in the
45 environment.

46 **Experimental section**

47 The GEMS can be separated into the equilibration components ('wet side'), and the measurement
48 components ('dry side') (Figure 1). In brief, the equilibration components include the follow-
49 ing features: filtered water is pumped through a membrane contactor cartridge containing a gas-
50 permeable membrane, the headspace of the cartridge is continuously recirculated and dried, and
51 gas is sampled via a capillary at a very low flow rate and transferred to the mass spectrometer. A
52 switching valve is used to alternate between sampling from the cartridge and sampling ambient
53 air, for calibration. The measurement components include metal alloy getters for purifying the gas
54 stream, a quadrupole mass spectrometer, vacuum pumps, and a laptop computer. We describe be-
55 low the final configuration that gave us the best results. We encourage scientists who are interested
56 in building their own systems to consult the Supporting Information, where we describe some al-
57 ternative configurations that were less effective. The Supporting Information also includes tables
58 of instrument settings (Tables S1–S2) suppliers and part numbers (Tables S3–S4) and photos and
59 schematics of the instrument (Figures S5–S8).

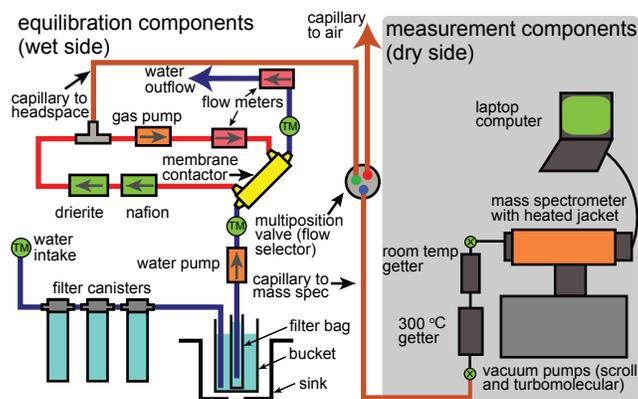


Figure 1: Schematic of the instrumental setup (not drawn to scale). See main text for description. See Figures S2–S4 for photos of the system.

Equilibration components

For shipboard installation, water from the ship’s underway seawater line passes through three 10” filter canisters containing reusable pleated filters (100, 20, and 5 μm nominal pore size) at a flow rate of $\sim 30 \text{ cm}^3 \text{ s}^{-1}$ and then into a bucket placed in a sink (Figure 1). Alternatively, any natural water source, such as water from a groundwater well or lake, can be continuously pumped with a submersible well pump, filtered, and used to fill the bucket. A two-layer filter bag consisting of 100 μm (outer) and 5 μm (inner) nominal pore size felt is placed inside the bucket. The filters are necessary to prevent the membrane contactor from clogging. Flexible PVC tubing and a gear pump is used to transfer water at a flow rate of $\sim 18 \text{ cm}^3 \text{ s}^{-1}$ from the filter bag to the membrane contactor and then to waste, down the sink drain (Figure 1). Our filter setup, water flow path, and gear pump is very similar to the configuration for the equilibrator inlet mass spectrometer developed by Cassar et al.(2009),¹⁴ except that we use the larger filter canisters to prolong the life of the disposable felt filter bags, due to our higher water flow rates. The filter canisters are not necessary when performing lab experiments with distilled or tap water.

The membrane contactor cartridge (Liqui-Cel Extra-Flow 2.5 x 8, model G540) contains hollow, tubular membranes composed of porous, hydrophobic polyethylene fiber. The tubes, called lumens, are 300 μm diameter and the total membrane surface area is 1.4 m^2 . Water flows through the membrane contactor, outside the lumens, and gas dissolved in the water transfers across the lumens

78 into the headspace (gas side) of the cartridge. Although liquid water does not cross the membrane,
79 water vapor transfers through the pores and can condense on the headspace side of the mem-
80 brane, reducing the gas transfer efficiency by clogging the pores.^{20,21} Therefore, the headspace is
81 continuously recirculated and dried to improve gas transfer efficiency across the membrane. The
82 headspace flows at $1.8 \text{ cm}^3 \text{ s}^{-1}$ through a Nafion tube surrounded by molecular sieves and cobalt
83 chloride indicator (PermaPure DM-110-24), then through a small piece of flexible PVC tubing
84 containing $\sim 10 \text{ g}$ of indicating Drierite (CaSO_4 , 10-20 mesh), then through a T-shaped fitting with
85 a capillary adapter for sampling the gas, and finally through a diaphragm pump before re-entering
86 the headspace (Figure 1). These drying techniques were selected because they do not require any
87 additional gas or power sources. The headspace is recirculated in the opposite direction to the wa-
88 ter, i.e., water enters and gas exits at the bottom of the cartridge. The recirculation loop increases
89 the effective headspace volume by less than 10 %, and therefore it likely has a negligible effect on
90 the response time. Without drying, the headspace partial pressure of water vapor (p_{H_2O}) is near
91 saturation equilibrium, since water is observed to condense on the headspace side. With drying,
92 p_{H_2O} in the headspace is somewhat lower and likely closer to ambient atmospheric p_{H_2O} . We do
93 not measure the gas humidity because, as discussed below, the vast majority of the water vapor is
94 removed by the getters before entering the mass spectrometer.

95 A critical design principle of the gas equilibration mass spectrometer (GEMS) is that the gas in
96 the headspace of the membrane contactor must be in equilibrium with the water flowing through
97 the membrane contactor. If this condition is met, the gas mole ratios in water can be calculated
98 from the measured headspace ratios, relative to air, and the gas solubility functions (Henry's law
99 coefficients). At equilibrium, the headspace is composed of all the gases that are dissolved in
100 the water, each at a partial pressure (p) yielding equilibrium with the water flowing through the
101 membrane contactor. This partial pressure of each gas can be calculated from its Henry's law
102 coefficient, which is a function of the temperature and salinity of the water. If air-equilibrated
103 water flows through the cartridge, the pressure of each gas in the headspace is equal to its pressure
104 in air. If water that is 5 % supersaturated in Ne flows through the cartridge, the partial pressure

105 of Ne will be 5 % higher in the headspace compared to air. When first setting up the membrane
106 contactor, we recommend allowing water to flow through the cartridge for at least 1 h, to allow
107 the headspace composition (which is initially air) to come into equilibrium with the water flowing
108 through the cartridge.

109 To verify that the headspace is at a similar pressure to the ambient air, we temporarily placed
110 a pressure measurement gauge (convectron), calibrated to air, in the headspace recirculation loop.
111 We found that the headspace pressure was within ~1 % of ambient air pressure when sampling
112 air-equilibrated water.

113 To maintain equilibrium, we ensure that the rate of gas flow out of the headspace and into the
114 mass spectrometer is negligible relative to the rate of gas transfer across the membrane. We use a
115 long, small-diameter capillary (0.05 mm ID, 5 m total length, deactivated fused silica) to achieve
116 this low flow rate. The estimated gas flow rate through the capillary is $\sim 8 \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$ ($\sim 7 \text{ cm}^3$
117 d^{-1}) based on a modified Hagen-Poiseuille equation. Cassar et al. (2009)¹⁴ found that the Hagen-
118 Poiseuille equation was a good approximation for capillary flow in a similar system. Calibration
119 of the instrument is performed by periodically sampling air through a second capillary of the same
120 dimensions.¹⁴

121 Accurate measurement of temperatures throughout the water flow path is critical, in order to
122 correct for the effects of changes in temperature on the saturation state of each gas. The temperature
123 is measured at the water intake (using a sensor with accuracy of $\pm 0.05 \text{ }^\circ\text{C}$), and immediately before
124 and after the membrane contactor using two thermistors (accuracy $\pm 0.1 \text{ }^\circ\text{C}$). The average of these
125 two temperatures is used as the equilibration temperature. The thermistors (temperature sensors)
126 are shown as green circles labeled TM in Figure 1. We reduce the magnitude of the temperature
127 change by placing foam insulation around the filter canisters, tubing, and the membrane contactor.

128 **Measurement components**

129 A multiposition Valco valve is used to alternate between the two capillaries. The valve is connected
130 to a 1 m long capillary to sample air, a 1 m long capillary to sample the headspace, and a common

131 4 m long capillary connected to the mass spectrometer. The valve to the mass spectrometer (Figure
132 1, blue circle) is always open, and the second open valve position switches from the headspace (red
133 circle) to air (green circle) to perform a calibration. Sample gas flows from the membrane contactor
134 (air), through the capillary and multiposition valve, through two chambers filled with reactive
135 metal alloy getters and then into the ion source of the quadrupole mass spectrometer (Hiden HAL
136 3F RC201). Vacuum is provided by a combined turbomolecular and dry scroll pumping system
137 (Agilent TPS-Compact). The pressure measured in the mass spectrometer is $\sim 1 \times 10^{-5}$ Pa while
138 sampling air or the headspace of the membrane contactor.

139 Removal of unwanted gases such as N_2 , O_2 , and H_2O from the gas stream greatly improves
140 the detection limit by reducing molecule-molecule collisions within the mass spectrometer, and
141 reduces matrix effects caused by differences in composition and pressure between the two gas
142 streams. Published methods of noble gas analysis purify the gas stream using low temperature
143 (cryogenic) traps and/or chemical purification.^{19,22–24} In-line purification with getters is ideal for a
144 portable system because it does not require any additional maintenance in the field, nor the trans-
145 port of cryogenic liquids. We used two custom-fabricated getter chambers (cylindrical stainless
146 steel containers) filled with SAES Getters St2002 pellets (Figures S7–S8). During operation, the
147 first can is heated to 300 °C and contains 100 g of getter; the second can is kept at room tempera-
148 ture and contains 30 g of getter. The heated getter breaks the C-H bonds in CH_4 , and adsorbs all
149 other gases except for H_2 and the noble gases. The room temperature getter adsorbs H_2 , from pure
150 H_2 gas and from the decomposed CH_4 , and also adsorbs all the other gases, at a lower efficiency
151 compared to the heated getter. We selected alloy St2002 due to its superior N_2 removal efficiency
152 (Figure S1). Reactivation of the getter surface is performed by heating both chambers to 400 °C
153 for 1 hr, and is required roughly once per month (when the signal intensity for N_2 becomes greater
154 than the signal intensity for ^{40}Ar). The getter lasts approximately one year before replacement is
155 needed. The temperature of both getter chambers is continuously recorded using thermocouples
156 in contact with the heater elements. Using this purification method, >98 % of the non-noble gas
157 content is removed from the gas stream before it enters the ion source, regardless of the initial gas

158 content (total pressure, humidity, and abundance of other gases).

159 The noble gases are measured with a quadrupole mass spectrometer operated with a secondary
160 electron multiplier (SEM) detector. The mole ratios are determined by selected ion monitoring.
161 Calibration with air, which has known and constant noble gas mole ratios,²⁵ is used to convert
162 the averaged ion ratios to the deviation from saturation equilibrium. We measure Ne, Ar, Kr, and
163 Xe. Helium is not measured because we found that He permeates through the capillary and/or the
164 cartridge (see Supporting Information), and Rn is not measured because its concentration is too
165 low (~6 orders of magnitude less abundant than Xe in seawater).

166 The Hiden Analytical instrument was selected because it has the ability to measure individual
167 selected ions at different electron energies, in a repeated sequence, without a loss in stability. We
168 measure ²²Ne with a reduced electron energy to prevent formation of doubly charged CO₂, which
169 is a potential isobaric interference. Although the getters remove >90 % of the CO₂, the signal
170 intensity for CO₂ after purification is sufficient to interfere with the ²²Ne measurement. Therefore,
171 we prevent the formation of the doubly-charged ion CO₂²⁺ by reducing the electron energy (cath-
172 ode voltage) below 37 V, as done by Hamme and Emerson²⁶ (see Supporting Information). We
173 measure ²²Ne at an electron energy of 35 V and all other masses at an electron energy of 55 V
174 (Table S1–S2). The precision and sensitivity for Ar, Kr, and Xe is improved at the higher electron
175 energy.

176 For Ar, we analyzed ³⁶Ar (0.337 % abundance) and/or ³⁸Ar (0.0629 % abundance). The pri-
177 mary isotope, ⁴⁰Ar, is 500–10 000 times more abundant in air than the other noble gases. The signal
178 intensity for ⁴⁰Ar is too high to be read accurately using the SEM at our operating pressure.²⁴ The
179 signal intensities for ³⁶Ar and ³⁸Ar are at least 40 and 8 times higher, respectively, than the other
180 noble gases we measure. In general, we found that measuring ³⁸Ar was preferred because it could
181 be measured on the same amplifier as ⁸⁴Kr, whereas ³⁶Ar had to be measured on a lower amplifier
182 due to its higher abundance. By minimizing the range of signal intensities, we minimize nonlinear-
183 ities in the detector response. For Kr, the primary isotope, ⁸⁴Kr (57.0 % abundance) was chosen.
184 For Xe, the least abundant gas, we measure both ¹²⁹Xe and ¹³²Xe (26.4 and 26.9 % abundance,

185 respectively), and take the average of the two signal intensities. Since Xe is the least abundant of
186 the gases we measure, measuring both isotopes and taking the average reduces the noise compared
187 to just measuring one isotope of Xe. Each measurement cycle (one measurement of each selected
188 ion) takes ~ 1 min; see Tables S1–S2 for further details on the mass spectrometer settings.

189 We place a custom-fabricated heater jacket set to 50 °C around the manifold, to reduce the
190 effects of room temperature change on the instrumental response, which is of particular concern
191 when operating the instrument in the field, where there may be large fluctuations in ambient tem-
192 perature. We use thermocouples to continuously monitor and record the room temperature and the
193 manifold temperature. The mass spectrometer and vacuum pumps are connected to an uninterrupt-
194 ible power supply (UPS, Eaton 9130) to isolate them from power fluctuations.

195 The mass spectrometer data is acquired and saved using the manufacturer’s software (MAS-
196 soft Pro 7). A custom Visual Basic program automates the valve switching between air and the
197 headspace, and records temperatures and flow rates. The data from both programs is plotted in real
198 time using Matlab.

199 The system described above was optimized for measurement of noble gas mole ratios. How-
200 ever, the equilibration components could potentially be used to equilibrate many other gases, given
201 that we achieve full equilibrium of Ne, Ar, Kr, and Xe, which span a factor of 10 range in solubility.
202 We have successfully obtained high-accuracy, high-precision measurements of O₂/Ar mole ratios
203 using the system described above, with the getter chambers eliminated.

204 **Data analysis**

205 In this section, we describe how to use the raw mass spectrometer data (extracted ion profile)
206 to calculate the mole ratios of the gases dissolved in water. As discussed above, if the rate of
207 gas removal from the headspace by the capillary is negligible relative to the rate of gas transfer
208 across the membrane, then full equilibration of the gases between the water flowing through the
209 membrane contactor and the headspace can occur.^{13,14}

210 We use the GEMS to determine the mole ratio of two gases (and the deviation of this ratio from

211 equilibrium), rather than their individual concentrations.¹⁴ If we recirculate air-equilibrated water
 212 through the membrane contactor, the measured ratios of any two noble gases are equivalent for the
 213 headspace versus air. However, the raw signal intensities for each gas in air versus the headspace
 214 are different by up to a few percent, and the magnitude of the offset can change with time. These
 215 offsets may be caused by slight differences in the rate of gas delivery to the mass spectrometer
 216 (e.g., due to differences in pressure between the headspace and air, or slight differences in the
 217 dimensions of the two capillaries), and/or differences in composition between the two gas streams
 218 causing matrix effects.^{14,19} Although obtaining the individual concentrations would be ideal, the
 219 noble gas mole ratios can be effectively used to quantify physical processes.^{3,11,27}

220 We use Henry's Law to determine the equilibrium molality of any inert gas, such as Ne

$$n_{Ne_{eq}} = p_{Ne_{air}} \cdot H_{Ne}(T, salinity) \quad (1)$$

221 where $n_{Ne_{eq}}$ is the molar concentration dissolved in water at equilibrium (mol kg^{-1}) and $p_{Ne_{air}}$ is
 222 the partial pressure of Ne in dry air (atm). H_{Ne} is the Henry's Law solubility coefficient of Ne
 223 ($\text{mol kg}^{-1} \text{ atm}^{-1}$) and is a function of the water temperature and salinity.^{28,29} We express the noble
 224 gas molar ratios in terms of the in situ deviation from the solubility equilibrium, often termed the
 225 saturation anomaly

$$\Delta \left(\frac{Ne}{Xe} \right) = \left[\frac{\left(\frac{n_{Ne}}{n_{Xe}} \right)_w}{\left(\frac{n_{Ne}}{n_{Xe}} \right)_{eq}} - 1 \right] \times 100\%, \quad (2)$$

226 where $(n_{Ne}/n_{Xe})_w$ is the molar ratio of the gases dissolved in water and $(n_{Ne}/n_{Xe})_{eq}$ is the molar
 227 ratio of the gases in the water at saturation equilibrium. Here, we show how the saturation anomaly,
 228 $\Delta(Ne/Xe)$, can be determined from measurements of $(Ne/Xe)_{hs}$ and $(Ne/Xe)_{air}$, the ratios in the
 229 headspace and air, respectively. Following from Equation 1 the equilibrium gas ratio $(Ne/Xe)_{eq}$
 230 is defined as

$$\left(\frac{Ne}{Xe} \right)_{eq} = \left(\frac{p_{Ne}}{p_{Xe}} \right)_{air} \left(\frac{H_{Ne}}{H_{Xe}} \right)_{T1} \quad (3)$$

231 where the subscript $T1$ indicates the in situ temperature (where the water was sampled). For

232 the membrane contactor, if the headspace is in equilibrium with the water passing through the
 233 cartridge, then we can calculate the ratio of the gases dissolved in water as

$$\left(\frac{Ne}{Xe}\right)_w = \left(\frac{pNe}{pXe}\right)_{hs} \left(\frac{H_{Ne}}{H_{Xe}}\right)_{T2}, \quad (4)$$

234 where the subscript *hs* indicates the headspace and *T2* indicates the equilibration temperature
 235 inside the membrane contactor. By substituting Eqns. 3 and 4 into Equation 2, we find

$$\Delta\left(\frac{Ne}{Xe}\right) = \left[\frac{\left(\frac{Ne}{Xe}\right)_{hs} \left(\frac{H_{Ne}}{H_{Xe}}\right)_{T2}}{\left(\frac{Ne}{Xe}\right)_{air} \left(\frac{H_{Ne}}{H_{Xe}}\right)_{T1}} - 1 \right] \times 100\%. \quad (5)$$

236 Finally, using the definition of (H_{Ne}/H_{Xe}) which follows from from Equation 1 at *T1* and *T2*, we
 237 obtain

$$\Delta\left(\frac{Ne}{Xe}\right) = \left[\frac{\left(\frac{Ne}{Xe}\right)_{hs} \left(\frac{Ne}{Xe}\right)_{eq,T2}}{\left(\frac{Ne}{Xe}\right)_{air} \left(\frac{Ne}{Xe}\right)_{eq,T1}} - 1 \right] \times 100\%. \quad (6)$$

238 Thus, the deviation of the gas ratios from solubility equilibrium can be determined by alternating
 239 between measurements of the noble gases in air and the headspace. The ratio in air is measured
 240 periodically (e.g., for a 40 min block after every 100–300 min of water sampling). We take the
 241 average of all the air measurements in each block (omitting the first and last 5 min), and then apply
 242 a linear interpolation between each pair of air measurements to calculate the air ratio at the time of
 243 each headspace measurement, as done by Cassar et al. (2009)¹⁴ for O₂/Ar.

244 We measure *T1* in situ, wherever the water is sampled. For example, on a ship *T1* is measured
 245 using a sensor mounted on the hull of the ship adjacent to the seawater intake. *T2* is determined
 246 from the average of two thermistors in the water flow path: one immediately before and one im-
 247 mediately after the membrane contactor. The salinity is measured once and we assume the in situ
 248 and equilibration salinities to be the same. We have observed *T2* to be up to 1.0 °C greater than
 249 *T1*, which results in a ~2.5 % correction to the calculated $\Delta(Ne/Xe)$ value.

250 **Results and Discussion**

251 **Precision**

252 To determine the precision of the GEMS, we recirculated water from a temperature-controlled
253 bath through the membrane contactor and collected data while continuously sampling from the
254 headspace only. We then performed calculations to simulate the process of switching between air
255 and the headspace (Figure 2). For these calculations, we used the ratios calculated from the raw
256 signal intensity (extracted ion profile), without adjustment to the molar abundances in water or air.
257 For example, the precision of the Ne/Kr ratio was calculated from the signal intensity of $^{22}\text{Ne}/^{84}\text{Kr}$.
258 We applied a linear interpolation to the raw ratio data, based on averaging 30 min of data every
259 340 min (i.e., simulating a 40 min measurement in air, with the first and last 5 minutes removed
260 before averaging). This timing is identical to the timing of the lab-based accuracy experiment
261 described below. A 7-min running mean filter was then applied to the 300-min intervals of data;
262 this averaging time is equal to the e-folding response time of Ne, which has the slowest response
263 rate of the gases we measure. We define the precision as the relative standard deviation (RSD) of
264 the difference between the filtered ratios and the interpolated ratios. In a temperature-controlled
265 room, the precision is 0.7 % or better for all gas ratios (0.7, 0.5, 0.5, 0.6, 0.2, and 0.6 % for
266 Ne/Xe, Ne/Kr, Ne/Ar, Ar/Xe, Ar/Kr and Kr/Xe, respectively). We report the precision for all
267 ratios as lighter gas/heavier gas for consistency. The relative precision (% RSD) is the same for
268 Ne/Xe as for Xe/Ne. Because the different noble gases we measure have different abundances and
269 physical properties, the gas ratios have varying precision and accuracy. We report the precision
270 and accuracy for all gas combinations since the utility of each gas ratio to study environmental
271 processes depends on the specific gases and on the precision/accuracy for that specific ratio. We
272 got very similar results (precision of 0.7 % or better for all gas ratios) when we measured air in
273 the lab continuously, instead of water. When determining the precision from measurements of the
274 headspace or air, we determine how similar each measurement is to the expected value. We did not
275 alternate between measuring air and the headspace because if air was being used to calculate the

276 expected headspace ratios, then any disequilibrium in the water with respect to air would bias the
277 calculated precision.

278 In the field, the precision was somewhat worse, likely due to room temperature change. When
279 we installed the mass spectrometer in an unheated garage, the mass spectrometer signal intensity
280 for each ion drifted with temperature, despite the heater jacket on the manifold. In a variable-
281 temperature environment, air calibrations should be performed more frequently. To determine the
282 precision, we measured air continuously and then averaged 30 min of data every 150 min. In
283 this environment, the precision while measuring air was 1.0 % or better for all gas ratios (1.0, 0.6,
284 0.5, 0.9, and 0.8 % for Ne/Xe, Ne/Kr, Ne/Ar, Ar/Xe, Ar/Kr and Kr/Xe, respectively). We did not
285 determine the precision while measuring water in the field because we did not have access to a
286 temperature-controlled water bath.

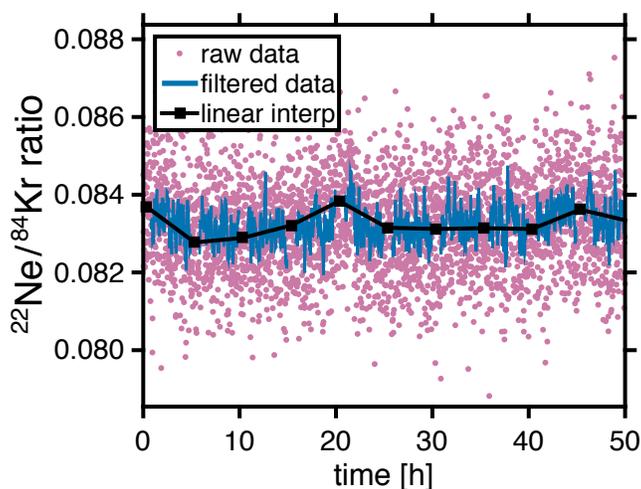


Figure 2: Measurements of $^{22}\text{Ne}/^{84}\text{Kr}$ signal intensity while sampling the headspace and recirculating air-equilibrated water through the membrane contactor. The pink dots show individual data points, the black line is a linear interpolation based on averaging 30 min of data every 340 min, and the blue line is the data after applying a 7-min running mean filter. The precision is calculated from the difference in magnitude between the blue and black lines.

287 Accuracy

288 To determine the accuracy of the GEMS, we compared the GEMS data to a published method¹⁹
289 (discrete samples analyzed by a laboratory-based mass spectrometer) during experiments in the

290 field and the lab. In the lab, using the GEMS, we recirculated water from an insulated 0.12 m³
291 tank filled with distilled water that was open to the lab air. The water in the tank was constantly
292 mixed using a submersible pump at the bottom of the tank. The temperature of the water was
293 changed during the experiment. A filter sock was placed directly into the water bath and a gear
294 pump connected to tubing was used to withdraw water from the filter sock and pump it through the
295 membrane contactor. For the discrete samples, water was withdrawn using a spigot on the bath.
296 Inside the tank, the spigot was connected to tubing, with the open end of the tubing placed next to
297 the filter sock, so that the water removed for discrete sample collection would be near the water
298 that entered the membrane contactor. Outside the tank, the other end of the spigot was connected
299 to tubing for sampling. In the lab experiment, we collected and analyzed one discrete sample at 10
300 time points over five days.

301 In the field experiment, water was pumped from Waquoit Bay, MA, using a submersible well
302 pump. The water passed through the canister filters and then into a bucket to overflow, as shown in
303 Figure 1. After the canister filters and before the bucket, a sampling valve was installed and used
304 to collect the discrete samples. For this experiment, we collected and analyzed one discrete sample
305 at eight time points over eight days.

306 The discrete samples were collected in copper tubes, sealed with a cold pressure welder and
307 extracted in the lab.³⁰ Noble gas abundances were measured on a pulse counting quadrupole mass
308 spectrometer.¹⁹ This method determines the concentration of each gas (in cm³_{STP} g⁻¹ or mol kg⁻¹),
309 with a combined standard uncertainty of 0.2–0.3 % for each gas. In order to compare the GEMS
310 data to the discrete samples, we must convert the GEMS measurements of saturation anomalies to
311 mole ratios. Therefore, the choice of solubility function directly influences our estimates of the
312 accuracy of the GEMS.

313 For Ne and Ar, we used the solubility determinations of Hamme and Emerson (2004)²⁸ who
314 determined the solubilities of Ne and Ar in fresh water and seawater with an accuracy of 0.30 and
315 0.13 % respectively, by equilibration with air. For Kr and Xe in fresh water (the lab experiment),
316 we used the solubility determinations of Benson and Krause (1976)²⁹ who determined solubilities

317 of all five stable noble gases in freshwater (but not salt water) with a stated accuracy of 0.1–0.2 %.
318 For the field experiment (sampling seawater), we used the solubility of Weiss and Kyser (1978)
319 for Kr,³¹ and the solubility of Wood and Caputi (1966)³² for Xe, fit by Hamme following the
320 procedure in Hamme and Emerson (2004), who determined the solubilities in both fresh water and
321 seawater.²⁸ Recent works have drawn the seawater solubilities of Kr and Xe into question because
322 they are not consistent with oceanic data and have not been verified by multiple investigators.⁷
323 Thus the Kr and Xe solubilities of Weiss and Kyser and Wood and Caputi have uncertainties of 1–2
324 %, ^{7,12} which results in increased uncertainty in our accuracy estimates during the field experiment
325 for all mole ratios except Ne/Ar.

326 We define the accuracy as the average magnitude (absolute value) of the relative percent differ-
327 ence between the GEMS and discrete samples, with both datasets expressed in terms of gas mole
328 ratios. We filtered the GEMS data with a 7-min running mean filter and then calculated the average
329 mole ratios over a 7-min period centered around the time each discrete sample was collected. The
330 choice of averaging time (from 3–15 min) did not significantly affect the estimated accuracy. The
331 mole ratios obtained by the GEMS are determined from the measured saturation anomaly and the
332 gas solubility at the in situ salinity and temperature.

333 In the lab experiment, the relative accuracy of the GEMS was 0.9 % or better for all gas mole
334 ratios (Figure 3). The experimentally-determined accuracy was 0.8, 0.4, 0.9, 0.8, 0.8, and 0.6 %
335 for the mole ratios of Ne/Xe, Ne/Kr, Ne/Ar, Ar/Xe, Ar/Kr, and Kr/Xe respectively. The relative
336 percent accuracy is the same for Ne/Xe as for Xe/Ne, and likewise for the other gas mole ratios.

337 In the field experiment, the accuracy of the GEMS was 0.6, 0.7, and 0.4 % for Ne/Kr, Ne/Ar,
338 and Ar/Kr (Figure S3). The accuracy of the ratios with Xe was substantially worse: 2.5, 2.0, and
339 2.4 % for Ne/Xe, Ar/Xe, and Kr/Xe, respectively. However, we found that we could improve the
340 accuracy for the ratios with Xe by using the discrete samples to calibrate the GEMS (Figures S2–
341 S4). We plotted the measured ratio, normalized to equilibrium for the GEMS versus the discrete
342 samples and calculated a linear fit. The slope, m , and intercept, b were used to calibrate the GEMS
343 data.

$$\left[\begin{array}{c} \left(\frac{n_{Ne}}{n_{Xe}} \right)_w \\ \left(\frac{n_{Ne}}{n_{Xe}} \right)_{eq} \end{array} \right]_{discrete} = m \left[\begin{array}{c} \left(\frac{n_{Ne}}{n_{Xe}} \right)_w \\ \left(\frac{n_{Ne}}{n_{Xe}} \right)_{eq} \end{array} \right]_{GEMS} + b \quad (7)$$

344 The R² values for the fit were 0.93, 0.85, and 0.73 for Ne/Xe, Ar/Xe, and Kr/Xe, respectively
 345 (Figure S2). Using this technique to adjust the GEMS data, the accuracy became 0.6, 0.4, and
 346 0.4 % for Ne/Xe, Ar/Xe, and Kr/Xe, respectively. Similarly, with calibration, the accuracy of the
 347 lab measurements also improved somewhat, to 0.6, 0.4 and 0.4 % for Ne/Xe, Ar/Xe, and Kr/Xe,
 348 respectively. Some of the error observed in the field may be associated with errors in the solubility
 349 of Kr and Xe. However, since the offset between the GEMS and discrete samples is not constant
 350 and seems to vary as a function of the magnitude of disequilibrium, not all of it can be explained
 351 by solubility errors.

352 We conclude that the GEMS can reliably obtain accuracy of 0.9 % or better for Ne/Kr, Ne/Ar,
 353 and Ar/Kr using air as the only calibration standard. For Xe, if accuracy of 0.9 % or better is
 354 desired, obtaining some discrete samples for calibration purposes is recommended.

355 We believe the reduced accuracy for Xe in the field experiment may be related to matrix ef-
 356 fects.¹⁹ Variability in the total pressure and/or the pressure of specific molecules may cause non-
 357 linearities in the relationship between gas pressure and signal intensity at the detector (e.g., due to
 358 altering the ionization efficiency for the gas of interest). Xe is likely to be the most sensitive to
 359 these matrix effects because it is the least abundant gas we measure (closest to the detection limit),
 360 and since its saturation state is the most variable.^{7,12} In unpurified air, the mole fractions of O₂
 361 and N₂ are ~ 10⁹ times greater than Xe . Therefore, even though the getters remove >98 % of
 362 the active (non-noble) gas content, the pressure of N₂ and O₂ is still far greater than the pressure
 363 of Xe after purification. Furthermore, in the field, biogenic gases such as O₂ and CO₂ will likely
 364 be more variable in abundance, and farther from equilibrium, compared to the lab experiment per-
 365 formed with distilled water. Therefore, we expect greater differences between the headspace and
 366 air composition in the field, leading to larger matrix effects.

367 Additionally, even if we could remove 100 % of the active gas, the pressure of ⁴⁰Ar would still

368 be 300 000 times greater than the pressure of ^{129}Xe , and therefore the measured pressure of Xe may
369 be affected by changes in the pressure of Ar.¹⁹ A matrix effect caused by other noble gases may be
370 more apparent at larger deviations from equilibrium. In our field dataset, the noble gas mole ratios
371 were on average farther from equilibrium, and also had larger maximum magnitudes compared to
372 the lab dataset. For example, the largest saturation anomalies measured for Ne/Xe, Ar/Xe, and
373 Kr/Xe were 6.4, 3.9, and 3.1 % in the field and 4.3, 1.7, and 2.1 % in the lab, respectively, based
374 on the discrete samples.

375 Notably, precision and accuracy are also degraded when the instrument experiences vibrations,
376 such as on a ship (see Supporting Information).

377 Since we only analyzed one sample at each time point, we cannot determine whether any of
378 the discrete samples may be inaccurate due to sampling or measurement problems; however, by
379 using samples at 8–10 time points, we believe we have a good estimate of the overall accuracy.
380 Comparing the two methods has an additional source of error: the discrete samples capture the
381 instantaneous gas composition at the time the tube was sealed, whereas the GEMS averages over
382 several minutes, with the e-folding time varying for each gas. The GEMS achieves similar accuracy
383 to other methods that are much more expensive and labor-intensive.

384 **Equilibration timescale**

385 When sampling the headspace, the signal intensity for each selected ion reflects a weighted average
386 of the concentration over the equilibration timescale of the system. To determine the equilibration
387 timescale, we switched between sampling water of two different gas compositions: air-equilibrated
388 water and freshly distilled water. We fit the instrument response to a kinetic equation.¹⁴ The signal
389 intensity or concentration, C , for each noble gas can be modeled as

$$C_t = [C_i - C_f] \exp(-t/\tau) \quad (8)$$

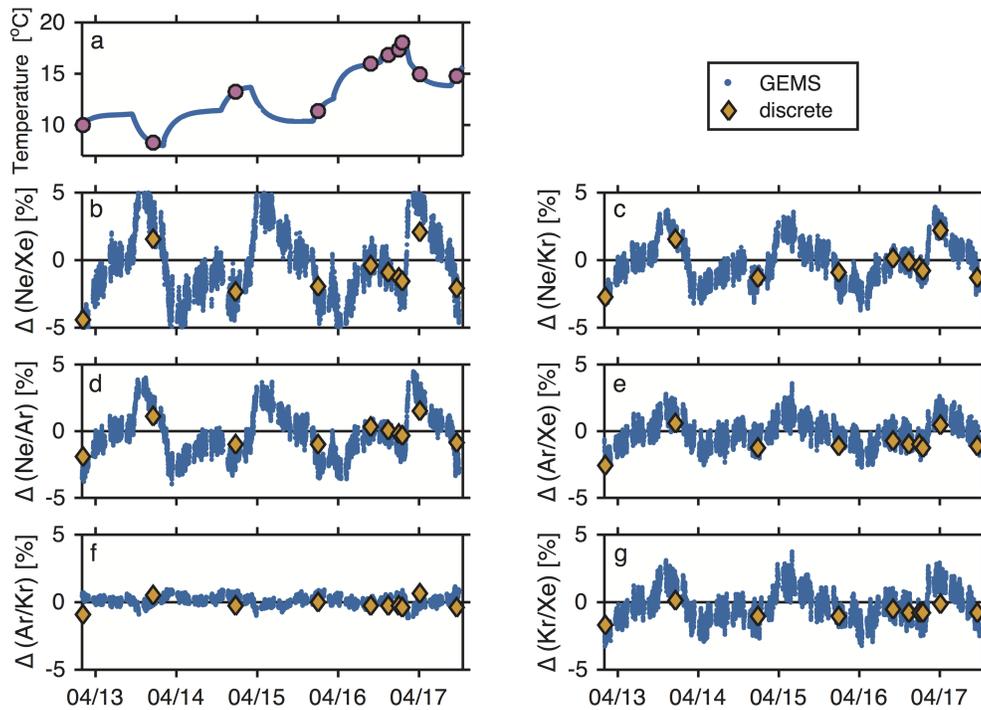


Figure 3: Results of a lab experiment to determine the accuracy of the GEMS. a) In situ temperature throughout the experiment (blue line) and the time each sample was collected (pink circles). b-g) Individual measurements by the GEMS filtered with a 7-min running mean filter (blue dots). Discrete samples (yellow diamonds), with the measured concentration converted to saturation anomalies. The height of the diamonds is equal to the measurement uncertainty.

390 where C_i is the initial signal intensity (before switching the water composition), C_f is the final
391 intensity (after stabilization), C_t is the intensity at any time t , and τ is the e-folding time of the
392 instrument. Specifically, $\tau = t_{1/2} / \ln(2)$, with $t_{1/2}$ the time at which the signal intensity is halfway
393 between C_f and C_i . By rearranging equation 8, we can plot the data as a linear equation of the
394 form $y = mx$ where $x = t$, $m = \tau^{-1}$, and

$$y = \ln \left(\frac{C_t - C_f}{C_i - C_f} \right). \quad (9)$$

395 For water at 20 °C and a water flow rate of $18 \text{ cm}^3 \text{ s}^{-1}$, the e-folding times were found to be
396 410(54) s for Ne, 240(80) s for Ar, 190(80) s for Kr, and 90(10) s for Xe, where the numbers in
397 parentheses are the standard uncertainty (Figure 4). These estimates are based on at least three
398 measurements of the e-folding time for each gas; each measurement took ~ 2 h. The e-folding
399 time increases with decreasing solubility. A greater proportion of the lower solubility gas must
400 transfer between the water and the headspace in order for the two phases to re-equilibrate, causing
401 the equilibration time to increase. Other investigators have noticed that lower solubility gases
402 equilibrate less efficiently across Liqui-Cel membrane contactors.¹⁴

403 **Pilot field study**

404 To demonstrate the utility of the GEMS, we conducted a pilot field study in Waquoit Bay, MA,
405 USA. We installed the mass spectrometer and laptop in an unheated boathouse, and we installed
406 the equilibration components just outside the boathouse. The filter and bucket were placed on
407 a bench, and the remainder of the equilibration equipment was installed inside a wooden box to
408 shelter it from precipitation. A hole in the the wall of the boathouse was used to connect the
409 capillary between the multiposition valve and the mass spectrometer.

410 To sample water, we deployed a submersible well pump ~ 60 m offshore, in an average water
411 depth of 1 m. The water pump and two temperature/salinity/depth sensors (RBR Concerto) were
412 attached to a hollow PVC pipe mounted on a cement block. The water pump was installed with

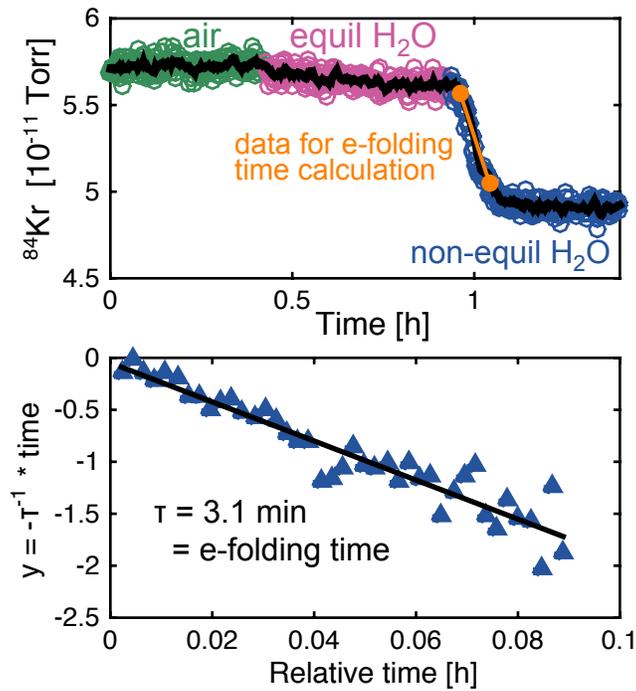


Figure 4: Results of an experiment to determine the equilibration timescale for each gas. a) ^{84}Kr signal intensity during an experiment switching from air, to equilibrated water, to non-equilibrated water. The orange circles and line show the portion of the data that is used to calculate the e-folding time. b) Calculation of the e-folding time from a linear regression of $y = -\tau^{-1}t$, with τ the e-folding time and t the time.

413 the intake at an average depth of 0.4 m, and the temperature/salinity/depth sensors were installed
414 at an average depth of 0.4 and 0.8 m. An additional temperature sensor ~ 1 m above the water level
415 was attached to the PVC pipe, to monitor air temperature. Wind speed data was taken from the
416 Waquoit Bay Carriage House weather station, 200 m north (inshore) of the water pump.³³

417 The GEMS collected data for one month. In Figure 5, we show the data from December 16–24,
418 the time period when discrete samples were collected for method validation purposes. We typi-
419 cally checked on the system twice per day (morning and early evening), and it otherwise operated
420 unattended. During these checks we replaced the filter socks (roughly once per day), replaced the
421 canister filters (once per week), and replaced the dessicant and membrane contactor (once every
422 five days). We also plotted the mass spectrometer data, flow rates, and temperatures, to verify that
423 the system was operating as intended. We obtained a near-continuous time-series with occasional
424 gaps resulting from the submersible pump coming out of the water at the lowest tides (e.g., mid-
425 night on Dec 19 and afternoon on Dec 21 in Figure 5). This type of study (sub-hourly measurement
426 frequency, over a month) would not be practical with traditional sampling and analysis methods.¹³

427 In Figure 5, the GEMS data for $\Delta(\text{Ne}/\text{Xe})$ was calibrated using the discrete samples, and the
428 other data is unadjusted. The error bars for $\Delta(\text{Ne}/\text{Xe})$ and $\Delta(\text{Ar}/\text{Kr})$ are larger in the field compared
429 to the laboratory-based experiment, due to the larger uncertainties in the seawater solubility of Kr
430 and Xe compared to the fresh water solubility. See the Accuracy section for more details.

431 The precision, accuracy, and response time of the system were sufficient to resolve substan-
432 tial variability in noble gas saturation anomalies throughout the time-series. This variability was
433 associated with changes in wind speed, water temperature, and air temperature (Figure 5). To
434 determine whether the observations were consistent with our scientific understanding of physical
435 controls on gas saturation state, we used a simple model. The model was forced with wind speed,
436 temperature, and salinity observations, and the gas exchange parameterization of Nicholson et al.
437 (2011),^{27,34} which includes separate terms for diffusive and bubble-mediated gas exchange. We
438 assumed a fixed 1 m water depth. We initialized the model on Dec 16, 12:30 pm using the mea-
439 sured saturation anomalies of the first discrete sample. This model is an oversimplification because

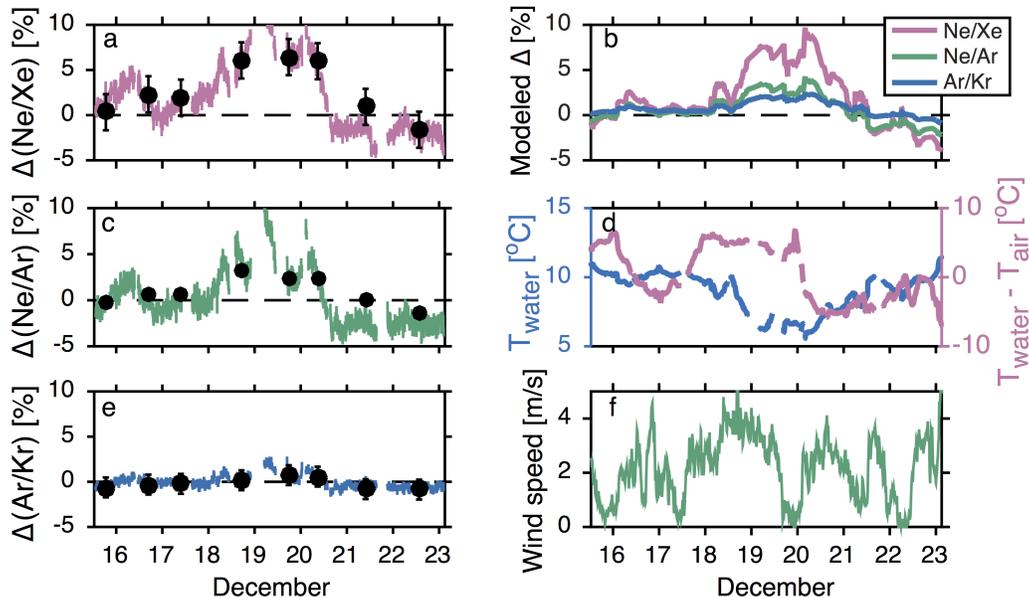


Figure 5: GEMS and discrete measurements of a) $\Delta(\text{Ne}/\text{Xe})$, c) $\Delta(\text{Ne}/\text{Ar})$, and e) $\Delta(\text{Ar}/\text{Kr})$ in Waquoit Bay, MA. The Ne/Xe data has been calibrated using discrete samples, as described in the Accuracy section. b) Modeled gas distributions forced by the measured temperature, salinity, and wind speed. d) Variability in water temperature (blue line) changes the measured saturation anomaly, and the air-water temperature difference (pink line) affects the air-sea gas flux. e) Wind speed also affects the gas flux. Date ticks represent midnight local time.

440 it does not account for the movement of water masses (e.g., due to tides) and the variable water
 441 depth. However, the model helps us to determine how much of the variability can be explained by
 442 air-sea gas exchange and changes in temperature/salinity.

443 The model predicted many similar features to the observations. For example, the model and
 444 observations show similar amplitude in the saturation anomalies, with Ne/Xe having the widest
 445 range in saturation anomalies and Ar/Kr the least. Additionally, the timing of changes is similar
 446 in the model and data. For example, the model and data show the saturation anomalies increasing
 447 from near-equilibrium to positive values on December 18–20, and decreasing from positive values
 448 to negative values on December 20–21. The changes in saturation anomalies are linked to changes
 449 in the water temperature and the air-water temperature difference. High resolution data such as
 450 this could be used to examine other processes such as tidally driven flows/mixing (e.g., by combin-
 451 ing the GEMS with current velocity measurements) and to infer the rates of biological processes
 452 (e.g., by combining the GEMS with O_2 measurements). In the Supporting Information, we de-

453 scribe in detail several potential applications of the GEMS, including lab-based tank experiments,
454 introduced tracer studies, and parameterizing physical versus biological gas fluxes.

455 **Comparison with other published methods**

456 The GEMS dramatically increases throughput, decreases labor, and decreases costs compared to
457 traditional discrete sampling and analysis methods. The GEMS has improved accuracy and time
458 resolution compared to another portable method that measures Ar and Kr, but not Ne or Xe.¹³
459 The accuracy is similar to^{22,35,36} or somewhat less accurate than^{7,19} laboratory-based methods that
460 cause much higher cost and labor. Additionally, the laboratory-based methods with higher pre-
461 cision require much more expensive instrumentation (over 250 000 USD), have higher analysis
462 costs (~500 USD per sample), and have lower sample throughput (~4 samples per day), since each
463 sample takes several hours to extract and analyze. In contrast, our system is less expensive to build
464 (~50 000 USD in 2013), requires minimal consumables, and can collect an endless number of
465 samples with a time resolution of 90–410 s. Thus, the GEMS enables continuous, real-time mea-
466 surements of four noble gases, with a sampling frequency (sub-hourly) that would be challenging
467 to achieve via traditional methods.¹³

468 The main disadvantage is that the described GEMS system does not determine the gas concen-
469 trations; instead it determines their mole ratios. In the future, we plan to test modifications to the
470 GEMS that will enable the determination of the gas concentrations, in addition to their mole ratios.
471 For example, the GEMS could be used along with a second mass spectrometer measuring O₂/Ar
472 ratios (e.g., an equilibrator inlet mass spectrometer,¹⁴ a membrane inlet mass spectrometer,^{16,18,37}
473 or the GEMS system described above, with the getter chambers eliminated) and a well-calibrated
474 sensor for O₂ concentration. The O₂/Ar ratio and the O₂ concentration could be used to derive the
475 Ar concentration,^{6,38} and the other noble gas concentrations could be determined from the GEMS
476 noble gas ratios and the Ar concentration. Another potential modification is changing the system
477 to measure individual samples, instead of a continuous gas stream.^{13,24}

478 **Conclusions**

479 We have described the gas equilibration mass spectrometer (GEMS), a new field-deployable method
480 for continuous measurement of the mole ratios of four noble gases (Ne, Ar, Kr, and Xe) dissolved
481 in water. In the lab, the precision is 0.7 % or better, and in a variable-temperature environment the
482 precision is 1.0 % or better. The accuracy is 0.9 % or better for all gas ratios in the lab. In the
483 field (and/or at greater disequilibrium) the accuracy is 0.7 % or better for Ne/Kr, Ne/Ar, and Ar/Kr
484 and 2.5 % or better for Ne/Xe, Ar/Xe, and Kr/Xe, but can be improved through calibration with
485 discrete samples to 0.6 % or better.

486 **Acknowledgement**

487 The authors thank Kevin Cahill, Josh Curtice, James Rassman, and Zoe Sandwith for their con-
488 tributions to lab and field work, Bill Jenkins for processing the noble gas data from discrete sam-
489 ples, and David Nicholson for discussions about the field data. The manuscript was improved
490 thanks to the thoughtful suggestions of two anonymous reviewers. Funding was provided by NSF
491 award OCE-1060840 and a WHOI Innovative Technology award to RHRS, and scholarships from
492 NSERC and CMOS to CCM.

493 **Supporting Information Available**

494 Lists of suppliers and parts numbers, photos of the system, a diagram of the getter chambers,
495 descriptions of some alternative configurations of the system, and further details on the calibration
496 of field data.

497 This material is available free of charge via the Internet at <http://pubs.acs.org/>.

498 **References**

- 499 (1) Stanley, R. H.; Jenkins, W. J. *The Noble Gases as Geochemical Tracers*; Springer, 2013; pp
500 55–79.

- 501 (2) Stanley, R.; Kirkpatrick, J.; Cassar, N.; Barnett, B.; Bender, M. *Global Biogeochem. Cycles*
502 **2010**, *24*, GB4001.
- 503 (3) Nicholson, D.; Emerson, S.; Caillon, N.; Jouzel, J.; Hamme, R. C. *J. Geophys. Res. Oceans*
504 **2010**, *115*.
- 505 (4) Stanley, R. H.; Jenkins, W. J.; Doney, S. C. *J. Mar. Res.* **2006**, *64*, 267–295.
- 506 (5) Loose, B.; Jenkins, W. J. *Geophys. Res. Lett.* **2014**, *41*, 2835–2841.
- 507 (6) Eveleth, R.; Timmermans, M.-L.; Cassar, N. *J. Geophys. Res. Oceans* **2014**, *119*, 7420–7432.
- 508 (7) Hamme, R. C.; Severinghaus, J. P. *Deep Sea Res. I* **2007**, *54*, 939–950.
- 509 (8) Aeschbach-Hertig, W.; Solomon, D. *The Noble Gases as Geochemical Tracers*; Springer,
510 2013; pp 81–122.
- 511 (9) Castro, M. C.; Goblet, P.; Ledoux, E.; Violette, S.; Marsily, G. *Water Resour. Res.* **1998**, *34*,
512 2467–2483.
- 513 (10) Stute, M.; Schlosser, P. *Climate Change in Continental Isotopic Records* **1993**, 89–100.
- 514 (11) Hamme, R.; Emerson, S. *Geophys. Res. Lett.* **2013**, *40*, 1149–1153.
- 515 (12) Stanley, R. H. R.; Jenkins, W. J.; Lott, D. E.; Doney, S. C. *J. Geophys. Res. Oceans* **2009**,
516 *114*.
- 517 (13) Machler, L.; Brennwald, M. S.; Kipfer, R. *Environ. Sci. Technol.* **2012**, *46*, 8288–8296.
- 518 (14) Cassar, N.; Barnett, B.; Bender, M.; Kaiser, J.; Hamme, R.; Tilbrook, B. *Anal. Chem.* **2009**,
519 *81*, 1855–1864.
- 520 (15) Kameyama, S.; Tanimoto, H.; Inomata, S.; Tsunogai, U.; Ooki, A.; Yokouchi, Y.; Takeda, S.;
521 Obata, H.; Uematsu, M. *Anal. Chem.* **2009**, *81*, 9021–9026.

- 522 (16) Virkki, V. T.; Ketola, R. A.; Ojala, M.; Kotiaho, T.; Komppa, V.; Grove, A.; Facchetti, S.
523 *Anal. Chem.* **1995**, *67*, 1421–1425.
- 524 (17) Marandino, C.; De Bruyn, W. J.; Miller, S. D.; Saltzman, E. S. *Atmos. Chem. Phys.* **2009**, *9*,
525 345–356.
- 526 (18) Tortell, P. *Limnol. Oceanogr.: Methods* **2005**, *3*, 24–37.
- 527 (19) Stanley, R. H. R.; Baschek, B.; Lott, D. E.; Jenkins, W. J. *Geochem. Geophys. Geosyst.* **2009**,
528 *10*, Q05008.
- 529 (20) Lv, Y.; Yu, X.; Tu, S.-T.; Yan, J.; Dahlquist, E. *J. Membr. Sci.* **2010**, *362*, 444–452.
- 530 (21) Wang, R.; Zhang, H.; Feron, P.; Liang, D. *Sep. Purif. Technol.* **2005**, *46*, 33–40.
- 531 (22) Sano, Y.; Takahata, N. *J. Oceanogr.* **2005**, *61*, 465–473.
- 532 (23) Severinghaus, J. P.; Grachev, A.; Luz, B.; Caillon, N. *Geochim. Cosmochim. Acta* **2003**, *67*,
533 325–343.
- 534 (24) Visser, A.; Singleton, M. J.; Hillegonds, D. J.; Velsko, C. A.; Moran, J. E.; Esser, B. K. *Rapid*
535 *Comm. Mass Spectrom.* **2013**, *27*, 2472–2482.
- 536 (25) US Standard Atmosphere. 1976.
- 537 (26) Hamme, R. C.; Emerson, S. R. *Mar. Chem.* **2004**, *91*, 53–64.
- 538 (27) Nicholson, D. P.; Emerson, S. R.; Khatiwala, S.; Hamme, R. C. An inverse approach to
539 estimate bubble-mediated air-sea gas flux from inert gas measurements. Proceedings of the
540 6th International Symposium on Gas Transfer at Water Surfaces, Kyoto University Press,
541 Kyoto, Japan. 2011.
- 542 (28) Hamme, R.; Emerson, S. *Deep-Sea Res. I* **2004**, *51*, 1517–1528.
- 543 (29) Benson, B. B.; Krause Jr, D. *The Journal of Chemical Physics* **1976**, *64*, 689–709.

- 544 (30) Jenkins, W.; Lott, D.; Cahill, K.; Curtice, J.; Landry, P. *Sampling and measuring helium*
545 *isotopes and tritium in seawater*; 2010, IOCCP Report No. 14.
- 546 (31) Weiss, R. F.; Kyser, T. K. *J. Chem. Eng. Data* **1978**, *23*, 69–72.
- 547 (32) Wood, D.; Caputi, R. *Solubilities of Kr and Xe in fresh and sea water*; Technical report, U.S.
548 Naval Radiological Defense Laboratory, San Francisco, CA, 1966.
- 549 (33) NOAA National Estuarine Research Reserve System System-wide Monitoring Program,
550 Centralized Data Management Office Website. <http://www.nerrsdata.org>, Accessed
551 January 1, 2016.
- 552 (34) Manning, C. C.; Nicholson, D. P. gas_toolbox: MATLAB code used in Manning et al.
553 GTWS-7 proceedings. Zenodo. <http://dx.doi.org/10.5281/zenodo.45293>, 2016.
- 554 (35) Brennwald, M. S.; Hofer, M.; Kipfer, R. *Environ. Sci. Technol.* **2013**, *47*, 8599–8608.
- 555 (36) Beyerle, U.; Aeschbach-Hertig, W.; Imboden, D. M.; Baur, H.; Graf, T.; Kipfer, R. *Environ.*
556 *Sci. Technol.* **2000**, *34*, 2042–2050.
- 557 (37) Kana, T. M.; Darkangelo, C.; Hunt, M. D.; Oldham, J. B.; Bennett, G. E.; Cornwell, J. C.
558 *Anal. Chem.* **1994**, *66*, 4166–4170.
- 559 (38) Hamme, R. C.; Cassar, N.; Lance, V. P.; Vaillancourt, R. D.; Bender, M. L.; Strutton, P. G.;
560 Moore, T. S.; DeGrandpre, M. D.; Sabine, C. L.; Ho, D. T.; Hargreaves, B. R. *J. Geophys.*
561 *Res.* **2012**, *117*, C00F12.

562 **Graphical TOC Entry**

563

