

Inter-comparison of salt effect correction for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements in seawater by
CRDS and IRMS using the Gas-H₂O equilibration method

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Abstract

1 The isotope composition of seawater is an efficient method for detecting mixing between water
2 masses. To measure long term or large scale hydrological processes at the ocean surface, it is
3 necessary to be able to precisely compare datasets produced by different laboratories. The
4 oxygen and hydrogen isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) composition of marine waters can be measured
5 using isotope ratio mass spectrometry (IRMS) and near-infrared laser absorption spectroscopy
6 (LS) techniques. The IRMS and equilibration method is thought to provide results on the
7 activity scale, while LS provides results on the concentration scale. However, the effect of
8 dissolved seawater salts on the measurement is not sufficiently assessed and seems sometimes
9 contradictory in the literature. For this purpose, we made artificial seawater and a pure NaCl
10 solution from a freshwater of known isotope composition. The solutions were measured by four
11 different laboratories allowing us to compare the two techniques. We show that minor
12 corrections are necessary to correct seawater measurements for the salt effect and report them
13 on the concentration scale. Interestingly, seawater measurements using LS (type Picarro)
14 coupled to a liner are not on the concentration scale and require a correction of $\sim 0.09\text{‰}$ for
15 $\delta^{18}\text{O}$, while the correction is relatively less significant for $\delta^2\text{H}$ ($\sim 0.13\text{‰}$). Moreover, we found
16 for IRMS measurements that the salt effect can differ between different laboratories but seems
17 reproducible for a given laboratory. A natural sea water sample was then analyzed by the
18 different laboratories participating in the study. We found that applying the corrections
19 increases the reproducibility of the isotope measurement significantly, with inter-laboratory
20 standard deviation decreasing from 0.06 to 0.02‰ and 0.55 to 0.23‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$,
21 respectively. Thus, comparing or merging sea water datasets produced in different laboratories
22 requires that each laboratory carries out its own calibration with artificial seawater and presents
23 measurements on the concentration scale.

24 1. Introduction

25 Since the pioneering study by Craig and Gordon (1965), the oxygen and hydrogen isotope
26 compositions of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) are commonly measured to investigate the hydrological
27 cycle. Most of the isotope applications concern freshwater (rain, ice, snow, water vapor and
28 river water) and the isotope variation is often considerably larger than the routine analytical
29 precision (Dansgaard, 1964, Vimeux, 2003, Masson-Delmotte et al., 2008, Kurita, 2011,
30 Benetti et al., 2014, 2015). Isotopes can also be used in oceanography to track formation and
31 transport processes in the various water masses (Craig and Gordon, 1965). The isotope
32 variations in marine waters are significantly smaller than in freshwaters (most of the ocean
33 waters have an isotope composition between -0.5 and $+1.5$ ‰ for $\delta^{18}\text{O}$ and -5 and $+10$ ‰ for
34 $\delta^2\text{H}$). For example, the oxygen isotope composition at the Weddell Sea surface only varies by
35 0.15 ‰ for $\delta^{18}\text{O}$ and by 2 ‰ for $\delta^2\text{H}$, while the amplitude of the salinity range can reach a unit
36 during summer (Weiss et al., 1979). These small variations measured off the Antarctica shelf
37 are investigated to quantify how sea ice processes and continental glacial melt input drive deep
38 water formation (Weiss et al., 1979, Meredith et al., 2008). In the present context of global
39 warming, the isotope composition of marine water is being used to detect changes in the
40 hydrological cycle, such as increasing sea ice or continental icecap melt (Benetti et al., 2016,
41 2017). Because a minor variation of less than 0.1 ‰ for $\delta^{18}\text{O}$ or 1 ‰ for $\delta^2\text{H}$ in a water mass
42 could reveal a significant hydrological process change, it is necessary to obtain the best
43 analytical accuracy for these measurements (better than 0.05 ‰ for $\delta^{18}\text{O}$ and 0.5 ‰ for $\delta^2\text{H}$).

44 Presently, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ can be measured using two different kinds of spectrometer,
45 based on different technologies: a) Isotope Ratio Mass Spectrometry (IRMS) and b) near-
46 infrared laser absorption spectrometry (LS). The two methods are described below:

47

48 a. Since the 1950s, the isotope composition of sea water has been traditionally measured
49 using IRMS, using both dual inlet and continuous flow methods. The IRMS measurements can
50 be carried out by using i. thermal conversion elemental analyser methods (TC/EA) (for $\delta^{18}\text{O}$
51 and $\delta^2\text{H}$), ii. metal reduction (uranium, chromium, zinc) of water (for $\delta^2\text{H}$), or iii. gas-sample
52 equilibration methods (for $\delta^{18}\text{O}$ and $\delta^2\text{H}$). The first two methods (i. and ii.) are not discussed in
53 this paper. We focus only on IRMS measurements after equilibration, which is a very common
54 method to measure $\delta^{18}\text{O}$ and $\delta^2\text{H}$. $\delta^{18}\text{O}$ ($\delta^2\text{H}$) measurements are obtained by equilibration
55 between a CO_2 (H_2) gas and the liquid (water) sample (cf. Epstein and Mayeda, 1953). These
56 measurements are reported on the activity scale, which reflect the stable isotopic composition
57 of the exchangeable water: only the free water molecules are able to exchange with the gas
58 during the equilibration, while the water molecules forming the hydration sphere of dissolved
59 ions do not participate in the exchange (Sofer and Gat, 1972, 1975, Skrzypek and Ford, 2014).
60 Because there is an isotope fractionation between the free water molecules and those forming
61 the hydration sphere, the stable isotope composition reported on the activity scale differs from
62 that reported on the concentration scale (that measures all water molecules: free and hydration
63 sphere). The "activity correction" increases with increasing salinity and depends on the ionic
64 composition of the saline solution. Notice that the two other IRMS methods (i. and ii., not
65 discussed in this paper) are thought to give measurements reported on the concentration scale.

66

67 b. In recent years, LS has been developed. The liquid sample is first injected into a
68 vaporizer, and then the water vapour is transferred to the analyser, containing a cavity filled
69 with circulating laser light *via* multiple mirrors. The technique uses the Beer-Lambert law to
70 calculate the concentrations of each species. Theoretically, all the water molecules analyzed
71 (free and hydration sphere) are injected to the vaporizer and the measurement is reported on the
72 concentration scale (Skrzypek and Ford, 2014). Presently, two commercial instruments

73 dominate the market: Picarro - Cavity Ring Down Spectroscopy (CRDS) and Los Gatos
74 Research - Integrated Cavity Output Spectroscopy (ICOS) (see detailed methods in Crosson et
75 al., (2002) and Baer et al., (2002)).

76

77 Most isotope measurements reported in the literature were carried out using the traditional
78 IRMS method. However, the new LS methods have advantages: the instruments are much
79 smaller, they are generally less expensive, they measure $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (also sometimes $\delta^{17}\text{O}$)
80 simultaneously on the same sample, and they allow continuous, in-situ measurements. They are
81 now distributed in many scientific laboratories and their use will probably increase in time. If
82 experimental conditions are optimal, both IRMS and LS methods can report precision
83 (reproducibility) better than $\sim 0.05\text{‰}$ for $\delta^{18}\text{O}$ and $\sim 1\text{‰}$ for $\delta^2\text{H}$ (1 SD), for freshwater and sea
84 water samples. The accuracy is often difficult to estimate while it is a crucial point to consider
85 for data comparisons between different laboratories. Laboratories place their data on the
86 VSMOW scale *via* normalization with internal standards, which have been previously
87 calibrated using international reference waters supplied by the International Atomic Energy
88 Agency (IAEA) in Vienna (Gonfiantini, 1978). Generally, clean/pure environmental
89 freshwaters present no issue for comparing measurements between different methods.
90 However, the presence of salt in the liquid samples has to be considered when using the IRMS
91 (with equilibration) and CRDS techniques, primarily in part because IRMS should provide data
92 on the activity scale, while CRDS on the concentration scale.

93 How to inter-compare $\delta^{18}\text{O}$ and $\delta^2\text{H}$ sea water measurements based on different
94 experimental protocols is the main purpose of this paper. We used artificial sea water (salinities
95 of 17.5, 35 and 70) prepared using a freshwater reference of known isotope composition
96 (salinity is expressed in the practical salinity scale of 1978, pss-78, with no unit). The solutions
97 were measured in four different laboratories to be able to evaluate the effect of the sea salt on

98 the measurement using IRMS coupled with equilibration method and LS. In the following, we
99 refer to the salt effect as the difference between the freshwater average reference values and the
100 saline solution. A natural sea water sample of salinity of 34.9 was also measured by the same
101 laboratories to assess the reliability of the estimated salt effect. First, we describe the present
102 state of knowledge in the field to introduce the contribution of this study.

103

104 2. Background

105

106 2.1 Salt effect with IRMS

107 Several studies have investigated the conversion from the activity to the concentration scale for
108 brine samples (sample containing more dissolved inorganic salt than typical seawater) (Feder
109 and Taube, 1952, Taube, 1954, Sofer and Gat, 1972, 1975, O' Neil and Truesdell, 1991, Kim et
110 al., 2012). In these studies, four artificial single-salt solutions (NaCl, KCl, MgCl₂ and CaCl₂)
111 were made by dissolving, at increasing molality, dry anhydrous salts in a freshwater of known
112 isotope composition. All the solutions were then measured by IRMS coupled with equilibration
113 between the liquid sample and the reference gas, to evaluate the separate effect of single salts
114 on the measurement. The individual effect of each salt on the IRMS measurement is given in
115 Figure 1. Sofer and Gat (1972, 1975) suggest two relationships calculated from a linear
116 combination of single salt effects as a function of the molality of the resulting solution
117 (Equation 1 and 2), assuming that the effects of single salts are cumulative. From Equation 1
118 and 2, the correction for a sea water at salinity of 35 ($m_{\text{Cl}^-}=0.56576$, $m_{\text{Na}^+}=0.48616$, $m_{\text{Mg}^{2+}}$
119 $=0.05475$, $m_{\text{Ca}^{2+}}=0.01065$, $m_{\text{K}^+}=0.01058$) is +0.06 ‰ for $\delta^{18}\text{O}$ and +0.55‰ for $\delta^2\text{H}$. Using
120 the data from Kim et al. (2012) and O' Neil and Truesdell (1991) and excluding the results from
121 Sofer and Gat (1972), we applied the same method to formulate Equation 3. The subsequent
122 correction for typical sea water S=35 is +0.06‰ for $\delta^{18}\text{O}$, which is in agreement with Sofer and

123 Gat (1972). The two linear combinations consider there is no effect from NaCl on the $\delta^{18}\text{O}$
124 measurement.

$$125 \quad \delta^2\text{H} = -0.4m_{\text{NaCl}} - 5.1m_{\text{MgCl}_2} - 6.1m_{\text{CaCl}_2} - 2.4m_{\text{KCl}} \quad (1)$$

$$126 \quad \delta^{18}\text{O} = 1.11m_{\text{MgCl}_2} + 0.476.1m_{\text{CaCl}_2} - 0.16m_{\text{KCl}} \quad (2)$$

$$127 \quad \delta^{18}\text{O} = 1.05m_{\text{MgCl}_2} + 0.416.1m_{\text{CaCl}_2} - 0.27m_{\text{KCl}} \quad (3)$$

128

129 While these studies are very careful to ensure the removal of the salt effect observed for
130 brine measurements, they are not appropriate to estimate with accuracy (within the normal
131 isotope measurement error) the salt effect for typical sea water. These studies reveal that the
132 salt effect for seawater measurement should be small ($\sim 0.06\text{‰}$ for $\delta^{18}\text{O}$ and $\sim 0.55\text{‰}$ for $\delta^2\text{H}$)
133 and close to the optimal precision of mass spectrometers. In particular, the studies with most
134 data (Sofer and Gat, 1972; 1975) report an experimental precision of ± 0.10 to 0.14‰ for $\delta^{18}\text{O}$
135 and $\pm 3\text{‰}$ for $\delta^2\text{H}$ which is not good enough to evaluate the small difference the salt effect makes
136 at salinities around 35. Moreover, most of the time the first artificial saline sample is
137 significantly different from the molality of seawater (the molality for each single salt in sea
138 water at $S=35$ is given in Figure 1 by the black dashed line), and the estimation of the salt effect
139 for typical seawater results from a linear extrapolation at zero salinity. Notice that while four
140 studies are available for $\delta^{18}\text{O}$ and allow comparisons, only Sofer and Gat (1975) measured the
141 four single salt effects, necessary to convert $\delta^2\text{H}$ sea water measurements into the concentration
142 scale.

143 Three other studies have been undertaken with the aim of providing artificial saline
144 solutions with lower salinities in order to evaluate the salt effect especially for sea water
145 (Lecuyer et al., 2009, Martineau et al., 2012, Bourg et al., 2001). Lecuyer et al. (2009) and
146 Martineau et al. (2012) found a salt effect at salinities around 35 of -0.15‰ for $\delta^{18}\text{O}$ and -2‰
147 for $\delta^2\text{H}$. They used salt from the sea salt marsh of Guerande (France), as representative of sea

148 water. However, the chemical composition given in their Table 1 indicates that this commercial
149 table salt is mainly composed of NaCl and is therefore not similar to typical sea water
150 composition. In addition to the table salt from Guerande, Martineau et al. (2012) also measured
151 the single NaCl effect by dissolving a pure reagent-grade NaCl salt in distilled water. The
152 estimated salt effect was found to be approximately the same for both solutions (not shown
153 here). In Figure 1, we show the $\delta^{18}\text{O}$ results based on the sea salt marsh of Guerande (no pure
154 NaCl solution available), while for $\delta^2\text{H}$ we show the results from the pure NaCl solution. In the
155 following, we consider the results from Lecuyer et al. (2009), as being the approximate effect
156 on the single salt NaCl. Figure 1 shows that while the different experiments are rather consistent
157 for the single salts KCl, MgCl₂ and CaCl₂, there is a strong disagreement for the NaCl effect on
158 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ between the different studies. O'Neil (1991) and Kim et al. (2012) found no effect
159 of NaCl on $\delta^{18}\text{O}$ (consistent with Sofer and Gat, 1972, but this result is not shown in their study),
160 while Lecuyer et al. (2009) found a significant offset between the measurement of the
161 freshwater and the NaCl solution. For the NaCl effect on $\delta^2\text{H}$, the two available studies of Sofer
162 and Gat (1975) and Martineau et al. (2012) also provide rather differing results (albeit with a
163 large scatter).

164 Bourq et al. (2001) evaluated the sea-salt effect using a solution composed of a mixture of
165 the different marine salts with a chemical composition proportional to seawater. They prepared
166 solutions with 0.5, 1 and 2 times the concentration of seawater (0.5SW, SW and 2SW).
167 Measurements were carried out using an equilibration device coupled to a Finnigan MAT252
168 mass spectrometer, and they reported reproducibility of 0.03‰ for $\delta^{18}\text{O}$ and 0.4‰ for $\delta^2\text{H}$. For
169 seawater, they found no effect on $\delta^{18}\text{O}$ over this range of concentration (up to 2SW) and a salt
170 effect of -1.7 ‰ for $\delta^2\text{H}$ at SW. These proposed corrections for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are different from
171 those described by Sofer and Gat (1972, 1975).

172

173 2.2 Salt effect with LS

174 The LS measurements are considered to be on the concentration scale and only a few
175 studies have investigated the salt effect on the oxygen and hydrogen isotope composition of sea
176 water (Skrzypek and Ford, 2014, Walker et al., 2016). However, measurement of saline
177 solutions using LS could be affected by: (1) an incomplete extraction/evaporation of water
178 within the vaporizer, and (2) a memory effect due to the water absorption on accumulated salt
179 (Skrzypek and Ford, 2014). Skrzypek and Ford (2014) show that (2) does not affect
180 significantly the measurements when the total load of salt in the vaporizer is below ~38.5 mg
181 (equivalent to ~100 sea water samples). Thus, this present study focuses on (1), providing that
182 the vaporizer is clean enough to run the measurements. Skrzypek and Ford (2014) measured
183 artificial sea water from a freshwater reference of known isotope composition, with
184 concentration of SW and 2SW. They found a $\delta^{18}\text{O}$ difference between the reference freshwater
185 and the saline solution of 0.09‰ for SW and 0.15‰ for 2SW and for $\delta^2\text{H}$ a difference of 1‰
186 for SW and 0.20‰ for 2SW. They conclude that for their set up (a Picarro Ltd. Analyzer L1115-
187 I with vaporizer V1102-I operating at 140°C) this effect is within the uncertainties of the
188 measurement (the precision reported by the manufacturer for this version is 0.10‰ for $\delta^{18}\text{O}$ and
189 1‰ for $\delta^2\text{H}$).

190

191 2.3 The added value of this study

192 The previous sections suggest that the salinity effect for both IRMS (with equilibration) and
193 LS measurements should be small for typical seawater at salinity 35, with a magnitude close to
194 the actual precision of the spectrometers (except the strongest effect of -1.7 ‰ on $\delta^2\text{H}$ observed
195 by Bourg et al., 2001). This makes this question sensitive, but not meaningless in ocean
196 sciences, where isotope variations can be very small. Data from the literature suggests that the
197 salt effect is sometimes not sufficiently assessed for typical seawater (e.g. precision not optimal,

198 range of salinity not relevant) and reveals contradictories in current literature (for sea salt as
199 well as for NaCl) (see previous sections). For these reasons, we decided to evaluate the salt
200 effect for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in four different laboratories, using either IRMS with equilibration or
201 LS techniques (Table 1). Note that only one laboratory provided $\delta^2\text{H}$ measurements using IRMS
202 with equilibration. We evaluate the salt effect for an appropriate range of salinities: we made
203 up artificial seawater at salinities of half normal salinity (0.5SW), normal salinity (SW) and
204 twice normal salinities (2SW). These solutions combine together the different salts present in
205 seawater (see section 3.1) and do not use the assumption of a cumulative effect of each single
206 salt (as assumed in the other studies, except in Bourg et al. (2001) and Skrzypek and Ford
207 (2014)). We also used a pure NaCl solution to investigate this single salt effect, due to
208 contradictions in the current literature (see Figure 1). The different solutions were then measured
209 using three different IRMS (and equilibration) and one LS instruments. For LS, the
210 measurement in the cavity requires the removal of the salt from the seawater because the sample
211 is analyzed in the vapor phase *via* a vaporizer. We tested three different protocols of LS
212 measurements: a direct injection of the seawater sample into the vaporizer, an injection through
213 a liner inserted in the vaporizer inlet, and a distillation of the saline sample prior to the
214 measurement, which is then injected to the vaporizer (see the supplementary material for a
215 detailed description of the distillation protocol). We also distributed a natural sea water sample
216 (salinity 34.9) to the different laboratories to assess the reliability of the estimated salt effect
217 correction from the artificial seawater (SW).

218

219 3. Methods

220

221 The four laboratories who participated in this inter-comparison exercise were: Institute of
222 Earth Sciences (IES) in Reykjavik (Iceland), British Geological Survey (BGS) in Keyworh

223 (UK), the Earth Sciences Research Group at the Vrije Universiteit Brussel (VUB) in Brussels
 224 (Belgium) and the Laboratoire d’Oceanographie et du Climat, Experimentation et Approches
 225 Numeriques (LOCEAN) in Paris (France). The BGS and IES laboratories participated in the
 226 WICO 2016 International Water Isotope Inter-Comparison Test. The small difference with
 227 freshwater $\delta^{18}\text{O}$ measurements from IAEA laboratories (less than 0.05‰) reveal the high
 228 precision routinely obtained at the BGS and IES laboratories. The methods of measurements
 229 are given in Table 1 and are described for each laboratory in sections 3.2 to 3.5. The artificial
 230 saline solutions and the natural seawater sample used in this study are described in section 3.1.
 231 The protocol elaborated to evaluate the salt effect is described in section 3.6.

232

Laboratory	Method	Measurements
IES	IRMS continuous flow–equilibration with CO_2	$\delta^{18}\text{O}$
	IRMS continuous flow–equilibration with H_2	$\delta^2\text{H}$
BGS	IRMS dual inlet–equilibration with CO_2	$\delta^{18}\text{O}$
VUB	IRMS continuous flow–equilibration with CO_2	$\delta^{18}\text{O}$
LOCEAN	PICARRO CRDS L2130-I + Distillation	$\delta^{18}\text{O}, \delta^2\text{H}$
	PICARRO CRDS L2130-I + Liner	$\delta^{18}\text{O}, \delta^2\text{H}$
	PICARRO CRDS L2130-I + Direct injection	$\delta^{18}\text{O}, \delta^2\text{H}$

233 Table 1: Methods and measurements for the four participating laboratories. Each laboratory
 234 received the initial freshwater reference, the three artificial seawater (0.5SW, SW, 2SW), the

235 three pure NaCl solutions (17.5, 35 and 70 g/l) and the natural seawater sample of
236 salinity=34.9.

237

238 3.1 The saline solutions

239 Artificial NaCl and seawater solutions were made from the LOCEAN freshwater internal
240 reference KONA II (with values on the VSMOW scale pre-measured by LOCEAN of
241 $\delta^{18}\text{O}=+0.51\text{‰}$ and $\delta^2\text{H}=+1.85\text{‰}$). This reference is stored in a steel bottle with a slight
242 overpressure of dry nitrogen to avoid evaporation and exchange with ambient air humidity. The
243 saline solutions were prepared by adding weighted amounts of solid salts (reagent grade purity)
244 to measured volumes of KONA II water (Table 2) to attain target concentrations. Solid salts
245 were weighed on a scale (precision of ± 0.1 mg) and dissolved in KONA II using a magnetic
246 stirrer. In the case of the artificial seawater, salts were dissolved successively. The salinity of
247 the artificial seawater solutions was measured with a salinometer (precision of $\pm 0.2\text{‰}$) yielding
248 salinities equal to 17.35, 33.80 and 65.17 for the 0.5SW, SW and 2SW samples, respectively.
249 The difference between the target and obtained salinity is due mostly to the error in the final
250 volume of the solution. Therefore, the ions within the artificial SW solutions are in the same
251 proportions as in natural seawater. 250 ml of each SW solution and 100 ml of each pure NaCl
252 solution were made and the solutions were subsampled into individual 25 ml tinted glass bottles
253 (GRAVIS).

254 The natural sample of sea water (salinity 34.9) was collected from the Icelandic shelf, off
255 Reykjavik around 64.2 °N/22.5 °W (November 2015). About three liters of this water were
256 collected and subsampled into 30 ml glass bottles (GRAVIS).

257

Salinity	NaCl	MgCl ₂	MgSO ₄	CaCl ₂	KCl	NaHCO ₃	Solution density	Volume
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g/kgSW	g	g	G	g	g	g	kg/litreSW	liters
17.5	13.516	1.247	1.685	0.582	0.37	0.103	1.01	0.248
35	27.03	2.494	3.369	1.163	0.739	0.206	1.023	0.244
70	54.06	4.988	6.738	2.326	1.478	0.412	1.05	0.238
NaCl (g/kg sol)	Density (kg/litre)	Volume sol. (litres)	NaCl (g)					
18	1.013	0.1	1.772					
35	1.024	0.1	3.583					
70	1.046	0.1	7.322					

258 Table 2: Calculations of the weighted amounts of solid salts and volumes of KONA II.

259

260 3.2 IES ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) laboratory

261 A Delta V Advantage IRMS coupled with a Gasbench II (continuous flow mode) was used
262 for the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements. 200 μl of sample water were loaded into 12 ml exetainers
263 (Labco Limited, UK), the vials were sealed with septa and all air is removed from the sample
264 vials by an automated, autosampler-assisted flushing procedure which uses a mixture of either
265 H_2 (for $\delta^2\text{H}$) or CO_2 (for $\delta^{18}\text{O}$) in He. The H_2 or CO_2 in the flushing He stream was used as the
266 equilibration gas. The equilibration time was $\sim 21^\circ\text{C}$ at 24 hours for $\delta^{18}\text{O}$ (+ 24 hours for the
267 last sample) and 1 hour for $\delta^2\text{H}$ using a Platinum catalyzer (+7 hours for the last sample). After
268 equilibration, the gas sampling system includes a two port needle which adds a gentle flow of
269 He into the sample vial, thus diluting and displacing sample gas. Water is removed from the
270 sample gas through diffusion traps.

271

272 3.3 BGS ($\delta^{18}\text{O}$) laboratory

273 An Isoprime100 IRMS coupled with the AquaPrep system (dual inlet mode) was used for
274 the analysis of $\delta^{18}\text{O}$. 200 μl of sample water were loaded into Labco Limited 3.7ml exetainers,
275 the exetainers were then evacuated (by expansion before pumping) to remove atmosphere then
276 flushed with CO_2 . The equilibration time was at least 12 hours (+25 hours for the last sample)
277 at $\sim 40^\circ\text{C}$. Each individual gas sample was then admitted to the cryogenic water trap to remove
278 any water vapour. The dry sample gas was then expanded into the dual inlet where it was
279 measured on the transducer before being expanded in the dual inlet bellows. Ionvantage
280 software then balanced the reference bellows relative to this volume and gases were admitted
281 to the IRMS. The sample and reference CO_2 gases enter alternatively into the mass spectrometer
282 through the dual changeover valve for isotope ratio measurement.

283

284 3.4 VUB ($\delta^{18}\text{O}$) laboratory

285 A Nu Instrument perspective IRMS coupled with a Gasbensch (Nu Instrument, Wrexham,
286 UK) (continuous flow mode) was used for $\delta^{18}\text{O}$. 12 ml exetainers (Labco Limited, UK) were
287 first flushed with He gas and capped with a rubber septum and aluminum seal. 500 μl of sample
288 was injected followed by an injection of 200 to 300 μl of CO_2 . The equilibration time was at
289 least 24 hours (+1 h30 for the last sample) at $\sim 21^\circ\text{C}$, while the sample is being shaken.

290

291 3.5 LOCEAN ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) laboratory

292 A PICARRO CRDS L2130-I Isotopic H_2O was used for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis. The
293 analyses were performed by running at least 6 injections per sample. The first 3 injections were
294 ignored to eliminate potential memory effects between samples and the remaining injections
295 were averaged. We used a 10 μl syringe from SGE (10F-CTC-5/0.47C). Here, we used three
296 different methods prior to CRDS measurements:

297

298 a. Sea water samples were distilled (see protocol in Appendix A). We elaborated this
299 method because over the long term, measuring freshwater samples decreases maintenance
300 problems, such as salt accumulation in the vaporizer of the PICARRO system and its potential
301 effect on the measurements (Skrzypek and Ford, 2014). Moreover, freshwater measurements
302 considerably increase the lifetime of the syringe, compared to seawater measurements.

303 b. The analyses uses a wire mesh inserted in the vaporizer inlet to trap about 80% of the
304 sea water salt (the liner was provided by Dave Hodell, University of Cambridge). The amount
305 of trapped salt was estimated by weighting the liner before and after the use. The life time of
306 the syringe is shorter than (a).

307 c. We directly inject sea water samples in the vaporiser. This method makes it necessary
308 to clean the vaporiser regularly to remove salt deposit within the vaporiser (after ~100
309 seawater samples, Skrzypek and Ford (2014)). The life time of the syringe is shorter than (a).

310

311 3.6 Protocol of salt effect evaluation

312

313 To evaluate the sea-salt effect, each laboratory measured the initial freshwater reference and
314 the three artificial seawaters (0.5SW, SW, 2SW). An accurate analytical precision was achieved
315 by repeating the measurements several times (more than one run) (except for the sole CRDS
316 measurement by direct injection at LOCEAN). The references used by the different laboratories
317 to convert the measurements to the VSMOW scale are given in Table 3. No significant
318 instrumental drift was evident during the IES, BGS and LOCEAN measurements and therefore
319 no drift correction was applied. For the VUB measurements, the instrumental drift of each run
320 was corrected using the internal standards, regularly inserted within the run. Then, the salt effect
321 was evaluated by subtracting the VSMOW value of the saline solution to the value of the initial
322 freshwater reference. In this manner, the salt effect corresponds to the correction needed to

323 convert the measurement into the concentration scale. This protocol has been similarly applied
324 for evaluating the NaCl effect.

325 Each laboratory also measured the natural seawater sample of salinity=34.9 (see section
326 3.1) to assess the corrections proposed from the artificial solutions. The same references (see
327 Table 3) have been used to convert the measurements to the VSMOW scale.

328

Laboratories	Reference	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
IES	KONA	-0.05	+0.46
	MIX	-3.26	-21.32
	EDP	-6.61	-44.3
BGS	CA-HI	-7.30	
	CA-LO	-39.30	
VUB	DO1	+6.91	
	NDO1	-0.79	
	NDO2	-7.38	
LOCEAN	Same as IES		

329

330 Table 3: Isotope composition of the references used by the different laboratories to
331 convert the measurements onto the VSMOW scale.

332

333 4. Results

334

335 4.1 Effect of sea salts on IRMS measurements (gas-sample equilibration method)

336 We tested the sea-salt effect on the IRMS measurements by analyzing the artificial
337 seawater solutions at salinity 17.5, 35 and 70 at IES, BGS and VUB. In each run, the freshwater

338 reference KONA II was also measured several times and the salt effect defined as the difference
 339 between the freshwater reference average values and the saline solution. The results are given
 340 in Table 4 and Figure 2. We also present in Figure 2 the results from the study of Bourg et al.
 341 (2001), as well as the extrapolated linear correction from Sofer and Gat (1972, 1975). All three
 342 laboratories show a salt effect for $\delta^{18}\text{O}$ with the amplitude of the effect increasing with salinity
 343 (except for BGS measurements for salinity 70) which is in contrast to Bourg et al. (2001) who
 344 detected no salt effect up to salinity 70. Interestingly, the salt effect for $\delta^{18}\text{O}$ measured by BGS
 345 is in the opposite direction to the other laboratories for salinities of 35. For $\delta^2\text{H}$, the trend is
 346 quite similar between IES and Bourg et al. (2001) but differs from the Sofer and Gat (1975)
 347 results.

348 Due to the current disagreement on the single salt NaCl effect (see Figure 1), we also
 349 measured pure NaCl solution at concentrations 17.5, 35 and 70. As for the sea-salt effect, results
 350 are presented in Table 4 and Figure 3. We also present the earlier results available over this
 351 range of salinity in Figure 3. For $\delta^{18}\text{O}$, the same trends were observed (decreasing at increasing
 352 NaCl concentration) but with different slopes for BGS, IES, VUB and Lecuyer et al. (2009).
 353 However, no effect was observed by Kim et al. (2012). For $\delta^2\text{H}$, similar trends were observed
 354 (decreasing at increasing NaCl concentration) between IES and Martineau et al. (2012), even if
 355 the dispersion can be strong for some $\delta^2\text{H}$ measurements.

356

		IES						BGS			VUB		
		$\delta^{18}\text{O}$ (‰)			$\delta^2\text{H}$ (‰)			$\delta^{18}\text{O}$ (‰)			$\delta^{18}\text{O}$ (‰)		
Samples		n	Mean	1SD	n	Mean	1SD	n	Mean	1SD	n	Mean	1SD
SW	17.5	12	+0.04	0.03	9	-0.45	0.99	3	+0.01	0.02	8	-0.03	0.06

	35	12	+0.07	0.04	9	-1.17	1.45	9	-0.07	0.04	8	+0.02	0.03
	70	12	+0.11	0.05	9	-2.73	1.39	3	-0.05	0.03	8	+0.09	0.07
NaCl	17.5	5	-0.03	0.05	3	+0.20	1.82	3	-0.05	0.02	8	-0.02	0.05
	35	8	-0.10	0.04	4	-0.05	0.73	9	-0.14	0.04	8	-0.03	0.06
	70	5	-0.16	0.06	3	-1.71	0.73	3	-0.19	0.01	8	-0.07	0.06

357

358 Table 4: Number of vials (n), mean salt effect and one standard deviation (1SD) for each
359 saline solution and each IRMS method. The salt effect is presented in ‰ as the difference
360 between the freshwater reference and the saline solution.

361 4.2 Effect of sea salts of the CRDS measurements

362 The sea salt effect was tested on the three different CRDS measurement methods
363 (distillation, liner or direct injection). The NaCl effect has only been measured for
364 measurements using the distillation method.

		Distillation					
		$\delta^{18}\text{O}$ (‰)			$\delta^2\text{H}$ (‰)		
Samples		n	Mean	1SD	N	Mean	1SD
SW	17.5	7	+0.06	0.05	7	+0.30	0.26
	35	8	+0.14	0.04	8	+0.57	0.12
	70	9	+0.23	0.04	9	+0.87	0.15
NaCl	17.5	2	+0.03	0.01	2	+0.08	0.04
	35	2	+0.03	0.02	2	+0.22	0.11
	70	2	+0.02	0.03	2	+0.22	0.09

		Liner					
		$\delta^{18}\text{O}$ (‰)			$\delta^2\text{H}$ (‰)		
		n	Mean	1SD	N	Mean	1SD
SW	17.5	4	+0.02	0.03	4	-0.10	0.04
	35	4	+0.09	0.03	4	+0.12	0.11
	70	3	+0.12	0.02	4	+0.39	0.23
		Direct injection					
		$\delta^{18}\text{O}$ (‰)			$\delta^2\text{H}$ (‰)		
		n	Mean	1SD	N	Mean	1SD
SW	17.5	1	+0.01	-	1	-0.07	-
	35	1	+0.07	-	1	+0.15	-

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Table 5: Number of vials (n), average salt effect and standard deviation for each salt solution and each CRDS method. Notice that there is only one measurement available for the direct injection method in order to avoid salt accumulation in the vaporiser.

Figure 4A shows that there is no effect of the distillation on the pure NaCl solutions for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, even at high concentration, while there is a near-proportional effect for the sea salt solution with increasing salinity for both isotopes. The sea salt effect at salinity 35 for CRDS measurements after our distillation method is +0.14‰ for $\delta^{18}\text{O}$ and +0.57‰ for $\delta^2\text{H}$. Moreover, the experiments show a sea salt effect, increasing with salinity, using the liner or by direct injection of sea water into the vaporizer (Figure 4B). The sea salt effect at salinity 35 for CRDS measurements by direction injection or using a liner is +0.07 to +0.09‰ for $\delta^{18}\text{O}$ and +0.12 to +0.15‰ for $\delta^2\text{H}$.

379 5.Discussion

380 5.1. Sea salts effect and corrections

381 For IRMS measurement using the gas-sample equilibration method, our results suggest
382 that the salt effect (1) is not insignificant even at salinity 35 and (2) could vary between
383 different laboratories (Figure 2). For CRDS measurements coupled with distillation, it is likely
384 that the sea salts left behind in the distillation process are partly hydrated with water isotopically
385 more positive than the distilled water. This statement is consistent with the fact that we do not
386 observe an effect with NaCl, an anhydrous salt in which no water molecule is left behind in the
387 solid phase during distillation (see Figure 4). When using a liner or direct injection with the
388 CRDS, it is likely that this effect is due to the incomplete extraction/evaporation of water from
389 the seawater samples into the vaporizer (heavier molecules stay preferentially to the hydrated
390 salt compared to the vapor). The same effect found for the two methods (liner or direct injection)
391 is consistent because there is the same amount of salt formation during vaporization of the
392 seawater samples. The only difference is about 80% of the salt can be easily removed by
393 changing the liner (estimated by weight difference, data not shown). In Figure 4B, we also
394 present data from Skrzypek and Ford (2014) who made two artificial sea waters at salinities of
395 35 and 70 and measured them by direct injection into a Picarro vaporizer/analyzer. The standard
396 deviation is 0.10‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$, higher than in our study because they used an
397 earlier version of the Picarro CRDS analyzer (the precision has since been improved by a factor
398 2 according to the manufacturer). They found a similar corrections for $\delta^{18}\text{O}$ at salinities of 35
399 and 70 and for $\delta^2\text{H}$ at salinity 70, while their proposed correction at salinity 35 for $\delta^2\text{H}$ is higher
400 than the one we propose. Nevertheless, the difference remains included in their estimated
401 uncertainties.

402

403 The correction needed to remove the sea salt effect at salinity 35 from the isotope
 404 measurements for each of the methods discussed here are summarized in Table 6 (results from
 405 Table 3 and 4 for salinity 35). The correction is the difference between the initial freshwater
 406 and the saline solution at salinity 35. We decided not to interpolate the correction using
 407 measurements at salinity 17.5, 35 and 70, as we cannot evaluate if the correction is linear.
 408 Nevertheless, the measurements at 17.5 and 70 can be used to have an idea of the trend of the
 409 correction.

410

	Laboratory	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
IRMS	IES	+0.07	-1.17
	BGS	-0.07	NA
	VUB	+0.02	NA
PICARRO	Distillation	+0.14	+0.57
	Liner	+0.09	+0.12
	Direct injection	+0.07	+0.15

411 Table 6: Estimated correction in ‰ for a seawater sample at salinity 35. NA = not available.

412 5.2 Assessment of corrections with a natural seawater sample

413 To check the consistency of the evaluated corrections, a natural sample of sea water of
 414 salinity 34.9 was measured several times by each laboratory according to the different methods.
 415 The results are presented in Figure 5. All the measurements are on the VSMOW scale, black
 416 dots corresponding to measurements without the correction and red dots to measurements using
 417 the correction factors derived in this study (Table 6). For $\delta^{18}\text{O}$ and $\delta^2\text{H}$, the dispersion is
 418 significantly smaller after correction. For $\delta^{18}\text{O}$, the standard deviation of the 6 measurements is

419 0.06‰ without correction and 0.02‰ with correction. For $\delta^2\text{H}$, the standard deviation of the 4
420 measurements is 0.55‰ without correction and 0.23‰ with correction. Thus, this test supports
421 the corrections estimated from the artificial seawater and the efficiency of the corrections to
422 improve inter-comparison amongst laboratories.

423

424 5.3 Recommendations

425

426 To facilitate the comparison of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ seawater measurements carried out using
427 different analytical methods, we suggest that the isotope values are presented on the
428 concentration scale. We recommend that all laboratories measuring the isotope composition of
429 seawater, using LS or IRMS using equilibration method, should evaluate the salt effect on the
430 measurement by preparing an artificial seawater at a salinity in the same range as in their
431 samples (see section 3.1). Then, the artificial solution should be measured in the same runs as
432 the initial freshwater reference. The salt correction can be estimated as the difference between
433 the freshwater reference and the saline solution measurement values. The measurements should
434 be repeated regularly throughout the lifetime of the instrumentation to assess the long-term
435 validity of the correction. The detailed procedure used in this study is described in the methods
436 section. We also recommend full descriptions be given of measurement methods, including
437 any correction that were applied. There is a shared interest in the marine geochemical
438 community to report $\delta^{18}\text{O}$ - $\delta^2\text{H}$ seawater values in a consistent and comparable manner. An
439 effort in this direction would lead to merged marine $\delta^{18}\text{O}$ - $\delta^2\text{H}$ datasets of greater value.

440

441 6. Conclusions

442

- 443 • Thanks to the improvements in instrumentation, the analytical precision of seawater $\delta^{18}\text{O}$ - $\delta^2\text{H}$
444 measurements has increased since the 1950s. Here we show that minor corrections are
445 necessary to remove the salt effect from measurements carried out with IRMS (and
446 equilibration) and from measurements carried out with LS.
- 447 • Our data reveal that the correction associated to measurements carried out with IRMS (and
448 equilibration) can differ between laboratories. These differences possibly result from slightly
449 different measurement protocols (e.g. equilibration and extraction protocol, sample
450 volume/vial).
- 451 • We found a significant salt effect for CRDS measurements carried out by injecting the
452 seawater directly or *via* a liner into the vaporiser, indicating that the measurements are not
453 initially in the concentration scale, as some water likely remains trapped on hydrated salts that
454 precipitate during evaporation.
- 455 • Considering the salt effect is a necessary step for accurately comparing datasets analysed in
456 different laboratories. We recommend being aware of these possible systematic differences
457 when comparing isotope datasets produced in different laboratories.
- 458 • We suggest that the concentration scale is the most relevant to precisely compare $\delta^{18}\text{O}$ - $\delta^2\text{H}$
459 seawater isotope data. We recommend that all laboratories measuring the isotope composition
460 of seawater, using LS or IRMS (and equilibration), should evaluate the salt effect specific to
461 their own analytical equipment by carrying out a series of tests on artificial seawater of known
462 isotope composition. These tests should be repeated during the lifetime of the instrument to
463 evaluate if the salt effect remains constant over a longer period of time for a given analytical
464 setup. Our experiments carried out over a period of time of less than 6 months and do not
465 allow to evaluate if the salt effect remains constant over a longer period of time for a given
466 analytical setup.

467 • Finally, when providing isotope data to international databases, we recommend that the
468 measurement method be fully described, including any corrections applied. Assembling
469 datasets based on measurements made by different groups using varying analytical approaches
470 is a complex undertaking. It is very important to ensure that datasets and methods are fully
471 documented, because investigating long term change in the oceanic freshwater budget or large
472 scale oceanic processes requires the highest precision we can attain.

473

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481 analysis.

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Appendix A : The sea water distillation process

The distillation line is shown in Figure A1. Before distillation, we provide partial vacuum in all glass compartments. Thus, we freeze 2 ml of the sample with liquid nitrogen and open the connection to the pump. When the void is sufficiently strong ($\sim 5.5 \cdot 10^{-2}$ mbar), we turn off the connection to the pump. Then, the water sample is heated to its boiling point and a cold trap is used to retrieve the distilled water. This operation lasts at least 15 minutes to allow reproductibility. The 15 minute duration is necessary to have the best precision, which is dependent on a full recovery of the water originally present in the seawater sample. The reproductibility of the method has been evaluated by distilling 15 times the same seawater samples at salinity 35 and measuring the 15 products with our Picarro instrument. We found a standard deviation of 0.04‰ for $\delta^{18}\text{O}$ and 0.24‰ for $\delta^2\text{H}$, showing the good reproducibility in the method. We elaborated on this method here because over the long term, measuring freshwater samples decreases maintenance problems, such as salt accumulation in the vaporizer and extends the very short lifetime of the syringe.

	$\delta^{18}\text{O}$	1SD	$\delta^2\text{H}$	1SD
1	+1.57	0.01	+5.37	0.07
2	+1.63	0.02	+5.74	0.18
3	+1.62	0.00	+5.81	0.18
4	+1.63	0.04	+5.86	0.21
5	+1.63	0.03	+5.89	0.21
6	+1.67	0.02	+5.91	0.05

7	+1.69	0.03	+6.26	0.16
8	+1.69	0.00	+6.13	0.18
9	+1.74	0.03	+6.41	0.22
10	+1.61	0.02	+5.86	0.14
11	+1.63	0.03	+5.84	0.14
12	+1.65	0.02	+6.07	0.22
13	+1.67	0.01	+5.91	0.10
14	+1.70	0.03	+6.09	0.05
15	+1.66	0.03	+5.97	0.01

500

501 Table A1: Measurements with a Picarro instrument of 15 distilled products from a same
502 seawater sample at salinity 35. The column SD indicates the standard deviation for each
503 isotopes based on the three last injections to the vaporiser (after removing the three first
504 injections).

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583

584 Caption

585

586 Figure

587

588 Figure 1: Estimation of the salt effect for the single salt (a) NaCl, (b) KCl, (c) MgCl and (d)
589 CaCl for $\delta^{18}\text{O}$ (left) and $\delta^2\text{H}$ (right). The Y-axis is the difference between the pure freshwater
590 and the salt solution (=salt effect) and the X-axis is the molality in mole.kg^{-1} . The dashed black
591 vertical line indicates the molality of the single salt in the standard mean sea water (S=35). Note
592 that Lecuyer et al. (2009) do not use a pure NaCl solution but natural sea salt marsh of Guerande
593 (France) (see exact composition in their Table 1).

594 Figure 2: Sea salt effect in ‰ in function of the salinity (A) for $\delta^{18}\text{O}$ and (B) for $\delta^2\text{H}$. The Y-
595 axis is the difference between the freshwater reference and the artificial sea water. The error
596 bar represents a 95% confidence interval

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599

600 Figure 3: Salt effect for pure NaCl solution in a function of the concentration. The Y-axis is
601 the difference between the freshwater reference and the artificial sea water (=the salt effect).
602 Note that Lecuyer et al. (2009) did not use a pure solution of NaCl but a sea salt from natural
603 sea salt marsh of Guerande (France) (see composition in their Table 1). The data from
604 Martineau et al. (2012) is the average of their two different runs presented in Figure 1 (pure
605 NaCl solution). The error bar represents a 95% confidence interval.

606

607 Figure 4: Estimation of the salt effect for $\delta^{18}\text{O}$ (left) and $\delta^2\text{H}$ (right) during (A) CRDS
608 measurement post distillation for artificial seawater and pure NaCl solution, and (B) CRDS

609 measurement with Liner or by direct injection to the vaporizer (only one measurement was done
610 by direct injection). The error bar represents a 95% confidence interval. The data from Skrzypek
611 and Ford (2014) are also presented (1 SD=0.10 ‰ for $\delta^{18}\text{O}$ and 1 SD=1‰ for $\delta^2\text{H}$, manufacturer
612 specification).

613

614 Figure 5: Comparison of the natural sea water sample at salinity 34.9. The measurements are
615 reported on the VSMOW scale. No correction was applied for the black dots, while the red dots
616 are corrected for the salt effect estimated from this study (Table 5). For $\delta^{18}\text{O}$ and $\delta^2\text{H}$, the
617 dispersion is smaller after correction. The error bar represents a 95% confidence interval (only
618 one measurement done by direct injection).

619

620 Figure A1: Schema of the distillation line : Step A : The sample is frozen and we did the vacuum
621 in the line. Step B: The distillation is running, the water vapor is trapped with liquid nitrogen.

622

623

Tables

624

625 Table 1: Methods and measurements for the four participating laboratories. Each laboratory
626 received the initial freshwater reference, the three artificial seawater (0.5SW, SW, 2SW), the
627 three pure NaCl solutions (17.5, 35 and 70 g/l) and the natural seawater sample of
628 salinity=34.9.

629 Table 2: Calculations of the weighted amounts of solid salts and volumes of KONA II.

630 Table 3: Number of measurement (n), mean salt effect and one standard deviation (1SD) for
631 each saline solution and each IRMS method. The salt effect is presented in ‰ as the
632 difference between the freshwater reference and the saline solution.

633 Table 4: Number of measurement (n), average salt effect and standard deviation for each salt
634 solution and each CRDS method.

635 Table 5: Estimated correction in ‰ for a seawater sample at salinity 35.

636 Table A1: Measurements with a Picarro instrument of 15 distilled products from a same
637 seawater sample at salinity 35. The column SD indicates the standard deviation for each
638 isotopes based on the three last injections to the vaporiser (after removing the three first
639 injections).