Inter-comparison of salt effect correction for $\delta^{18}O$ and δ^2H measurements in seawater by CRDS and IRMS using the Gas-H$_2$O equilibration method

M. Benetti[1], A. E. Sveinbjörnsdóttir[1], R. Ólafsdóttir[1], M.J. Leng[2], C. Arrowsmith[2], K. Debondt[3], F. Fripiat[4], G. Aloisi[5]

1. Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland

2. NERC Isotope Geosciences Facilities, British Geological Survey, Nottingham NG12 5GG, UK

3. dpt of Anaytical and Environmental Geochemistry (AMGC)Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels, Belgium

4. Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

5. LOCEAN, Sorbonne Universités, UPMC/CNRS/IRD/MNHN, Paris, France

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 ($\delta^{18}O$ and $\delta^{2}H$) 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 ~0.09‰ for

15   $\delta^{18}O$, while the correction is relatively less significant for $\delta^{2}H$ (~0.13‰). 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 $\delta^{18}O$ and $\delta^{2}H$,

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 ($\delta^{18}O$ and δ^2H) 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 $\delta^{18}O$ and –5 and +10‰ for

34   δ^2H). For example, the oxygen isotope composition at the Weddell Sea surface only varies by

35   0.15‰ for $\delta^{18}O$ and by 2‰ for δ^2H, 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 $\delta^{18}O$ or 1‰ for δ^2H 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 $\delta^{18}O$ and 0.5‰ for δ^2H).

44   Presently, $\delta^{18}O$ and δ^2H 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 $\delta^{18}O$

51   and $\delta^{2}H$), ii. metal reduction (uranium, chromium, zinc) of water (for $\delta^{2}H$), or iii. gas-sample

52   equilibration methods (for $\delta^{18}O$ and $\delta^{2}H$). 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 $\delta^{18}O$ and $\delta^{2}H$. $\delta^{18}O$ ($\delta^{2}H$) 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 Sprectroscopy (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 $\delta^{18}O$ and δ^2H (also sometimes $\delta^{17}O$)

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 ~0.05‰ for $\delta^{18}O$ and ~1‰ for δ^2H (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 $\delta^{18}O$ and δ^2H 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, $MgCl_2$ and $CaCl_2$)

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_{Cl^-} =0.56576, m_{Na^+} =0.48616, $m_{Mg^{2+}}$

119 =0.05475, $m_{Ca^{2+}}$= 0.01065, m_{K^+}= 0.01058) is +0.06 ‰ for $\delta^{18}O$ and +0.55‰ for δ^2H. 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 $\delta^{18}O$, which is in agreement with Sofer and

123   Gat (1972). The two linear combinations consider there is no effect from NaCl on the δ^{18}O

124   measurement.

125        $\delta^2 H = -0.4 m_{NaCl} - 5.1 m_{MgCl2} - 6.1 m_{CaCl2} - 2.4 m_{KCl}$ (1)

126        $\delta^{18}O = 1.11 m_{MgCl2} + 0.476.1 m_{CaCl2} - 0.16 m_{KCl}$ (2)

127        $\delta^{18}O = 1.05 m_{MgCl2} + 0.416.1 m_{CaCl2} - 0.27 m_{KCl}$ (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 (~0.06‰ for δ^{18}O and ~0.55‰ for δ^2H)

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 δ^{18}O

135   and ±3‰ for δ^2H 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 δ^{18}O and allow comparisons, only Sofer and Gat (1975) measured the

141   four single salt effects, necessary to convert δ^2H 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 δ^{18}O and –2‰

147   for δ^2H. 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 $\delta^{18}O$ results based on the sea salt marsh of Guerande (no pure

154   NaCl solution available), while for δ^2H 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, $MgCl_2$ and $CaCl_2$, there is a strong disagreement for the NaCl effect on

158    $\delta^{18}O$ and δ^2H between the different studies. ONeil (1991) and Kim et al. (2012) found no effect

159   of NaCl on $\delta^{18}O$ (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 δ^2H, 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   Bourg 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 $\delta^{18}O$ and 0.4‰ for δ^2H. For

169   seawater, they found no effect on $\delta^{18}O$ over this range of concentration (up to 2SW) and a salt

170   effect of -1.7 ‰ for δ^2H at SW. These proposed corrections for $\delta^{18}O$ and δ^2H 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 $\delta^{18}O$ difference between the reference freshwater

185   and the saline solution of 0.09‰ for SW and 0.15‰ for 2SW and for δ^2H 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 $\delta^{18}O$ and

189   1‰ for δ^2H).

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 δ^2H 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 $\delta^{18}O$ and δ^2H in four different laboratories, using either IRMS with equilibration or

201 LS techniques (Table 1). Note that only one laboratory provided δ^2H 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 contradictons 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 $\delta^{18}O$ 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$_2$	$\delta^{18}O$
	IRMS continuous flow–equilibration with H$_2$	δ^2H
BGS	IRMS dual inlet–equilibration with CO$_2$	$\delta^{18}O$
VUB	IRMS continuous flow–equilibration with CO$_2$	$\delta^{18}O$
LOCEAN	PICARRO CRDS L2130-I + Distillation	$\delta^{18}O,\delta^2H$
	PICARRO CRDS L2130-I + Liner	$\delta^{18}O,\delta^2H$
	PICARRO CRDS L2130-I + Direct injection	$\delta^{18}O,\delta^2H$

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    $\delta^{18}O$=+0.51‰ and δ^2H =+1.85‰). 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 ± 0.2‰) 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	MgCl₂	MgSO₄	CaCl₂	KCl	NaHCO₃	Solution density	Volume

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/kgsol)	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

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

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

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

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

273   An Isoprime100 IRMS coupled with the AquaPrep system (dual inlet mode) was used for

274   the anlaysis of $\delta^{18}O$. 200µl 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 ~40°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 ($\delta^{18}O$) laboratory

285   A Nu Instrument perspective IRMS coupled with a Gasbensh (Nu Instrument, Wrexham,

286   UK) (continuous flow mode) was used for $\delta^{18}O$. 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 (+11h30 for the last sample) at ~21°C, while the sample is being shaken.

290

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

292   A PICARRO CRDS L2130-I Isotopic H_2O was used for $\delta^{18}O$ and δ^2H 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	$\delta^{18}O$ (‰)	δ^2H (‰)
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 $\delta^{18}O$ 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 $\delta^{18}O$ measured by BGS

345 is in the opposite direction to the other laboratories for salinities of 35. For $\delta^{2}H$, 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 $\delta^{18}O$, 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 $\delta^{2}H$, 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 $\delta^{2}H$ measurements.

356

		IES						BGS			VUB		
		$\delta^{18}O$ (‰)			$\delta^{2}H$ (‰)			$\delta^{18}O$ (‰)			$\delta^{18}O$ (‰)		
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

Table 4: Number of vials (n), mean salt effect and one standard deviation (1SD) for each

saline solution and each IRMS method. The salt effect is presented in ‰ as the difference

between the freshwater reference and the saline solution.

4.2 Effect of sea salts of the CRDS measurements

The sea salt effect was tested on the three different CRDS measurement methods

(distillation, liner or direct injection). The NaCl effect has only been measured for

measurements using the distillation method.

		Distillation					
		$\delta^{18}O$ (‰)			$\delta^{2}H$ (‰)		
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					
		$\delta^{18}O$ (‰)			δ^2H (‰)		
		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					
		$\delta^{18}O$ (‰)			δ^2H (‰)		
		n	Mean	1SD	N	Mean	1SD
SW	17.5	1	+0.01	-	1	−0.07	-
	35	1	+0.07	-	1	+0.15	-

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 $\delta^{18}O$ and δ^2H, 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 $\delta^{18}O$ and +0.57‰ for δ^2H. 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 $\delta^{18}O$ and +0.12 to +0.15‰ for δ^2H.

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 $\delta^{18}O$ and 1‰ for $\delta^{2}H$, 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 $\delta^{18}O$ at salinities of 35

399 and 70 and for $\delta^{2}H$ at salinity 70, while their proposed correction at salinity 35 for $\delta^{2}H$ 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	$\delta^{18}O$ (‰)	δ^2H (‰)
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 $\delta^{18}O$ and δ^2H, the dispersion is

418   significantly smaller after correction. For $\delta^{18}O$, the standard deviation of the 6 measurements is

419   0.06‰ without correction and 0.02‰ with correction. For δ^2H, 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 δ^{18}O and δ^2H 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 thorughout 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 δ^{18}O-δ^2H seawater values in a consistent and comparable manner. An

439   effort in this direction would lead to merged marine δ^{18}O-δ^2H datasets of greater value.

440

441   6. Conclusions

442

443 • Thanks to the improvements in instrumentation, the analytical precision of seawater δ^{18}O-δ^2H

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 traped 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 δ^{18}O-δ^2H

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

482   Appendix A : The sea water distillation process

483

484   The distillation line is shown in Figure A1. Before distillation, we provide partial

485   vacuum in all glass compartments. Thus, we freeze 2 ml of the sample with liquid nitrogen and

486   open the connection to the pump. When the void is sufficiently strong (~5.5 10^{-2} mbar), we turn

487   off the connection to the pump. Then, the water sample is heated to its boiling point and a cold

488   trap is used to retrieve the distilled water. This operation lasts at least 15 minutes to allow

489   reproductibility. The 15 minute duration is necessary to have the best precision, which is

490   dependent on a full recovery of the water originally present in the seawater sample. The

491   reproductibility of the method has been evaluated by distilling 15 times the same seawater

492   samples at salinity 35 and measuring the 15 products with our Picarro instrument. We found a

493   standard deviation of 0.04‰ for $\delta^{18}O$ and 0.24‰ for δ^2H, showing the good reproducibility in

494   the method. We elaborated on this method here because over the long term, measuring

495   freshwater samples decreases maintenance problems, such as salt accumulation in the vaporizer

496   and extends the very short lifetime of the syringe.

497

498

499

	$\delta^{18}O$	1SD	δ^2H	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 distillated 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).

505

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507

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582

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 $\delta^{18}O$ (left) and δ^2H (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 $\delta^{18}O$ and (B) for δ^2H. 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

597

598

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 $\delta^{18}O$ (left) and δ^2H (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 $\delta^{18}O$ and 1 SD=1‰ for δ^2H, 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 $\delta^{18}O$ and δ^2H, 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 vaccum

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.

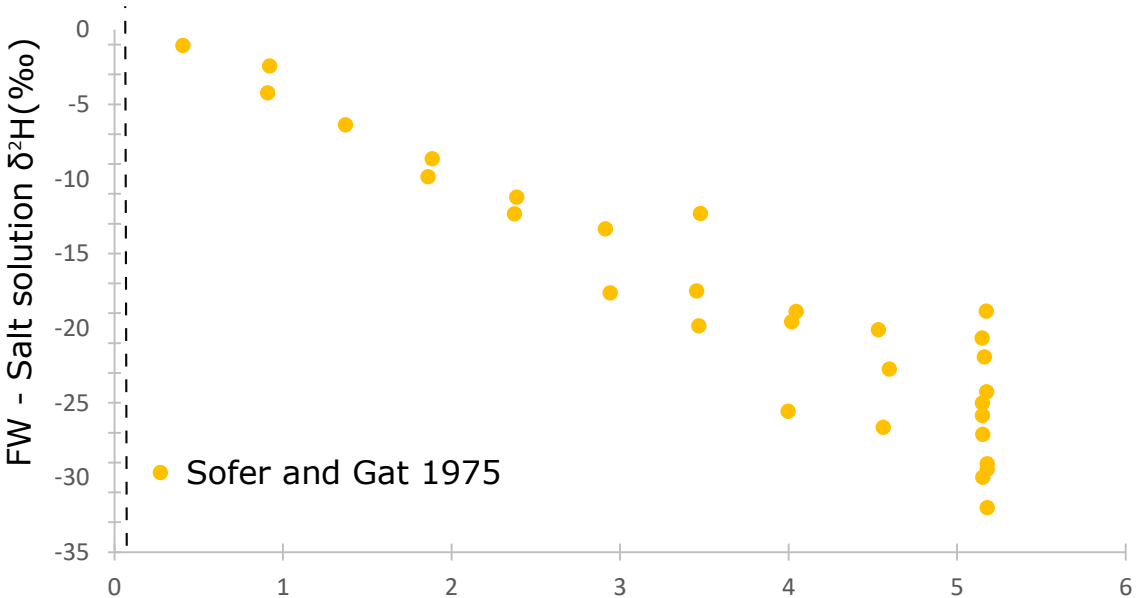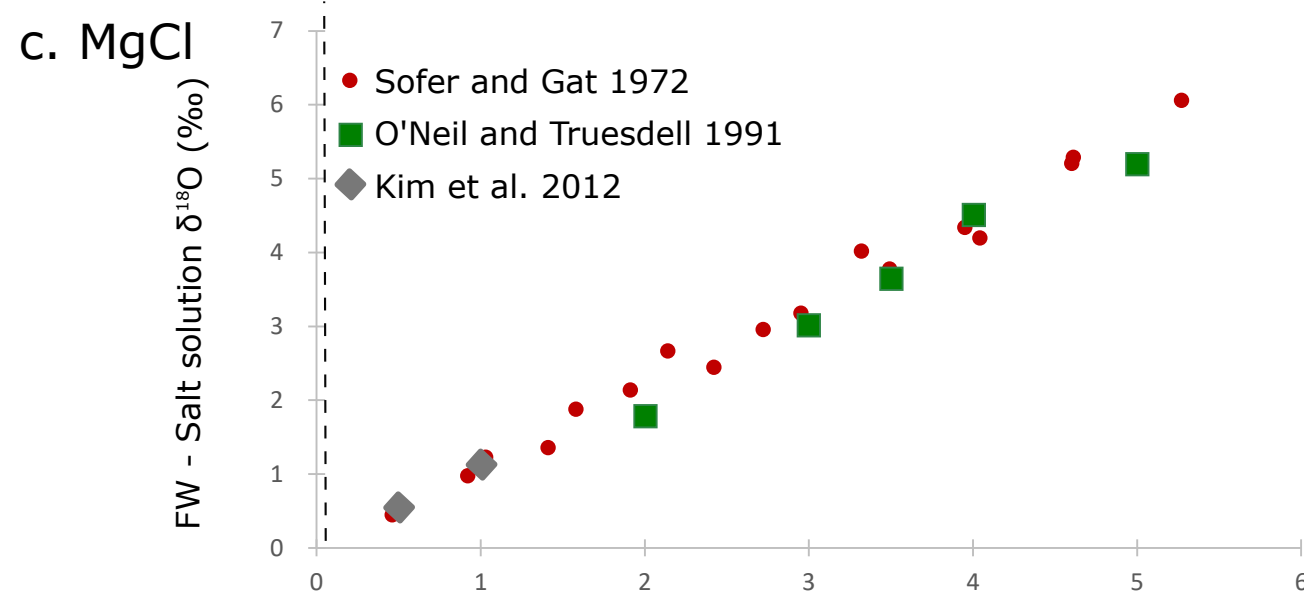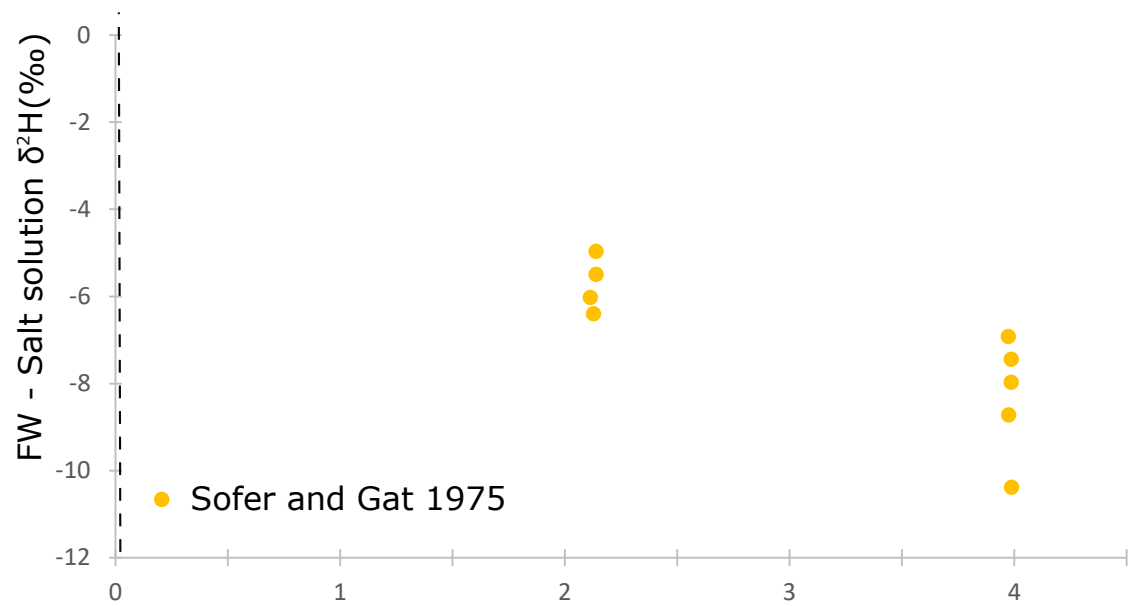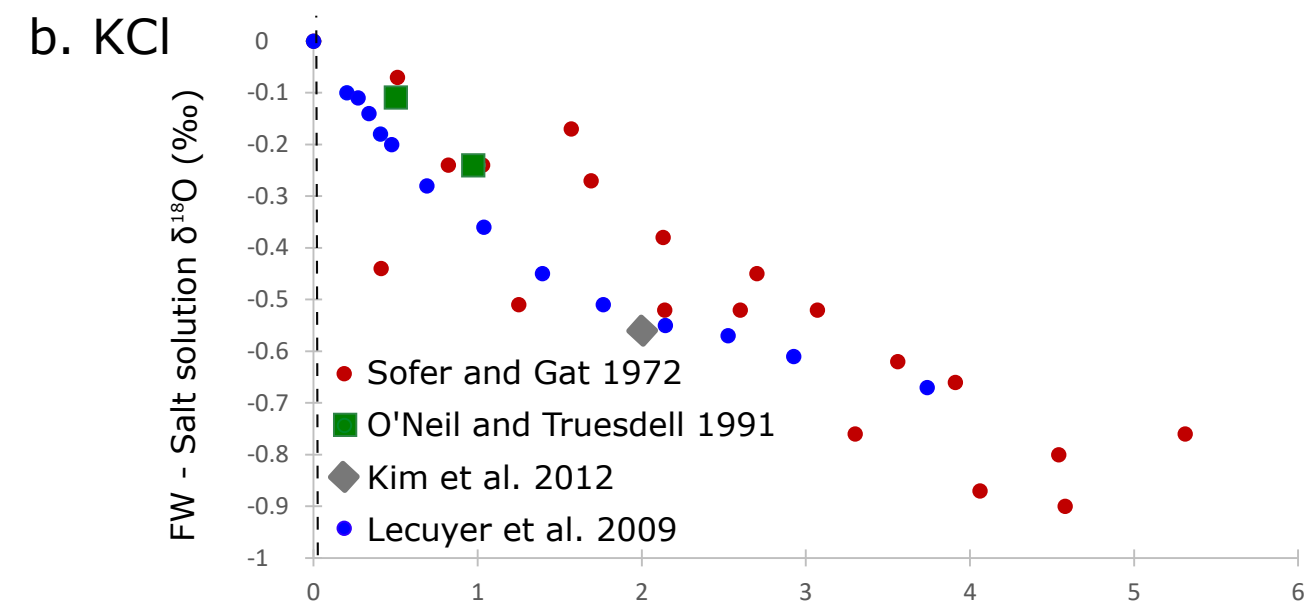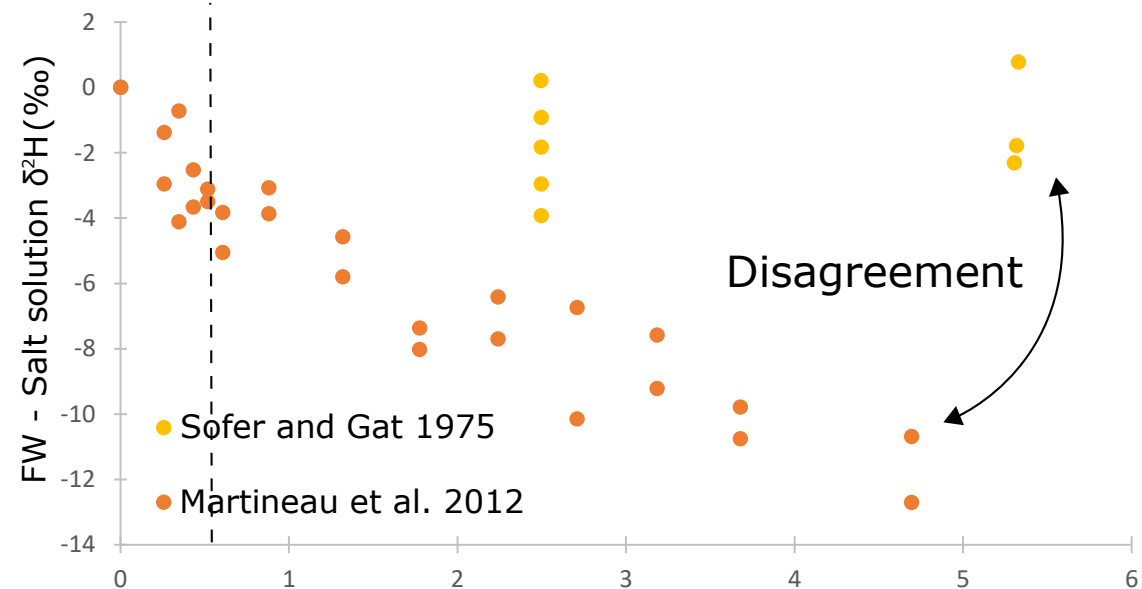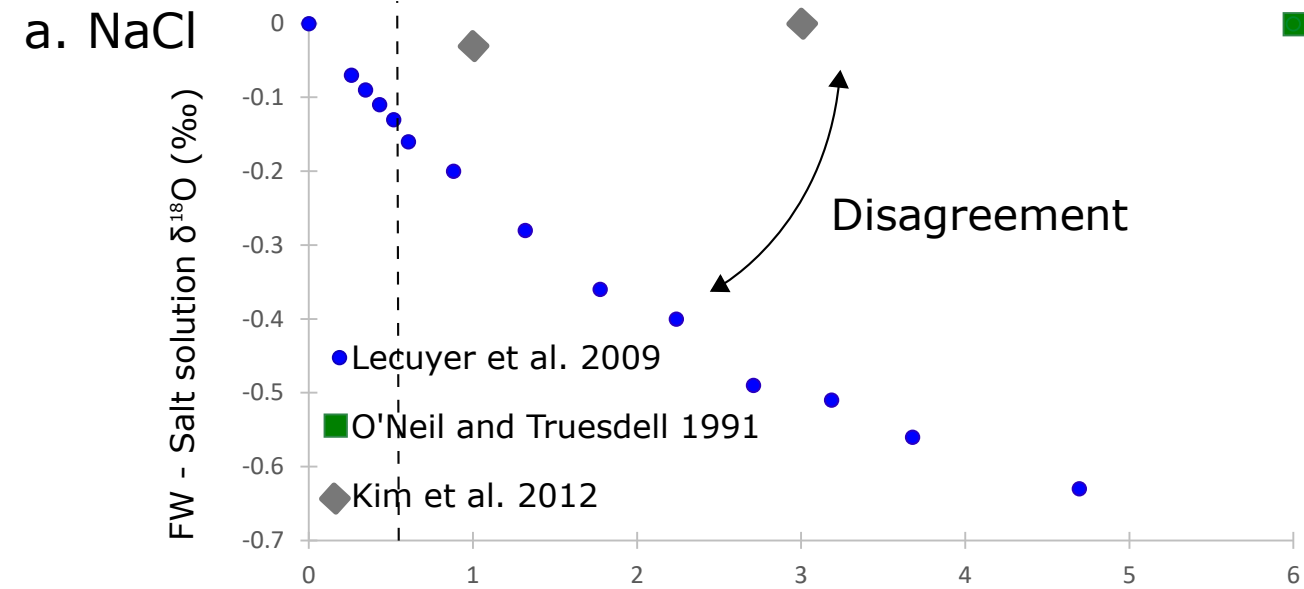629   Table 2: Calculations of the weighted amounts of solid salts and volumes of KONA II.

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

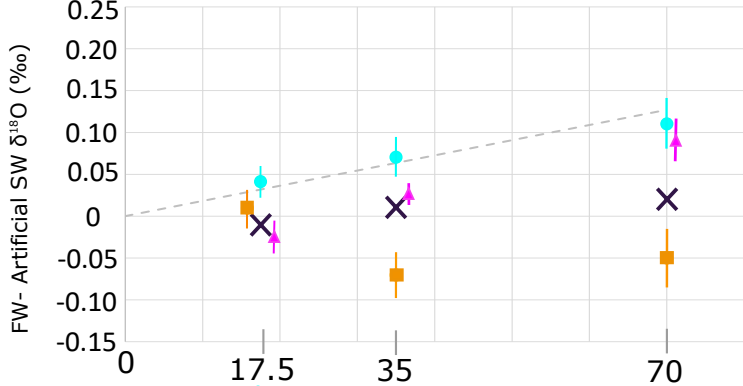632   difference between the freshwater reference and the saline solution.

633   Table 4: Number of measurement (n), average salt effect and standard deviation for each salt

634   solution and each CRDS method.

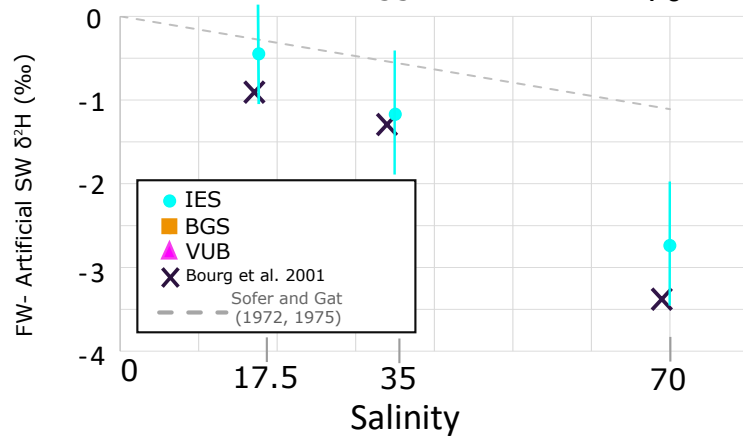635   Table 5: Estimated correction in ‰ for a seawater sample at salinity 35.

636   Table A1: Measurements with a Picarro instrument of 15 distillated 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
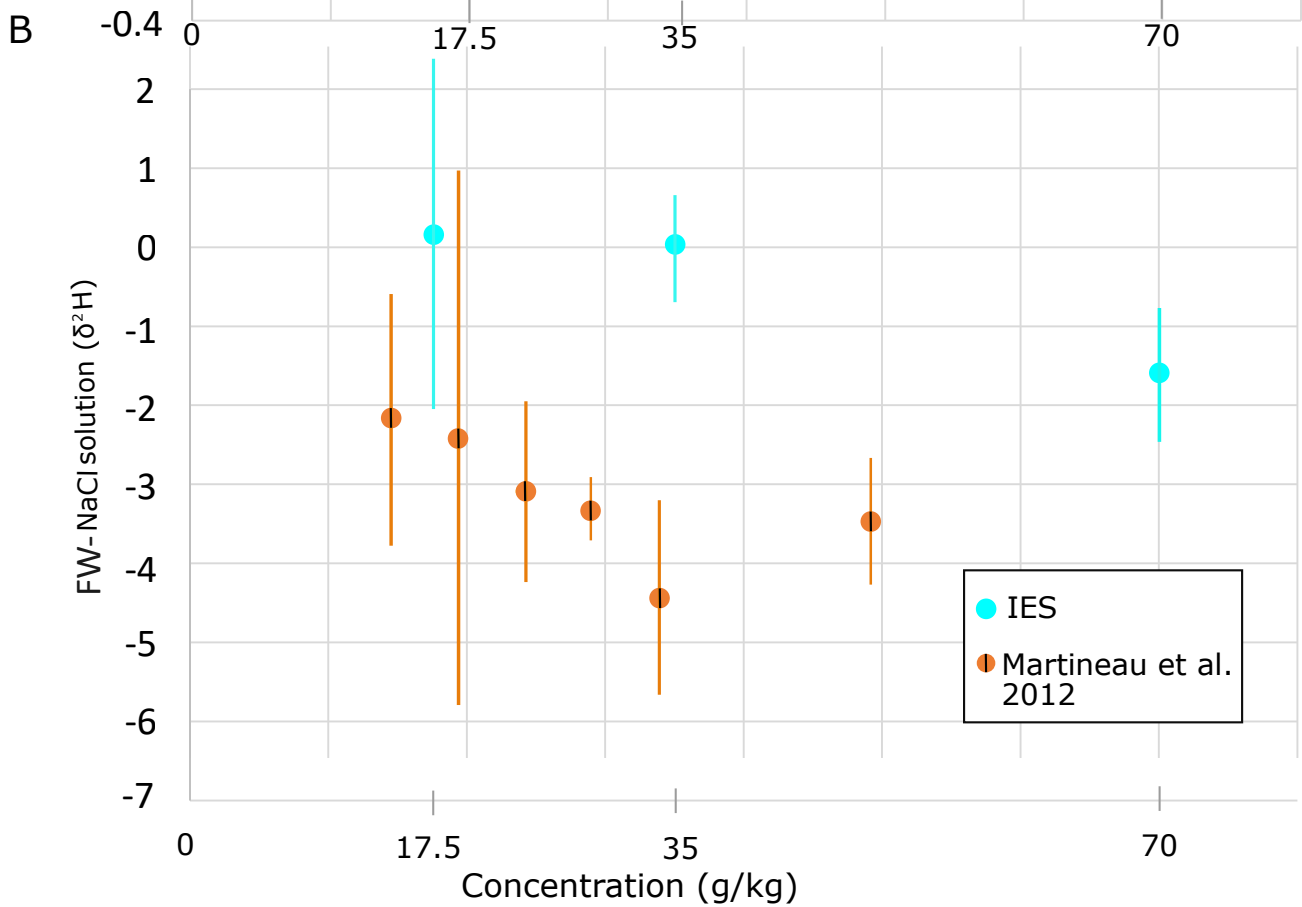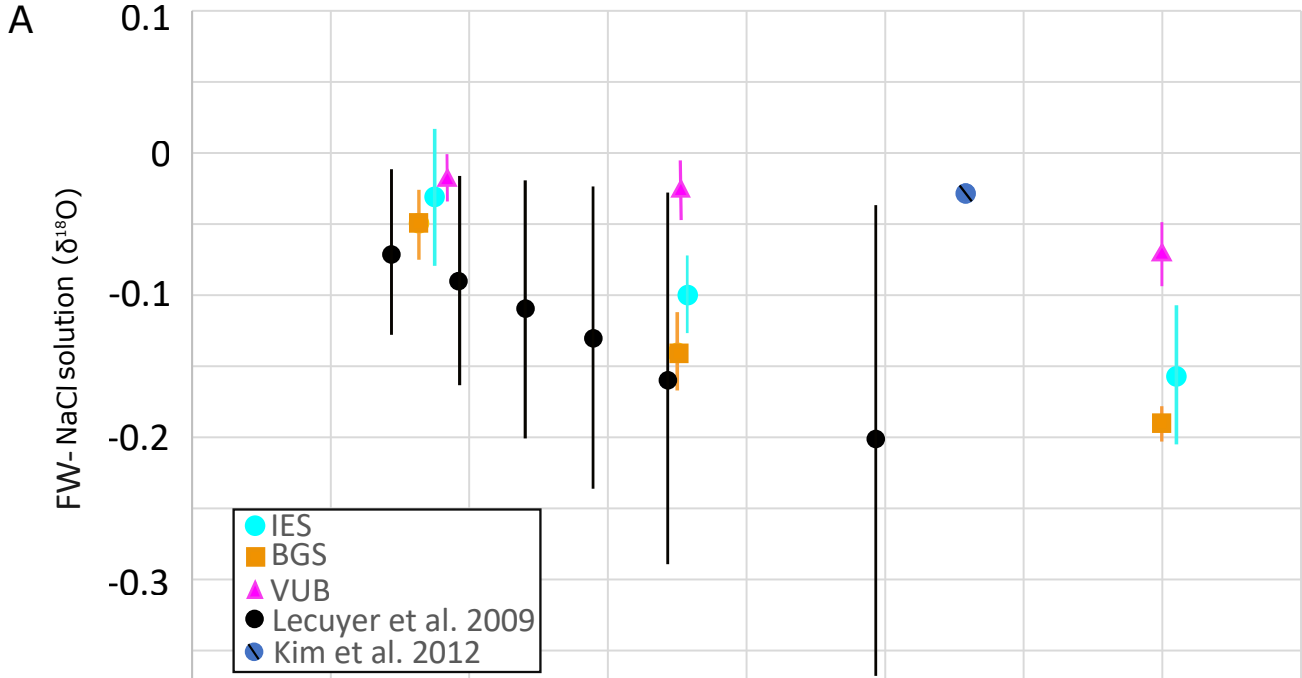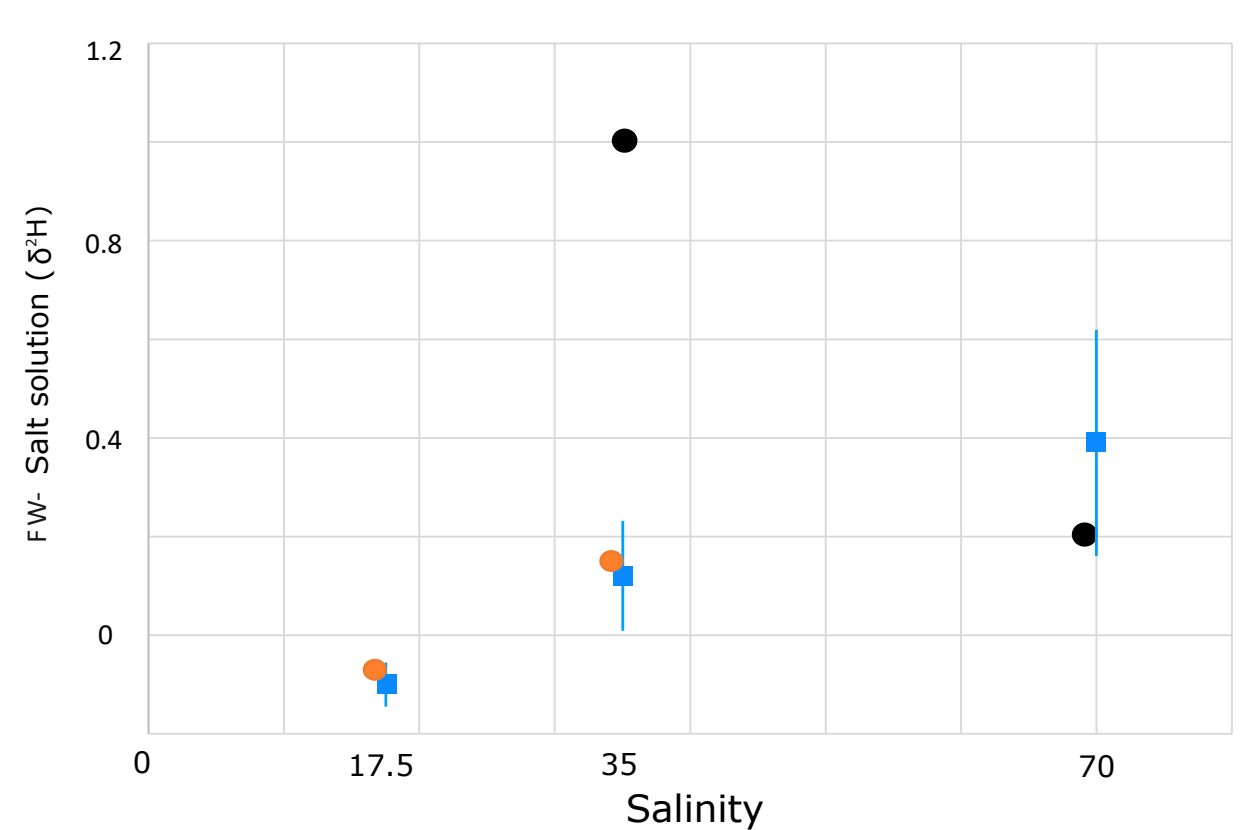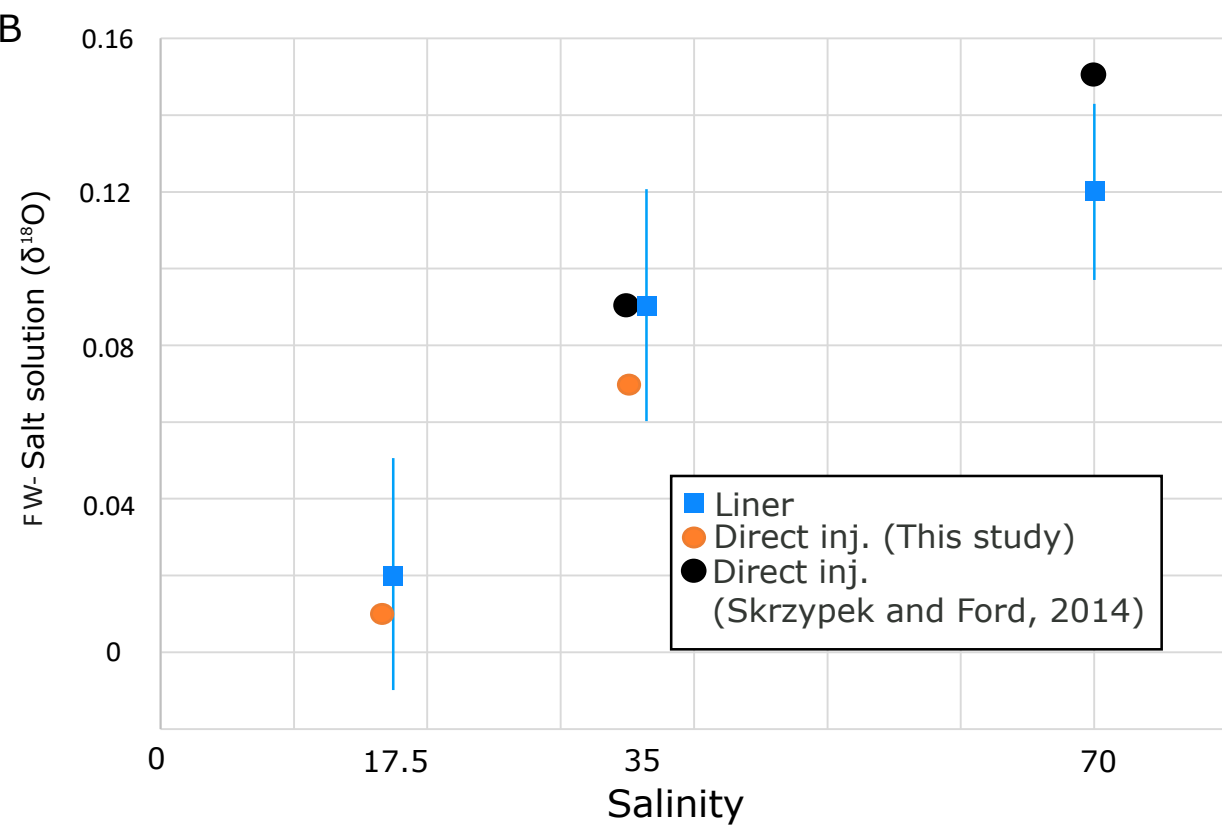
639   injections).

a. NaCl — FW - Salt solution δ¹⁸O (‰) vs Molality: Lecuyer et al. 2009; O'Neil and Truesdell 1991; Kim et al. 2012. Disagreement noted. δ²H (‰) vs Molality: Sofer and Gat 1975; Martineau et al. 2012. Disagreement noted.

b. KCl — FW - Salt solution δ¹⁸O (‰) vs Molality: Sofer and Gat 1972; O'Neil and Truesdell 1991; Kim et al. 2012; Lecuyer et al. 2009. δ²H (‰) vs Molality: Sofer and Gat 1975.

c. MgCl — FW - Salt solution δ¹⁸O (‰) vs Molality: Sofer and Gat 1972; O'Neil and Truesdell 1991; Kim et al. 2012. δ²H (‰) vs Molality: Sofer and Gat 1975.

d. CaCl — FW - Salt solution δ¹⁸O (‰) vs Molality: Sofer and Gat 1972; O'Neil and Truesdell 1991; Kim et al. 2012. δ²H (‰) vs Molality: Sofer and Gat 1975.

A

FW- Artificial SW δ¹⁸O (‰)

B

FW- Artificial SW δ²H (‰)

Legend:
- IES
- BGS
- VUB
- Bourg et al. 2001
- Sofer and Gat (1972, 1975)

Salinity

A

open valve

pumping

frozen
sample

2 ml

liquid
nitrogen

B

close valve

2 ml

distilled
sample

boiling
water

liquid
nitrogen