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# 1 Thermal properties of standard seawater up to high pressure 2 in stable and metastable states

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## 5 Abstract

6 In this work, a consolidated experimental apparatus for measuring the density of  
7 liquids, such as high pressure and metastable states, based on the isochoric method,  
8 was exploited to measure thermal properties of seawater. Density of standard seawater  
9 was measured in a wide range of temperature and pressure, specifically from (261.15 to  
10 313.15) K and up to 110 MPa. All terms contributing to the uncertainty in determining  
11 the volume and the mass of the specimen were evaluated, obtaining a relative expanded  
12 uncertainty of seawater density around 0.05 % ( $k = 2$ ). Experimental results were  
13 fitted by using a 8-parameters function of specific volume as a function of temperature  
14 and pressure. Using the obtained expression, density, isobaric thermal expansion, and  
15 isothermal compressibility of seawater were calculated from (263.15 to 313.15) K and  
16 for pressures between (1 and 105) MPa. A comparison with the predictions obtained  
17 by the Thermodynamic Equation of Seawater - 2010 (TEOS-10) shows a general good  
18 agreement that worsens when metastable states are considered.

19 *Keywords:* seawater, density, pycnometer, metastable states, thermal properties

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## 20 1. Introduction

21 Seawater is not only the environment where more than 200 thousands documented  
22 species live, but it is also the reservoir of the thermal energy of our planet. The dis-  
23 tribution of the energy content is driven by geographical variations of the temperature,  
24 the pressure and the density that are at the origin of small and large scale circulations  
25 (Wright et al., 2011). Furthermore, the energy exchanges between seawater and the at-  
26 mosphere significantly contribute to the formation and to the evolution of ordinary and  
27 extraordinary climate events. To monitor and provide predictive models for forecast and  
28 climate change, accurate measurements of physical and chemical properties of seawater  
29 are strongly demanded. Beside the role played to sustain the Earth's ecosystem and  
30 climate, seawater is also exploited as cooling fluid in power stations, as heating fluid  
31 for the regasification of liquefied natural gas (LNG) and as feed stock to produce fresh  
32 water by desalination processes. For all the applications, it is necessary to have accurate  
33 predictions for the density of the fluid, at high pressure and at different temperatures, to  
34 optimize the production of the industrial plants (Safarov et al., 2009, 2013).

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35 The density of seawater changes as a function of the depth below sea surface. Specif-  
36 ically, the pressure range in oceanic seawater is from 0.1 MPa at the sea surface to ap-  
37 proximately 108.6 MPa at the deepest level. The ocean temperature ranges, on average,  
38 approximately from (273.15 to 313.15) K. In addition to density, derived properties are  
39 useful to understand real ocean processes. For example, thermal expansivity is needed to  
40 figure out great gradients due to hot (close to critical temperature) seawater vents from  
41 ocean floor (Safarov et al., 2012).

42 Seawater freezing point is around 271 K; however, it can be cooled to lower tem-  
43 peratures without crystallization (supercooled seawater). This phenomenon is observed  
44 both in Antarctic and Arctic oceans, occurring as a consequence of the melting of ice  
45 shelves at depth (ice shelves cavity) and the formation of sea ice at the surface. As  
46 shown in Haumann et al. (2020), the deep vertical extent of the supercooled seawater  
47 column can be important for both vertical heat transport and for the vertical transport of  
48 salt, carbon, oxygen, and nutrients. Furthermore, supercooled seawater is the basis for  
49 the creation of the "platelet ice", which forms by nucleation in supercooled layers of sea-  
50 water near ice shelves, both in Antarctica and Arctic, under particular conditions able to  
51 generate and maintain supercooling (Hoppmann et al., 2020). Platelet ice involves both  
52 physical processes and biogeochemical cycles, hosting the associated peculiar ecosys-  
53 tem (Katlén et al., 2020).

54 The thermodynamic modelling of seawater poses many problems since the system is  
55 composed by a large number of different dissolved salts in small quantities, but strongly  
56 interacting. For this reason, a complete description of the interactions as a function of  
57 the composition has been avoided in favor of the adoption of salinity as a new indepen-  
58 dent variable, defined on the basis of chemical properties. Although the introduction  
59 of salinity allowed to solve practical problems, the chosen definition is not unique and  
60 still debated, as claimed by Seitz et al. (2011) and Feistel (2018).

61 Since 2010, the thermodynamic of seawater is described by the Thermodynamic  
62 Equation of Seawater - 2010, or TEOS-10 (IOC et al., 2010), in terms of absolute salin-  
63 ity,  $S_A$ , defined as the mass fraction of dissolved material per kilogram of seawater.  
64 However, the validity of TEOS-10 and the experimental values in the literature do not  
65 include the liquid metastable region.

66 Considering these aspects, in the present work standard seawater density is mea-  
67 sured and modeled in a wide range of temperature and pressure. The pseudo-isochoric  
68 method (pycnometry) was exploited to carry out density measurements up to 110 MPa,  
69 to cover the whole natural range of ocean pressure, and for temperatures down to 261 K,  
70 to investigate (even partially) supercooled seawater. These measurements were used  
71 to implement a function of density able to operate in the entire range of temperature  
72 and pressure here investigated, and to be used to derive the thermal properties, such as  
73 isothermal compressibility and isobaric thermal expansivity.

## 74 2. Materials and method

75 To measure the density of seawater, and with the aim of carrying out measurements  
76 even in metastable conditions, the isochoric method was exploited. As for the previ-  
77 ous work Romeo et al. (2018), the method was chosen because of its versatility and

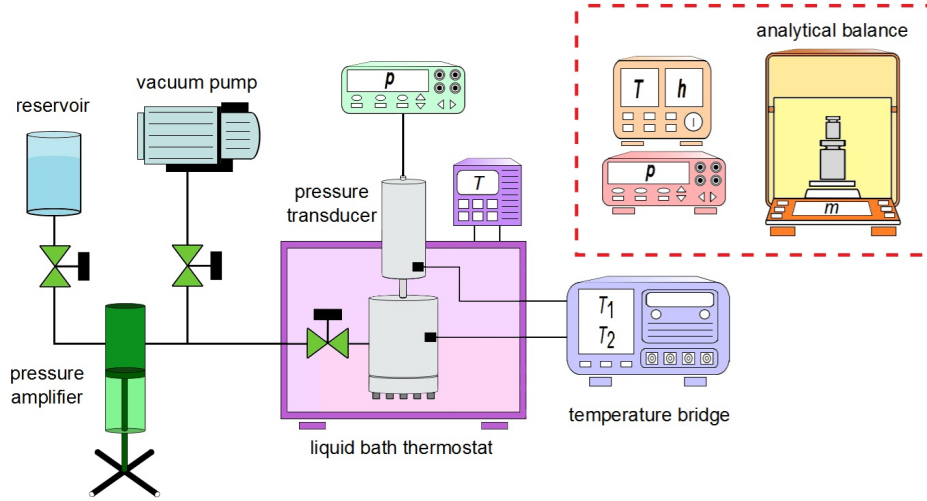


Figure 1: Schematic representation of the experimental apparatus for carrying out density measurements of standard seawater.

78 capability to operate in hard working conditions without being affected by the physical  
79 properties of the fluid (Goodwin et al., 2003).

80 This technique basically consists in measuring the mass and the volume of the mea-  
81 suring pycnometric cell. The main element of the experimental apparatus, the pyc-  
82 nometer, was designed and realized at Istituto Nazionale di Ricerca Metrologica and  
83 used in Romeo et al. (2018), where details on the pycnometer construction features and  
84 on the experimental setup can be found. The pycnometer was pressurized several times  
85 to test the sealing and the pressure stabilization was obtained up to 120 MPa.

86 The experimental apparatus schematically represented in Fig. 1 was arranged to  
87 control both temperature and pressure. A liquid bath thermostat (with a stabilization of  
88  $\pm 0.01$  K), where the pycnometer is placed, is used to control the temperature, which is  
89 measured by two platinum resistance thermometers (PT100). The latter are sited one on  
90 the pycnometer main body and the other one on the pressure transducer. The thermome-  
91 ters are connected in 4-wire configuration to an industrial thermometer bridge. While  
92 the pycnometer is connected to a capacitance high pressure transducer with a full-scale  
93 range of 200 MPa for the pressure measurements. A high-pressure circuit consisting of  
94 a pressure amplifier and a system of valves are arranged to connect to the tank at am-  
95 bient conditions, fill the pycnometer, and increase the pressure inside. To complete the  
96 measurement, an analytical balance with a resolution of 0.1 mg, stainless steel standard  
97 weights to measure the mass, and sensors to monitor ambient temperature, pressure and  
98 relative humidity to calculate air density, is used.

99 To start the measuring procedure, the pycnometer is filled to a certain pressure using  
100 the pressure amplifier and the high pressure circuit. Then, it is placed into the thermo-  
101 static liquid bath. The temperature is slowly decreased, so that the sample reaches the  
102 metastable liquid condition avoiding crystallization. To this scope, it is required from

103 1 hour up to 3 hours (at the lower temperatures) to change the temperature by 1 K be-  
 104 low the triple point. The temperature and the pressure are recorded at the equilibrium:  
 105 when temperature and pressure stabilization is within 0.01 K and 0.2 MPa, respectively  
 106 (usually around one hour is required). At the end of the cycle, the pycnometer is taken  
 107 off the thermostat and carefully cleaned and dried from the thermostatic liquid (ethanol)  
 108 before the weighing for the mass determination.

109 Once the measurements were complete, the density of seawater sample was mea-  
 110 sured by a commercial vibrating tube densimeter at atmospheric pressure, with an un-  
 111 certainty of 30 ppm as estimated by Romeo et al. (2019), to verify the composition had  
 112 not changed.

### 113 2.1. Determination of the mass

114 The mass of seawater was determined by means of the gravimetric method. Weigh-  
 115 ing was performed using a commercial analytical balance employed as a comparator  
 116 with stainless steel standard masses (Davidson et al., 2004), by the double substitution  
 117 method (OIML R111-1, 2004). Therefore, the mass  $M$  was obtained by the value of  
 118 the certified standard weights,  $M_{\text{eq}}$ , and the difference of the readings,  $\Delta R$ :

$$M = M_{\text{eq}} + \Delta R. \quad (1)$$

119 Seawater mass,  $m$ , was obtained by the difference between the mass of the pycnome-  
 120 ter filled with the seawater sample,  $M_{\text{ssw}}$ , and the mass of the empty pycnometer,  $M_0$ ,  
 121 corrected for the buoyancy, by the following relation

$$m = M_{\text{ssw}} \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right) - M_0 \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right), \quad (2)$$

122 where  $\rho_{\text{air}}$  is the density of air during the weighing, and  $\rho_{\text{std}} = 8 \text{ g} \cdot \text{cm}^{-3}$  is the standard  
 123 weights density.

### 124 2.2. Determination of the volume

125 The gravimetric method was also adopted to measure the volume of the pycnometer  
 126 (Lorefice et al., 2014). Thus, the pycnometer was weighted both empty and filled with  
 127 ordinary bi-distilled water (used as reference fluid) at the temperature  $T_0$  and pressure  
 128  $p_0$ , corresponding to a thermodynamic state of water density known with low uncer-  
 129 tainty (0.003 % for the thermodynamic state here investigated). Water density is pro-  
 130 vided by the equation of state of the International Association for Properties of Water  
 131 and Steam, i.e., IAPWS-95 formulation by Wagner and Pruss (2002).

132 The pycnometer mass (empty and filled with water) was measured by comparison  
 133 with standard weights by the double substitution method, using the analytical balance as  
 134 comparator. During the weighing, atmospheric parameters were monitored to correct  
 135 for the buoyancy in air. So that, the reference volume was determined as

$$V_0(T_0, p_0) = \frac{M_{\text{ref}} - M_0}{\rho_{\text{ref}}(T_0, p_0) - \rho_{\text{air}}} \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right), \quad (3)$$

136 where  $M_{\text{ref}}$  is the mass of the pycnometer filled with ordinary water,  $M_0$  is the mass  
 137 of the empty pycnometer,  $\rho_{\text{ref}}$  is the reference water density,  $\rho_{\text{air}}$  is the air density, and  
 138  $\rho_{\text{std}} = 8 \text{ g} \cdot \text{cm}^{-3}$  is the standard weights density. The reference volume of the pycnome-  
 139 ter at  $T_0 = (293.21 \pm 0.01) \text{ K}$  and  $p_0 = (50.8 \pm 0.2) \text{ MPa}$  is  $V_0 = (11.655 \pm 0.002) \text{ cm}^3$ .

140 To account for the variation of the volume as a function of temperature,  $T$ , and  
 141 pressure,  $p$ , the value of  $V_0$  was corrected by the thermal expansion coefficient and the  
 142 compressibility coefficient, as follows

$$V(T, p) = V_0(T_0, p_0)[1 + \alpha(T - T_0) + \beta(p - p_0)], \quad (4)$$

143 where  $\alpha$  and  $\beta$  are the thermal expansion and the isothermal compressibility of the  
 144 pycnometer, respectively.

145 The values of  $\alpha$  and  $\beta$  were determined experimentally, by performing measuring  
 146 cycles with a reference fluid, i.e., ordinary water. Measurements were carried out using  
 147 bi-distilled water, between (275 and 313) K and from (50 to 100) MPa. Considering the  
 148 change of volume of Eq. 4, a function derived from the definition of density was used  
 149 (see Romeo et al. (2018) for details). By fitting this linear function of both temperature  
 150 and pressure, considering the literature density values of the IAPWS-95 formulation for  
 151 each measurement, the  $\alpha$  and  $\beta$  were obtained:

$$\alpha = (2.2 \pm 0.2) \cdot 10^{-5} \text{ K}^{-1}$$

$$\beta = (7.5 \pm 0.2) \cdot 10^{-5} \text{ MPa}^{-1}.$$

152 For the studied temperature and pressure range, variations of the elastic properties  
 153 with temperature and pressure were within the declared uncertainty. For this reason,  
 154 they are considered constant over the whole examined  $T - p$  range.

### 155 3. Uncertainty analysis

#### 156 3.1. Contribution of mass measurement

157 For the uncertainty analysis, according to Eq. 2, the mass of seawater is a function  
 158 of all the quantities involved in the weighing procedure:

$$m = m(\Delta R, d, M_{\text{eq}}, \rho_{\text{air}}, \rho_{\text{std}}).$$

159 Therefore, the relative uncertainty in the estimation of seawater mass,  $u(m)/m$ , was  
 160 calculated with the uncertainty propagation formula by

$$\frac{u(m)}{m} = \frac{1}{m} \left[ \sigma^2(\Delta R) + \left( \frac{d}{\sqrt{6}} \right)^2 + u^2(M_{\text{eq}}) + \left( \frac{\partial m}{\partial \rho_{\text{air}}} \right)^2 u^2(\rho_{\text{air}}) + \left( \frac{\partial m}{\partial \rho_{\text{std}}} \right)^2 u^2(\rho_{\text{std}}) \right]^{\frac{1}{2}}, \quad (5)$$

161 where  $\sigma(\Delta R)$  is the standard deviation of the the difference of readings,  $d$  is the digital  
 162 resolution of the analytical balance as a triangular distribution (BIPM et al., 2008),

163  $u(M_{\text{eq}})$  is the uncertainty of the standard weights, provided by the calibration certificate.  
 164 The uncertainties of the standard weights density,  $u(\rho_{\text{std}})$ , and air density,  $u(\rho_{\text{air}})$ , were  
 165 negligible in the overall uncertainty. The sources of uncertainty affecting the mass  
 166 measurement and associated relative magnitudes are listed in Table 1. The relative  
 167 uncertainty of seawater mass is estimated to be 0.015%.

### 168 3.2. Contribution of the reference volume

169 According to Eq. 3, the uncertainty of the pycnometer reference volume,  $V_0$ , was  
 170 obtained taking into account the contributions of the mass of the reference fluid ( $\Delta M =$   
 171  $M_{\text{ref}} - M_0$ ), the densities of the reference fluid, air of laboratory and standard weights,  
 172 and the filling temperature and pressure:

$$V_0 = V_0(\Delta M, \rho_{\text{ref}}, \rho_{\text{air}}, \rho_{\text{std}}, T_0, p_0) . \quad (6)$$

173 Applying the uncertainty propagation to Eq. 3, the relative uncertainty,  $u(V_0)/V_0$ , is  
 174 assessed by

$$\begin{aligned} \frac{u(V_0)}{V_0} = \frac{1}{V_0} \left[ \left( \frac{\partial V_0}{\partial \Delta M} \right)^2 u^2(\Delta M) + \left( \frac{\partial V_0}{\partial \rho_{\text{ref}}} \right)^2 u^2(\rho_{\text{ref}}) + \left( \frac{\partial V_0}{\partial \rho_{\text{air}}} \right)^2 u^2(\rho_{\text{air}}) + \right. \\ \left. \left( \frac{\partial V_0}{\partial \rho_{\text{std}}} \right)^2 u^2(\rho_{\text{std}}) + \left( \frac{\partial V_0}{\partial T_0} \right)^2 u^2(T_0) + \left( \frac{\partial V_0}{\partial p_0} \right)^2 u^2(p_0) \right]^{\frac{1}{2}} . \quad (7) \end{aligned}$$

175 The uncertainty of the reference fluid mass,  $u(\Delta M) = 0.002$  g, is given by the sum  
 176 of the squares of the standard deviation of the readings difference, the balance reso-  
 177 lution, and the standard weights uncertainty. As for the mass, the contributions of the  
 178 uncertainties of the standard weights density,  $u(\rho_{\text{std}})$ , and the air density,  $u(\rho_{\text{air}})$ , resulted  
 179 negligible in the overall uncertainty. As stated in Wagner and Pruss (2002), the uncer-  
 180 tainty of IAPWS-95 for water density at 293.21 K and 50.8 MPa is  $u(\rho_{\text{ref}}) = 0.003$  %.  
 181 The uncertainty  $u(T_0)$  of the temperature measurement is due to the calibration fit, the  
 182 resolution of the instrument and the reading repeatability, and its value is within 0.01 K.  
 183 The uncertainty of the pressure measurements  $u(p_0)$  is due to the pressure transducer  
 184 used and the measurement repeatability and it is 0.2 MPa.

185 The uncertainty of the pycnometer reference volume  $V_0$  is lower than 0.01%; all  
 186 the contributions considered and the associated relative magnitude are summarized in  
 187 Table 1.

### 188 3.3. Volume uncertainty analysis

189 According to Eq. 4, the uncertainty of the pycnometer volume was determined con-  
 190 sidering the volume  $V$  as a function of the reference volume  $V_0$ , the thermal expansion  
 191 coefficient  $\alpha$ , the isothermal compressibility coefficient  $\beta$ , the temperature  $T$  and the  
 192 pressure  $p$ :

$$V = V(V_0, \alpha, \beta, T, p) .$$

193 The volume relative uncertainty,  $u(V)/V$ , was estimated by using the standard formu-  
 194 lation for the uncertainty propagation, as follows

$$\frac{u(V)}{V} = \frac{1}{V} \left[ \left( \frac{\partial V}{\partial V_0} \right)^2 u^2(V_0) + \left( \frac{\partial V}{\partial \alpha} \right)^2 u^2(\alpha) + \left( \frac{\partial V}{\partial \beta} \right)^2 u^2(\beta) + \left( \frac{\partial V}{\partial T} \right)^2 u^2(T) + \left( \frac{\partial V}{\partial p} \right)^2 u^2(p) \right]^{\frac{1}{2}}, \quad (8)$$

195 where  $u(V_0)$  is  $0.002 \text{ cm}^3$ . The uncertainties of the  $\alpha$  and  $\beta$  coefficients,  $u(\alpha)$  and  $u(\beta)$ ,  
 196 are due to the fitting process for their estimations; other sources of uncertainty are neg-  
 197 ligible.

198 The uncertainty on temperature,  $u(T) = 0.01 \text{ K}$ , was calculated by the uncertainty of  
 199 the calibration fit, the instrument resolution, the reading repeatability and the tempera-  
 200 ture gradient measured between the two thermometers. The uncertainty of the pressure  
 201 transducer  $u(p)$  is  $0.01 \text{ MPa}$ ; this value includes the declared uncertainty of the instru-  
 202 ment at the full-scale and the repeatability.

203 In Table 1, all contributions to the relative uncertainty of the volume along with  
 204 their relative values are reported.

#### 205 3.4. Density uncertainty analysis

206 From the perspective of the uncertainty calculation, because seawater was measured  
 207 by the pseudo-isochoric method, density is a function of mass, volume, and absolute  
 208 salinity

$$\rho = \rho(m, V, S_A).$$

209 Applying the uncertainty propagation formula, the relative uncertainty of seawater den-  
 210 sity is expressed by

$$\frac{u(\rho)}{\rho} = \frac{1}{\rho} \left[ \left( \frac{\partial \rho}{\partial m} \right)^2 u^2(m) + \left( \frac{\partial \rho}{\partial V} \right)^2 u^2(V) + \left( \frac{\partial \rho}{\partial S_A} \right)^2 u^2(S_A) \right]^{\frac{1}{2}}, \quad (9)$$

211 where  $u(m)$  is the mass uncertainty and is  $0.002 \text{ g}$ , while  $u(V)$  is the uncertainty of the  
 212 volume at the measured temperature and pressure, whose value is  $0.003 \text{ cm}^3$ . Since  
 213 the absolute salinity of the sample was not measured by the authors, its uncertainty,  
 214  $u(S_A)$ , was assumed starting from the value estimated by Le Menn (2011), combined  
 215 with the value reported in McDougall et al. (2012). Table 1 summarizes all sources  
 216 of uncertainty that play a role in the uncertainty budget of seawater density, and their  
 217 relative magnitude.

218 The largest contribution to the uncertainty is due to the volume, as expected con-  
 219 sidering the many quantities involved in its measurement. The expanded relative un-  
 220 certainty of seawater density is  $0.05 \%$  with a coverage factor  $k = 2$ , considering the  
 221 worst case scenario.



Table 1: Uncertainty budget of standard seawater density ( $S_A = 35.158 \text{ g}\cdot\text{kg}^{-1}$ )

Uncertainty source	Relative magnitude %
<b>Mass</b>	<b>0.015</b>
Reading standard deviation	0.015
Balance resolution	0.001
Standard weights mass	negligible
Air density	negligible
Standard weights density	negligible
<b>Volume</b>	<b>0.021</b>
Reference volume	0.014
Mass of the reference fluid	0.013
Reference water density	0.003
Air density	negligible
Standard weights density	negligible
Temperature	0.001
Pressure	0.002
Thermal expansion coefficient	0.008
Compressibility coefficient	0.015
Temperature	0.001
Pressure	0.001
<b>Salinity</b>	<b>&lt;0.001</b>
<b>COMBINED UNCERTAINTY (<math>k = 2</math>)</b>	<b>0.05</b>

#### 4. Results

The density measurements were carried out for a sample of standard seawater delivered by OSIL (Batch P160), with certified practical salinity  $S_p = 34.993$ , i.e., absolute salinity  $S_A = 35.158 \text{ g}\cdot\text{kg}^{-1}$ . Measurements were carried out at temperatures from about (261.15 to 313.15) K and in the pressure range between (21 to 110) MPa, for five samples of standard seawater of the same batch. All experimental densities along the constant-mass curves are listed in Table 2, where the values reported in italics identify metastable states.

Fig. 2 shows the pressure measurements as a function of temperature for each measuring cycle performed at constant mass. The measured thermodynamic states include also supercooled seawater region: the metastable equilibrium states. The plot of the densities as a function of temperature, along curves at constant mass, is reported in Fig. 3.

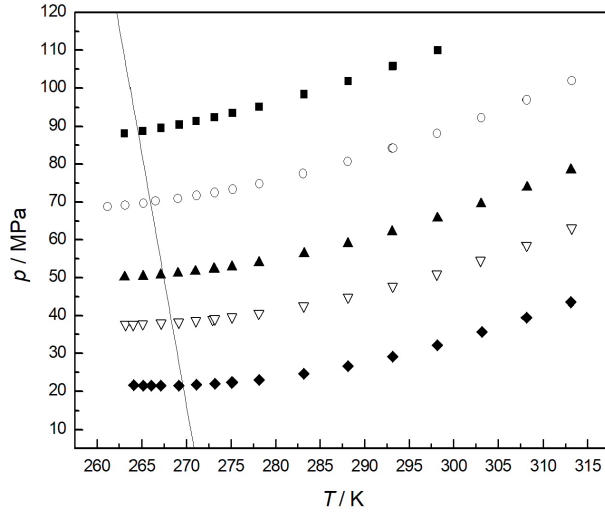


Figure 2: Pressure as a function of temperature at constant mass:  $\blacksquare$ ,  $m = 12.482$  g;  $\circ$ ,  $m = 12.371$  g;  $\blacktriangle$ ,  $m = 12.253$  g;  $\nabla$ ,  $m = 12.174$  g;  $\blacklozenge$ ,  $m = 12.069$  g; —, melting curve.

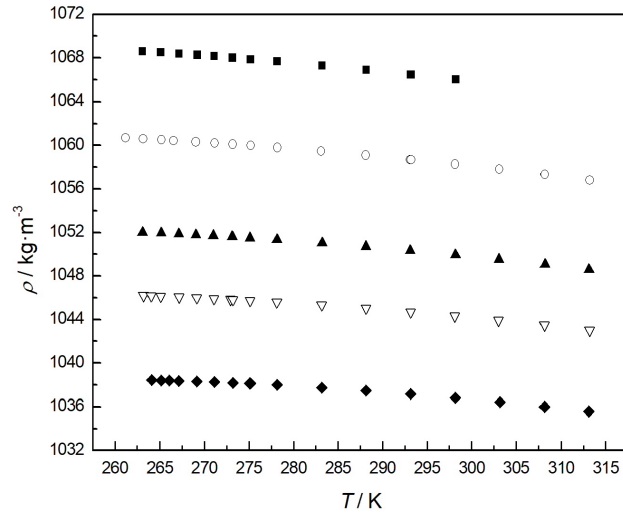


Figure 3: Density of standard seawater ( $S_A = 35.158$  g·kg $^{-1}$ ) as a function of temperature at constant mass:  $\blacksquare$ ,  $m = 12.482$  g;  $\circ$ ,  $m = 12.371$  g;  $\blacktriangle$ ,  $m = 12.253$  g;  $\nabla$ ,  $m = 12.174$  g;  $\blacklozenge$ ,  $m = 12.069$  g.

Table 2: Density  $\rho$  of standard seawater ( $S_A = 35.158 \text{ g}\cdot\text{kg}^{-1}$ ) at temperature  $T$  and pressure  $p$ , for different masses  $m$ . The uncertainty associated with all values of density is 0.05 %. Entries in italics are the measurements carried out in metastable equilibrium.

$T / \text{K}$	$p / \text{MPa}$	$\rho / \text{kg}\cdot\text{m}^{-3}$	$T / \text{K}$	$p / \text{MPa}$	$\rho / \text{kg}\cdot\text{m}^{-3}$
$m = 12.482 \text{ g}$					
<i>263.10</i>	<i>88.10</i>	<i>1068.60</i>	275.18	93.55	1067.87
265.10	88.72	1068.50	278.18	95.16	1067.67
267.14	89.55	1068.39	283.20	98.43	1067.29
269.20	90.44	1068.26	288.17	101.82	1066.90
271.10	91.33	1068.15	293.13	105.71	1066.47
273.12	92.37	1068.02	293.21	105.84	1066.46
273.15	92.39	1068.01	298.23	109.96	1066.01
$m = 12.371 \text{ g}$					
<i>261.20</i>	<i>68.76</i>	<i>1060.68</i>	283.10	77.51	1059.46
<i>263.17</i>	<i>69.17</i>	<i>1060.60</i>	288.10	80.67	1059.09
<i>265.16</i>	<i>69.67</i>	<i>1060.52</i>	293.09	84.20	1058.70
266.55	70.26	1060.44	293.21	84.23	1058.69
269.05	70.94	1060.32	298.13	88.07	1058.27
271.15	71.73	1060.21	303.10	92.28	1057.82
273.17	72.47	1060.10	308.17	96.95	1057.33
275.20	73.36	1059.98	313.22	101.96	1056.81
278.18	74.79	1059.80			
$m = 12.253 \text{ g}$					
<i>263.10</i>	<i>50.17</i>	<i>1052.00</i>	278.15	54.00	1051.34
<i>265.15</i>	<i>50.37</i>	<i>1051.93</i>	283.21	56.37	1051.03
<i>267.13</i>	<i>50.71</i>	<i>1051.86</i>	288.16	59.02	1050.70
269.05	51.19	1051.77	293.10	62.14	1050.34
271.00	51.68	1051.69	298.20	65.73	1049.93
273.12	52.32	1051.59	303.09	69.52	1049.52
273.17	52.24	1051.59	308.21	73.90	1049.05
275.13	52.87	1051.50	313.14	78.48	1048.58
$m = 12.174 \text{ g}$					
<i>263.22</i>	<i>37.61</i>	<i>1046.18</i>	278.13	40.59	1045.59
<i>264.02</i>	<i>37.60</i>	<i>1046.16</i>	283.16	42.50	1045.32
<i>265.12</i>	<i>37.78</i>	<i>1046.12</i>	288.15	44.86	1045.02
<i>267.15</i>	<i>37.98</i>	<i>1046.06</i>	293.17	47.76	1044.67
269.14	38.25	1045.99	298.12	50.96	1044.30
271.07	38.62	1045.91	303.05	54.53	1043.91
272.95	38.94	1045.84	308.16	58.51	1043.48
273.20	39.11	1045.82	313.20	63.10	1043.00
275.14	39.61	1045.74			
$m = 12.069 \text{ g}$					
<i>264.10</i>	<i>21.57</i>	<i>1038.44</i>	278.15	23.05	1037.99
<i>265.16</i>	<i>21.54</i>	<i>1038.42</i>	283.18	24.64	1037.75

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266.05	21.54	1038.39	288.15	26.67	1037.48
267.14	21.53	1038.37	293.15	29.17	1037.16
269.15	21.54	1038.32	298.16	32.13	1036.82
271.13	21.71	1038.26	303.17	35.70	1036.42
273.21	21.98	1038.19	308.14	39.46	1036.01
275.05	22.34	1038.12	313.11	43.54	1035.58
275.16	22.34	1038.12			

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235 The experimental densities of this work were compared to the density values pro-  
 236 vided by TEOS-10 formulation. Figs. 4 and 5 show the deviations of the measurements  
 237 from TEOS-10 equation as a function of temperature and pressure, respectively. All the  
 238 deviations are within  $\pm 0.02\%$ , so considering the experimental uncertainty all measure-  
 239 ments are in good agreement with TEOS-10. From Fig. 4, it is possible to note that most  
 240 of the largest deviations correspond to the lowest temperature, and in particular to mes-  
 241 tatable states. Also observing Fig. 5, it is clear that the largest deviations correspond  
 242 to the lowest pressures, thus measurements carried out in the metastable region.

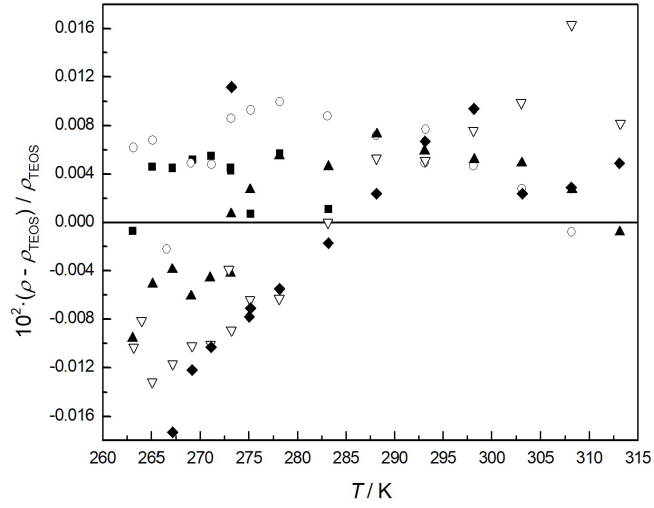


Figure 4: Deviations of experimental seawater density from the values of TEOS-10 (zero line) as a function of temperature: ■,  $m = 12.482$  g; ○,  $m = 12.371$  g; ▲,  $m = 12.253$  g; ▽,  $m = 12.174$  g; ◆,  $m = 12.069$  g.

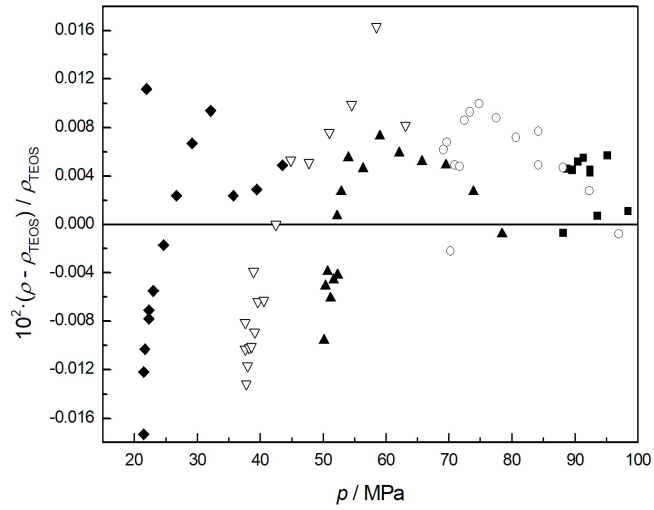


Figure 5: Deviations of experimental seawater density from the values of TEOS-10 (zero line) as a function of pressure: ■,  $m = 12.482$  g; ○,  $m = 12.371$  g; ▲,  $m = 12.253$  g; ▽,  $m = 12.174$  g; ◆,  $m = 12.069$  g.

Table 3: Coefficients for the interpolation function of density (Eq. 10) determined from the experimental densities, temperatures and pressures by means of the least squares method.

parameter	value	unit
$a$	0.182915	$\text{m}^3 \cdot \text{kg}^{-1} \cdot \text{MPa}$
$b$	$6.97805 \cdot 10^{-4}$	$\text{m}^3 \cdot \text{kg}^{-1}$
$c$	659.033	MPa
$t_a$	$-4.66555 \cdot 10^{-5}$	$\text{K}^{-2}$
$t_b$	8.82548	$\text{K}^{-1}$
$t_c$	$1.40672 \cdot 10^{-3}$	$\text{K}^{-1}$
$t_d$	$-6.07869 \cdot 10^{-5}$	$\text{K}^{-2}$
$t_e$	$-5.93252 \cdot 10^{-8}$	$\text{K}^{-3}$

## 243 5. Derived thermal properties

244 The measurements presented in this work, together with the experimental results of  
 245 Romeo et al. (2019), carried out by means of a commercial vibrating tube densimeter  
 246 at atmospheric pressure, were regressed to identify a model to calculate density. The  
 247 model was chosen to be slender and handy, trying to balance the need for a very limited  
 248 number of parameters and good accuracy. The model used is the following 8-parameters  
 249 equation:

$$v(T, p) = \frac{a[1 + t_a(T - T_0)^2]}{p + c[1 + t_c(T - T_0) + t_d(T - T_0)^2 + t_e(T - T_0)^3]} + b[1 + t_b(T - T_0)], \quad (10)$$

250 where  $v(T, p)$  is the specific volume and  $a, b, c, t_a, t_b, t_c, t_d, t_e$  are parameters, whose  
 251 values are shown in Tab. 3. Validity of Eq 10 was checked analyzing the residuals  
 252 of the fit. In Figs. 6 and 7, relative difference between fit-predicted and experimental  
 253 densities as a function of temperature and pressure, respectively, are shown. Residuals  
 254 spread within  $\pm 0.012\%$  and most of them within  $\pm 0.007\%$ , so widely less than the  
 255 experimental uncertainty.

256 Equation 10 was used to calculate seawater density, isothermal compressibility and  
 257 isobaric thermal expansion, in the temperature range between (263.15 to 313.15) K,  
 258 with step of 10 K, and in the pressure range between (1 to 105) MPa. The set of den-  
 259 sity, isothermal compressibility and thermal expansivity data is reported in Tab. 4.  
 260 Fig. 8 shows the densities obtained by Eq. 10 as a function of pressure along isotherms.  
 261 Comparison between the calculated densities and TEOS-10 values is reported in Fig. 9.  
 262 The deviations scatter within  $\pm 0.015\%$ . Based on these results, Eq. 10 can be used to  
 263 calculate density within the fitted  $T - p$  range with the same uncertainty value stated  
 264 for the experimental density, i.e., 0.05 %.

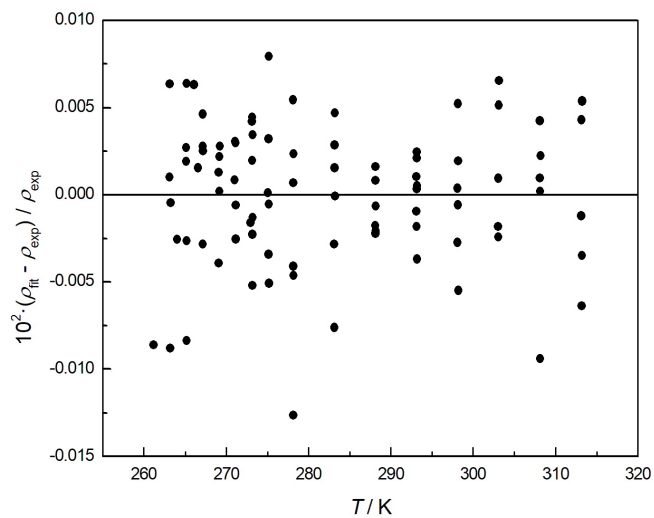


Figure 6: Percentage residuals of the fit (predicted density versus experimental density) as a function of temperature.

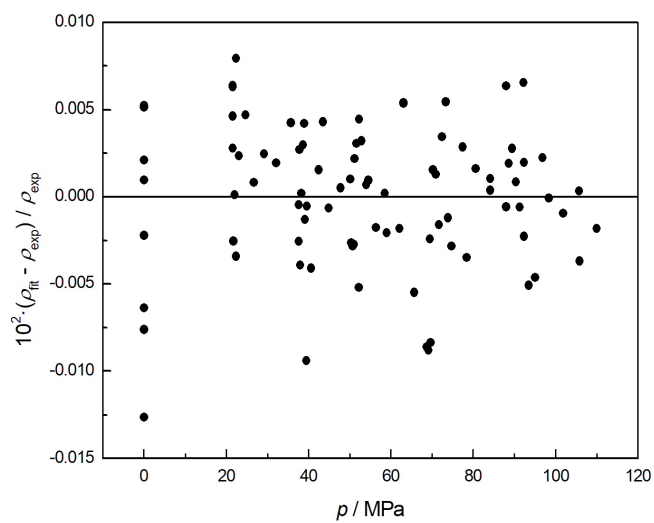


Figure 7: Percentage residuals of the fit (predicted density versus experimental density) as a function of pressure.

Table 4: Density  $\rho$  of standard seawater ( $S_A = 35.158 \text{ g}\cdot\text{kg}^{-1}$ ) at temperature  $T$  and pressure  $p$ , calculated by using Eq.10 along with the isothermal compressibility  $\kappa$  and the isobaric thermal expansion  $\alpha$ . Entries in italics refer to metastable states of liquid seawater.

$p / \text{MPa}$	$\rho / \text{kg}\cdot\text{m}^{-3}$	$\kappa / \text{GPa}^{-1}$	$10^4 \cdot \alpha / \text{K}^{-1}$
<i><math>T = 263.15 \text{ K}</math></i>			
<i>1.00</i>	<i>1028.23</i>	<i>0.4969</i>	<i>-0.818</i>
<i>15.00</i>	<i>1035.27</i>	<i>0.4779</i>	<i>-0.321</i>
<i>30.00</i>	<i>1042.57</i>	<i>0.4587</i>	<i>0.178</i>
<i>45.00</i>	<i>1049.62</i>	<i>0.4407</i>	<i>0.645</i>
<i>60.00</i>	<i>1056.45</i>	<i>0.4237</i>	<i>1.083</i>
<i>75.00</i>	<i>1063.06</i>	<i>0.4077</i>	<i>1.493</i>
<i>90.00</i>	<i>1069.46</i>	<i>0.3926</i>	<i>1.879</i>
<i>105.00</i>	<i>1075.66</i>	<i>0.3926</i>	<i>2.241</i>
<i><math>T = 273.15 \text{ K}</math></i>			
1.00	1028.37	0.4655	0.500
15.00	1034.97	0.4484	0.861
30.00	1041.82	0.4310	1.226
45.00	1048.45	0.4147	1.568
60.00	1054.87	0.3993	1.891
75.00	1061.09	0.3848	2.195
90.00	1067.12	0.3710	2.481
105.00	1072.66	0.3580	2.752
<i><math>T = 283.15 \text{ K}</math></i>			
1.00	1027.29	0.4431	1.581
15.00	1033.56	0.4272	1.834
30.00	1040.08	0.4111	2.090
45.00	1046.39	0.3959	2.332
60.00	1052.51	0.3816	2.560
75.00	1058.44	0.3680	2.777
90.00	1064.20	0.3551	2.982
105.00	1069.78	0.3429	3.177
<i><math>T = 293.15 \text{ K}</math></i>			
1.00	1025.17	0.4280	2.517
15.00	1031.23	0.4129	2.677
30.00	1037.51	0.3976	2.840
45.00	1043.60	0.3831	2.995
60.00	1049.51	0.3694	3.143
75.00	1055.24	0.3564	3.284
90.00	1060.79	0.3441	3.419
105.00	1066.19	0.3324	3.548
<i><math>T = 303.15 \text{ K}</math></i>			
1.00	1022.15	0.4195	3.376
15.00	1028.07	0.4047	3.451

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30.00	1034.21	0.3897	3.528
45.00	1040.16	0.3756	3.604
60.00	1045.93	0.3622	3.677
75.00	1051.53	0.3495	3.749
90.00	1056.96	0.3374	3.818
105.00	1062.23	0.3260	3.886
$T = 313.15 \text{ K}$			
1.00	1018.28	0.4172	4.219
15.00	1024.14	0.4023	4.209
30.00	1030.22	0.3873	4.202
45.00	1036.11	0.3731	4.198
60.00	1041.82	0.3597	4.198
75.00	1047.36	0.3470	4.200
90.00	1052.73	0.3350	4.205
105.00	1057.94	0.3235	4.212

265 In Fig. 10 the derived isothermal compressibility as a function of pressure, along  
 266 isotherms is shown. Compressibility results are compared to TEOS-10 values and  
 267 shown in Fig. 11. Difference of isothermal compressibility are lower than  $0.005 \text{ GPa}^{-1}$   
 268 and, as expected, are higher for the isotherm of supercooled seawater. This latter is  
 269 also the only isotherm for which the differences have an opposite trend compared to  
 270 the others. Calculated isobaric thermal expansion as a function of pressure and repre-  
 271 sented along isotherms are reported in Fig. 12. Whereas in Fig. 13, expansivities of  
 272 this work and TEOS-10 are compared. Differences are lower than  $0.24 \cdot 10^{-4} \text{ K}^{-1}$ , and  
 273 the two isotherms at the extreme temperatures show the highest differences, which are  
 274 at the lowest pressure. Instead, for the intermediate temperatures, the differences are  
 275 nearly constant.

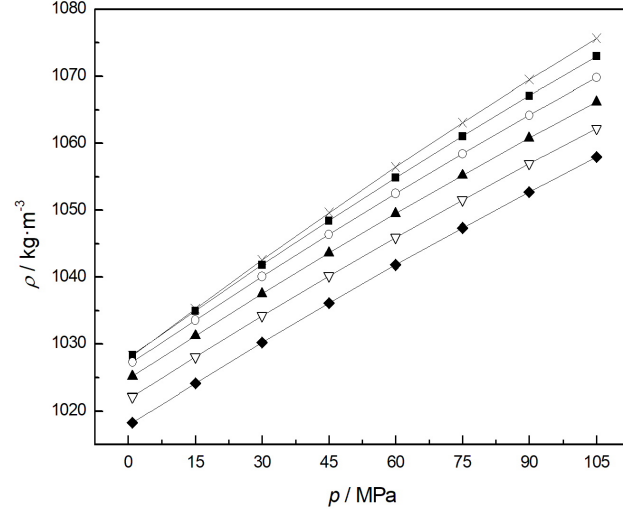


Figure 8: Density of seawater calculated by the fit (Eq. 10) as a function pressure, along isotherms:  $\times$ ,  $T = 263.15$  K;  $\blacksquare$ ,  $T = 273.15$  K;  $\circ$ ,  $T = 283.15$  K;  $\blacktriangle$ ,  $T = 293.15$  K;  $\nabla$ ,  $T = 303.15$  K;  $\blacklozenge$ ,  $T = 313.15$  K.

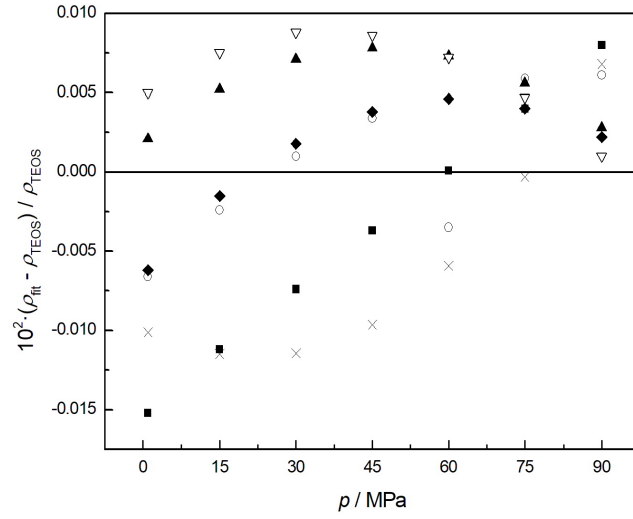


Figure 9: Percentage deviations of seawater densities calculated by the fit (Eq. 10) from the values of TEOS-10 (zero line) as a function pressure, along isotherms:  $\times$ ,  $T = 263.15$  K;  $\blacksquare$ ,  $T = 273.15$  K;  $\circ$ ,  $T = 283.15$  K;  $\blacktriangle$ ,  $T = 293.15$  K;  $\nabla$ ,  $T = 303.15$  K;  $\blacklozenge$ ,  $T = 313.15$  K.

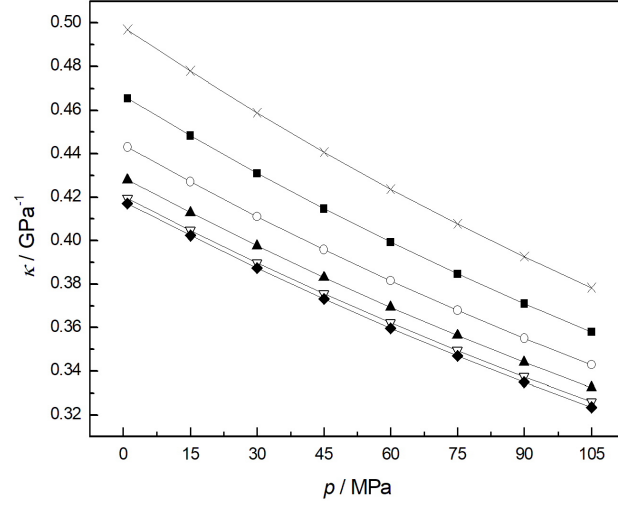


Figure 10: Isothermal compressibility of seawater as a function of pressure:  $\times$ ,  $T = 263.15$  K;  $\blacksquare$ ,  $T = 273.15$  K;  $\circ$ ,  $T = 283.15$  K;  $\blacktriangle$ ,  $T = 293.15$  K;  $\nabla$ ,  $T = 303.15$  K;  $\blacklozenge$ ,  $T = 313.15$  K.

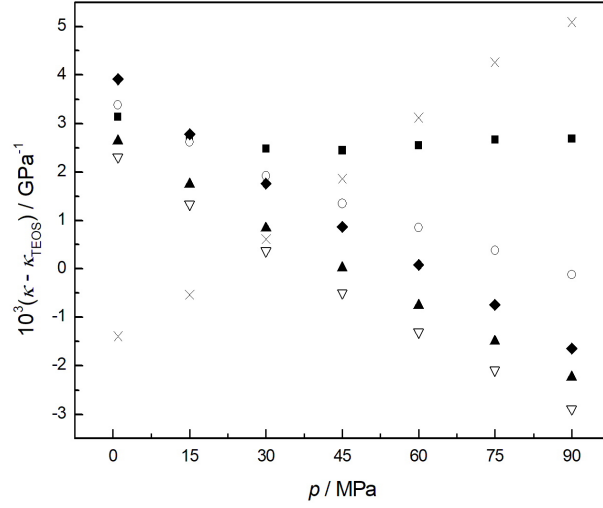


Figure 11: Deviations of isothermal compressibility derived in this work from data calculated by TEOS-10 as a function of pressure:  $\times$ ,  $T = 263.15$  K;  $\blacksquare$ ,  $T = 273.15$  K;  $\circ$ ,  $T = 283.15$  K;  $\blacktriangle$ ,  $T = 293.15$  K;  $\nabla$ ,  $T = 303.15$  K;  $\blacklozenge$ ,  $T = 313.15$  K.

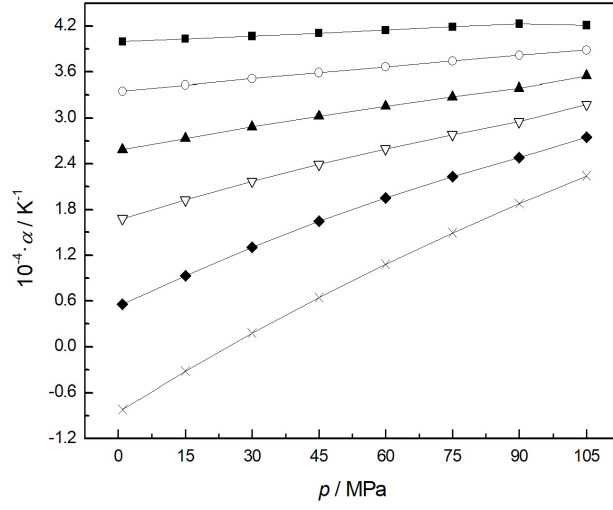


Figure 12: Isobaric thermal expansion of seawater as a function of pressure:  $\times$ ,  $T = 263.15$  K;  $\blacksquare$ ,  $T = 273.15$  K;  $\circ$ ,  $T = 283.15$  K;  $\blacktriangle$ ,  $T = 293.15$  K;  $\nabla$ ,  $T = 303.15$  K;  $\blacklozenge$ ,  $T = 313.15$  K.

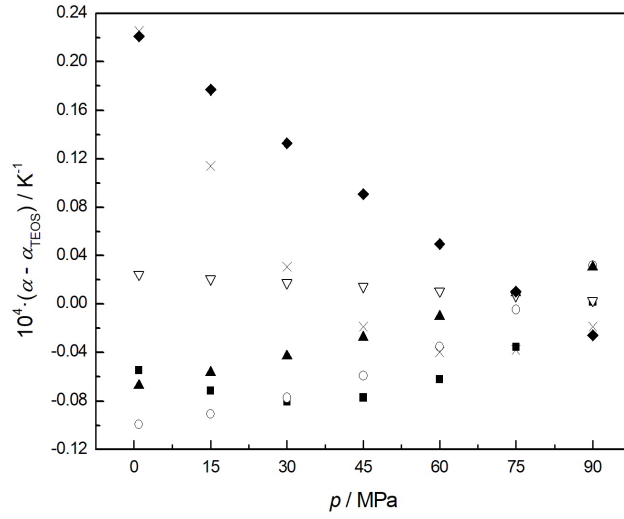


Figure 13: Deviations of isobaric thermal expansion derived in this work from data calculated by TEOS-10 as a function of pressure:  $\times$ ,  $T = 263.15$  K;  $\blacksquare$ ,  $T = 273.15$  K;  $\circ$ ,  $T = 283.15$  K;  $\blacktriangle$ ,  $T = 293.15$  K;  $\nabla$ ,  $T = 303.15$  K;  $\blacklozenge$ ,  $T = 313.15$  K.

## 276 6. Conclusions

277 In this work, with the pseudo-isochoric method, density of standard seawater ( $S_A =$   
278  $35.158 \text{ g}\cdot\text{kg}^{-1}$ ) was measured. Measurements were carried out by means of a calibrated  
279 pycnometer of known volume as a function of temperature and pressure. The mass of  
280 seawater was determined by the gravimetric method. Seawater density was obtained for  
281 temperatures between (261.15 to 313.15) K and in the pressure range from about (21 to  
282 110) MPa, thus partially covering the supercooled region, with an estimated expanded  
283 relative uncertainty of 0.05 %, with  $k = 2$ . The experimental values were compared  
284 to the equation of state of TEOS-10 (IOC et al., 2010). Considering the experimental  
285 uncertainty, all the measurements are in agreement with TEOS-10 data within  $\pm 0.02$  %.

286 Starting from the high pressure experimental data, along with the measurements at  
287 atmospheric pressure of Romeo et al. (2019), a 8-parameters function of specific vol-  
288 ume as a function of temperature and pressure was implemented. The function is able to  
289 determine seawater density from (263.15 to 313.15) K and from (1 to 105) MPa, with  
290 an uncertainty of 0.05 %. Additionally, from the calculated densities, the isothermal  
291 compressibilities and the isobaric thermal expansivities were derived and compared  
292 with the values of TEOS-10, resulting within  $\pm 0.005 \text{ GPa}^{-1}$  and  $\pm 0.24 \cdot 10^{-4} \text{ K}^{-1}$ , re-  
293 spectively.

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