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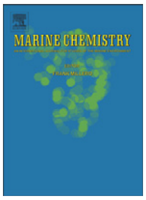

The effect of composition on the density of South Pacific Ocean waters

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ABSTRACT

The conductivities and densities were measured on 331 samples collected in the South Pacific Ocean during the P18 CLIVAR (Climate Variability and Predictability) cruise. The relative densities ($\rho-\rho^0$) were compared to those determined from the equation of state of seawater. The excess densities ($\Delta\rho=\rho_{\mathrm{Meas}}-\rho_{\mathrm{Calc}}$) ranged from ± 0.003 kg m^{-3} in surface waters to 0.015 kg m^{-3} in deep waters due to additions of nutrients and carbonates. The values of $\Delta\rho$ were found to be a linear function of the increases of ΔNTA, $\Delta Si(OH)_4$ and ΔNO_3 in the deep waters ($\sigma=0.002$ to 0.005 kg m^{-3}). The best correlations of $\Delta\rho$ with changes in concentration of $\Delta Si(OH)_4$ are (N = 331) given by

$$\Delta\rho\,/\,\mathrm{kg\ m^{-3}} = -1.7\cdot 10^{-3} + 9.4\cdot 10^{-5}\Delta\mathrm{Si(OH)_4} \quad \left(\sigma = 0.0043\ \mathrm{kg\ m^{-3}}\right).$$

Correlation of the South Pacific data with earlier measurements made in the North Pacific and Indian oceans (N = 596) are given by

$$\Delta\rho\,/\left(\mathrm{kg\ m^{-3}}\right) = -1.7\cdot 10^{-3} + 9.44\cdot 10^{-5}\Delta\mathrm{Si(OH)_4} \quad \left(\sigma = 0.0043\ \mathrm{kg\ m^{-3}}\right).$$

The excess densities can also be accounted for by determining the change in the absolute salinity (S_A) of seawater. The values of ΔS have been estimated from

$$\Delta S = 50\ \Delta\mathrm{NTA} + 68\ \Delta\mathrm{SiO_2} + 63\ \Delta\mathrm{HNO_3} + 82\ \Delta\mathrm{H_3PO_4}.$$

The values of $\Delta\rho$/kg m^{-3} calculated from the estimated values of S_A agreed with the measured densities with a standard error of ± 0.004 kg m^{-3}. Values of S_A determined from density measurements also show a correlation with $\Delta Si(OH)_4$. The Indian and South Pacific values have been fitted to ($\sigma=0.0044$)

$$\Delta S = -2.4\cdot 10^{-3} + 1.06\cdot 10^{-4}\ \Delta\mathrm{Si(OH)_4}.$$

An error of ± 0.0044 g kg^{-1} in S_A is equivalent to and error of ± 0.003 kg m^{-3} in the density (which is the precision of the density measurements).

1. Introduction

Changes in the composition of seawater result in variations of the conductance–density relationship (Brewer and Bradshaw, 1975; Connors and Weyl, 1968). The limitations of the conductivity method to determine the salinity or density of seawater have been examined by several workers (Brewer and Bradshaw, 1975; Millero et al., 1976a, b, 1978, 2008a; Millero and Kremling, 1976; Poisson et al., 1980, 1981; Millero, 2000). Studies to examine the limitations of the International Equation of State of Seawater (Millero and Poisson, 1981) have also been discussed (Millero et al., 1978; Millero, 2000; Millero et al., 1976a,b,c,d; Millero and Kremling, 1976; Poisson et al., 1980). Brewer and Bradshaw (1975) were the first to estimate the relationship between changes in the calculated density or sigma-T and changes in the composition of ocean waters. They found that changes in salinity of 0.015 could result in changes in σ_T of 0.012 due to changes in the composition of seawater due to the oxidation of plant material. Brewer and Bradshaw (1975) suggested that the excess density, $\Delta\rho$/kg m^{-3} = ρ(meas) − ρ(calc) could be estimated by examining the changes in total alkalinity (TA), total carbon dioxide (TCO_2) and silicate ($\Delta Si(OH)_4$). They also pointed out that these small changes in the density could affect the global circulation of world ocean waters along

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constant density surfaces. Millero et al. (1976b) modified their work using a more reliable partial molar volume for $Si(OH)_4$ and considering the effect of added NO_3 to the excess density.

The theoretical equations were examined by Millero et al. (1976b) using measurements of the density and conductivity of samples of seawater collected during the GEOSECS cruises. They found excess densities in deep waters were (0.005 ± 0.0015) kg m^{-3} in the North Atlantic and (0.016 ± 0.0036) kg m^{-3} in the North Pacific. The differences between the measured and calculated excess densities using model equations found to be ± 0.003 kg m^{-3} in the North Atlantic and ± 0.004 kg m^{-3} in the North Pacific.

Millero et al. (1978) made density measurements on 124 samples collected in the North Pacific along 35N. The excess densities ranged from 0.0038 kg m^{-3} in surface waters (0–490 m) to 0.021 in deep waters (1000–5834 m). The measured values of the excess density calculated from model equations agreed with the measured value over the entire depth range to 0.005 kg m^{-3}.

Millero et al. (1978) also examined the densities in the North Pacific due to changes in the absolute salinity (S_A) defined by (Millero et al., 2008a)

$$S_A = S + \Delta S = S + \Sigma\, M_i\, \Delta n_i \tag{1}$$

where S is the Practical Salinity and M_i is the molecular weight and Δn_i is the change in moles of added nutrients, silicates and carbonates compared to the values in the surface waters of the North Atlantic which have negligible concentrations of $Si(OH)_4$, NO_3 and PO_4. The change in the salinity, ΔS, due to the addition of μmol kg^{-1} of $CaCO_3(s)$, $SiO_2(s)$, HNO_3 and H_3PO_4 can be estimated by (Millero et al., 1978)

$$\Delta S = 50 \cdot 10^{-6} \Delta NTA + 64 \cdot 10^{-6}\ \Delta SiO_2 + 63 \cdot 10^{-6}\ \Delta HNO_3 + 82 \cdot 10^{-6}\ \Delta H_3PO_4. \tag{2}$$

It should be pointed out that the Si entering the oceans is $SiO_2(s)$ not $Si(OH)_4$ used in earlier studies (Millero et al., 1978, 2008b). For deep waters with $Si(OH)_4 = 160$ μmol kg^{-1}, $\Delta NTA = 80$ μmol kg^{-1}, $HNO_3 = 37$ μmol kg^{-1} and $H_3PO_4 = 2.5$ μmol kg^{-1}, the contributions to ΔS are respectively, 0.0102, 0.004_0, 0.001_7 and 0.000_2 g kg^{-1}. Since the change in the density due to salinities near 35.0 is not a strong function of salinity ($\Delta\rho = 0.752$ kg m^{-3} ΔS), one can convert Eq. (2) into changes in Δρ using

$$\Delta\rho \,/\, \text{kg m}^{-3} = 3.79\ 10^{-5} \Delta NTA + 4.84\ 10^{-5}\ \Delta Si(OH)_4 + 4.77\ 10^{-5}\ \Delta NO_3 + 6.2\ 10^{-5}\ \Delta PO_4. \tag{3}$$

(where the concentrations of the normalized alkalinity, $\Delta NTA = NTA - 2318$ μmol kg^{-1}, silicate and nitrate are in μmol kg^{-1}). This equation is valid as long as the amounts of added salts are low. The measured excess densities in the North Pacific agreed with those calculated from Eq. (2) on the average of ± 0.0043 kg m^{-3}. In more recent work, measurements in the Indian Ocean of the excess density (Millero et al., 2008a) have been examined using the equation (N = 135)

$$\Delta\rho \,/\, \text{kg m}^{-3} = -2.7 \cdot 10^{-3} + 7.66 \cdot 10^{-5} \Delta Si(OH)_4. \tag{4}$$

The measurements agreed with the values calculated from this equation with a standard error of $\sigma = 0.0027$ kg m^{-3}.

In this paper, we present new (N = 337) density and conductivity measurements on samples collected in the South Pacific on the P18 CLIVAR (Climate Variability and Predictability) cruise. These measurements have been combined with our earlier measurements to derive equations that represent a larger area of the world oceans.

2. Experimental methods

The samples were collected in 125 cm^3 HDPE bottles and sealed with parafilm until analysis back in the lab. The Practical Salinities were measured with a portasal salinometer calibrated with standard seawater. The densities were measured on the Paar 500 densimeter at 25.000 ± 0.003 °C in the laboratory. Although salinity was measured at sea, it was re-measured back in the lab at the same time as the density to account for any evaporation that may have occurred after collection. The measurements on standard seawater were reproducible to $\sigma = 0.003$ kg m^{-3}. All of the measurements were made relative to the density of water which is based on the equations of Kell (1975) adjusted to the 1990 temperature scale (Spieweck and Bettin, 1992). The new measurements of the relative density $(\rho - \rho^0)$ have been compared to those determined from the equation of state of seawater (Millero and Poisson, 1981). These relative densities are not strongly affected by changes in the temperature scale or the absolute value for the density of pure water. Measurements on standard seawater (P146) of known Practical Salinity yielded densities at 25 °C that agreed with the equation of state to $\sigma = 0.003$ kg m^{-3}, which is the precision of the measurements.

3. Results and calculations

The measured values of Δρ/kg m^{-3} at 25 °C for all the samples collected in the Pacific Ocean are tabulated in Table 1 along with the station, salinity, concentrations of $Si(OH)_4$, NO_3 and PO_4 and changes in ΔNTA are also given in Table 1. The values of Δρ as a function of depth (db) are shown in Fig. 1. The surface values show a scatter of ± 0.005 kg m^{-3} and the deep waters have an average of ~0.011 kg m^{-3}. Part of the scatter is related to changes in the composition of seawater not being directly related to depth. The values of Δρ/kg m^{-3} as a function of $\Delta Si(OH)_4$, ΔNO_3, ΔPO_4 and ΔNTA (μmol kg^{-1}) are shown in Figs. 2 and 3. The results have been fitted to equations of the

$$\Delta\rho \,/\, kg\ m^{-3} = a + b\ \Delta[i] \tag{4}$$

The concentration values of the constituents i are in μmol kg^{-1} and the coefficients a and b are given in Table 2 along with the standard error of the fits. The intercepts are close to zero except for NO_3 and PO_4. As shown in earlier studies (Millero et al., 2008a), the results as a function of $\Delta Si(OH)_4$ or ΔNTA give the best fit. Since the values of $\Delta Si(OH)_4$ are more readily available, the equation for silicate is suggested as the best to use for the South Pacific

$$\Delta\rho \,/\, \text{kg m}^{-3} = -2.7 \cdot 10^{-3} + 7.66 \cdot 10^{-5}\ \Delta Si(OH)_4 \quad x\left(\sigma = 0.0027\ \text{kg m}^{-3}\right). \tag{5}$$

The excess densities calculated at the absolute salinity using Eq. (2) were also examined. The differences between the measured and calculated values using this equation yielded standard error in the differences of ± 0.003 kg m^{-3}.

4. Global ocean density estimates

The excess densities measured in the North Pacific, Indian and South Pacific oceans as a function of $\Delta Si(OH)_4$ are shown in Fig. 4. All available data were fitted to the equation (N = 599)

$$\Delta\rho \,/\, \text{kg m}^{-3} = -1.7 \cdot 10^{-3} + 9.44 \cdot 10^{-5}\ \Delta Si(OH)_4 \quad x\left(\sigma = 0.0026\ \text{kg m}^{-3}\right). \tag{6}$$