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Constraints on the salinity–oxygen isotope relationship in the central tropical Pacific Ocean

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ABSTRACT

Uncertainties surround the relationship between salinity and the stable isotopic composition of seawater, largely due to a dearth of modern seawater isotope data. Here we report 191 new, paired measurements of salinity and seawater oxygen isotopes ($\delta^{18}O_{sw}$) taken from the central tropical Pacific in May 2012, from the surface to 4600 m depth. We observe significant correlations between $\delta^{18}O_{sw}$ and salinity across the study region, with slopes ranging from 0.23 to 0.31‰/psu for the mixed layer, and 0.35–0.42‰/psu for waters between the mixed layer and 500 m depth. When considering $\delta^{18}O_{sw}$–salinity across averages of individual water masses in the region, slopes range from 0.21 to 0.40‰/psu, albeit with appreciable scatter. Surface salinity and $\delta^{18}O_{sw}$ data corresponding to the North Equatorial Countercurrent are significantly higher than previously observed, which we attribute to a weak westerly current and dry conditions in the region during the May 2012 cruise. Subsurface (80–500 m) salinity values from 2012 are significantly lower than corresponding values from pre-existing regional data, highlighting a different latitudinal sampling distribution, while subsurface $\delta^{18}O_{sw}$ is not significantly different. Thus, in May 2012, $\delta^{18}O_{sw}$ in this region could not be used to distinguish between subsurface water masses of different salinities. Unlike other regions where the surface 'freshwater endmember' is close to the $\delta^{18}O$ value of regional precipitation, the freshwater endmember implied by our dataset (−10.38‰) is consistent with a strong evaporative influence. Paired $\delta^{18}O$–δD values of precipitation and surface seawaters have similar slopes (5.0, 5.1), and relatively low intercepts (1.4, 0.8) indicating isotopic variability in both reservoirs is also partly controlled by evaporation.

1. Introduction

Variations in tropical Pacific Ocean temperature and atmospheric circulation have large-scale impacts on global climate. As such, it is important to quantify tropical Pacific ocean–atmosphere variability across a range of timescales, through the generation and analysis of paleoclimate proxy records from this region. Many of the most important records of past climate variability from the tropical Pacific are based on proxies linked to the stable isotopic composition of seawater. In particular, carbonate records of $\delta^{18}O$ derived from fossil corals and marine microfossils are key indicators of past changes in ocean temperature and salinity (e.g., Dunbar et al., 1994; Cole et al., 2000; Gagan et al., 2000; Lea et al., 2000; Tudhope et al., 2001; Koutavas et al., 2002; Stott et al., 2002; Cobb et al., 2003; Correge, 2006; Oppo et al., 2009; Thompson et al., 2011; Koutavas and Joanides, 2012; Cobb et al., 2013; Leech et al., 2013; McGregor et al., 2013). Given that both temperature and the $\delta^{18}O$ value of seawater ($\delta^{18}O_{sw}$) contribute to carbonate $\delta^{18}O$ variability, independent constraints on temperature derived from Mg/Ca in foraminifera (Nurnberg et al., 1996; Lea et al., 1999; Elderfield and Ganssen, 2000) or Sr/Ca in corals (Alibert and McCulloch, 1997; Beck et al., 1997; Gagan et al., 1998; Nurhati et al., 2009; Nurhati et al., 2011) allow for the explicit reconstruction of $\delta^{18}O_{sw}$ variability. Such estimates may provide information about past salinity, given the strong empirical relationship between the $\delta^{18}O_{sw}$ and salinity (Craig and Gordon, 1965b; Fairbanks et al., 1997).

$\delta^{18}O_{sw}$ variability is often interpreted in the context of hydroclimate variability as evaporation and precipitation affect both $\delta^{18}O_{sw}$ and salinity (Fairbanks et al., 1997; LeGrande and Schmidt, 2006). However, recent work on the tropical Pacific salinity budget indicates that changes in salinity are controlled by a combination of surface forcing, advection, and vertical mixing (Hasson et al., 2013). The relative importance of each of these terms in shaping the spatiotemporal variability of $\delta^{18}O_{sw}$ remains uncertain. These factors, as well as the extra degree of freedom provided by the stable isotopic composition of precipitation may drive variability $\delta^{18}O_{sw}$–salinity relationship. Model simulations have already highlighted the $\delta^{18}O_{sw}$–salinity relationship likely varies temporally

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(Schmidt, 1999; Oppo et al., 2007; Schmidt et al., 2007; LeGrande and Schmidt, 2011), yet how the real world $\delta^{18}O_{sw}$–salinity relationship varies on different timescales remains unknown. How well available $\delta^{18}O_{sw}$–salinity data approximate mean $\delta^{18}O_{sw}$–salinity conditions is also unclear, given that short, episodic seawater $\delta^{18}O$ sampling efforts likely alias substantial seasonal and interannual variability (Abe et al., 2009).

Currently, there is a dearth of $\delta^{18}O_{sw}$ data from the tropical Pacific, which hinders our understanding of these potential complexities of the $\delta^{18}O_{sw}$–salinity relationship. Here we present 191 new, paired salinity–$\delta^{18}O_{sw}$ values sampled in the central tropical Pacific in May 2012. These new data more than double the number of stable isotope observations in the central tropical Pacific, and more than triple the number of observations from the subsurface and deep ocean of this region. Although we are adding substantially to the $\delta^{18}O_{sw}$ database with these new data, our new dataset still represents only three weeks, and is thus subject to the temporal biases inherent in most $\delta^{18}O_{sw}$ data, which tend to be collected over short periods of time. We present the new data in the subsequent sections, investigate the $\delta^{18}O_{sw}$–salinity relationship across different depths and water masses, and compare the new dataset to previous observations from the region.

2. Materials and methodology

Seawater and rain samples for water isotope analysis ($N = 177$, $N = 6$) were taken from May 2 to May 23, 2012, during cruise MGL08-12 to the Line Islands Ridge. The sampling range encompasses −0.22°S to 20.8°N, 161.5°W–156.0°W, with the majority of samples from south of 10°N (Fig. 1). Additional surface seawater ($N = 14$) and daily rain samples ($N = 10$) were taken at Kiritimati during a land-based field expedition from May 16 to May 30, 2012. Shipboard and island rain samples were collected daily in a separatory funnel filled with a layer of mineral oil to prevent evaporation. Cruise seawater samples were taken from an uncontaminated seawater intake line ~3 m below the surface and from 10-liter niskin bottles attached to a 24-position rosette. The cruise salinity values are derived from a SBE-21 SEACAT Thermosalinigraph installed in the seawater intake line, and an SBE 9/11plus V5.1 g CTD attached to the 24-position rosette. Salinity samples from Kiritimati were collected in 60 mL amberglass bottles simultaneously with seawater samples for isotope analysis, and were measured with a Mettler Toledo conductivity meter (±0.2 psu precision), maintaining a constant sample temperature of 25 °C in a dry bead heat block.

Stable isotope samples were sealed in 3.5 ml crimp-top vials with butyl rubber stoppers and aluminum seals. Both seawater and precipitation $\delta^{18}O$ and δD values were measured at Georgia Institute of Technology on a Picarro L1102-I water isotope analyzer. Samples were calibrated using three internal water standards ($\delta^{18}O$ −16.49, −4.84, 0.93‰, δD −98.3‰, −27.5‰, −27.0‰) analyzed at the beginning and end of each 45-sample run (Moerman et al., 2013). These internal standards, are calibrated against NIST-VSMOW, NIST-GISP, and NIST-SLAP. Instrument drift was assessed with an internal standard measured after every ninth sample. Each rainwater sample was measured three times. Coefficients that correct for instrument memory of the previous sample were applied to the rainwater data after measurement. For seawater samples, changes in memory with the addition of salts to the instrument precluded using memory coefficients. Instead, we measured each sample six times and averaged the last three values for each sample. Long-term instrument reproducibility is ±0.1‰ for $\delta^{18}O$ and ±0.8‰ for δD (1σ). Data are reported as ‰ VSMOW. All seawater data will be archived on the Goddard Institute for Space Studies (GISS) global seawater oxygen-18 database (http://data.giss.nasa.gov/o18data/) (Schmidt et al., 1999), and all precipitation isotope data will be archived on the Global Network of Isotopes in Precipitation (GNIP) database (IAEA/WMO, 2006).

$\delta^{18}O_{sw}$ and salinity values from May 2012 water samples are compared to 78 paired $\delta^{18}O_{sw}$ and salinity values archived in the GISS global seawater oxygen-18 database (Schmidt et al., 1999). These data are from 5°S–20°N, 175°W–140°W, a region that expands beyond, but is centered on, the area in which the new data were collected. Central tropical Pacific $\delta^{18}O_{sw}$ and salinity values include data from January–February 1991 ($N = 60$) (Laube-Le'Enfant, 1996), data of unknown month and year ($N = 12$) from the mid 20th century (Epstein and Mayeda, 1953; Craig and Gordon, 1965a), and November–December 1973 data ($N = 6$) from the Geochemical Open Sections Study (GEOSECS) database (Ostlund et al., 1987). This combined dataset is biased toward January and February 1991, as the majority of the data come from Laube-Le'Enfant (1996). Daily precipitation stable isotope values are compared to monthly $\delta^{18}O$ and δD values ($N = 23$, 1962–1964) from Kiritimati available from GNIP (IAEA/WMO, 2006).

3. Results and discussion

3.1. Paired $\delta^{18}O_{sw}$ and salinity observations

Ninety-five seawater samples are from the surface mixed layer, estimated at 75 m from CTD casts between the equator and 10°N. May 2012 surface, mixed layer $\delta^{18}O_{sw}$ values range from 0.22 to 0.68‰ (Figs. 1, 2) with a mean of 0.47 ± 0.12‰ (1σ standard deviation). As apparent in Fig. 2, the mean surface $\delta^{18}O_{sw}$ value from off the coast of Kiritimati (0.38 ± 0.07‰) is slightly fresher than the mean $\delta^{18}O_{sw}$ value from the open ocean at nearby latitudes (0.56 ± 0.08‰). This may be due to submonthly variability — Kiritimati experienced more precipitation from May 15–May 30 relative to earlier in the month when the cruise samples were taken. Or, potential groundwater flux may be driving lower salinity and $\delta^{18}O_{sw}$ values near the island shore. Given this potential bias, we exclude the Kiritimati seawater measurements from regression analyses.

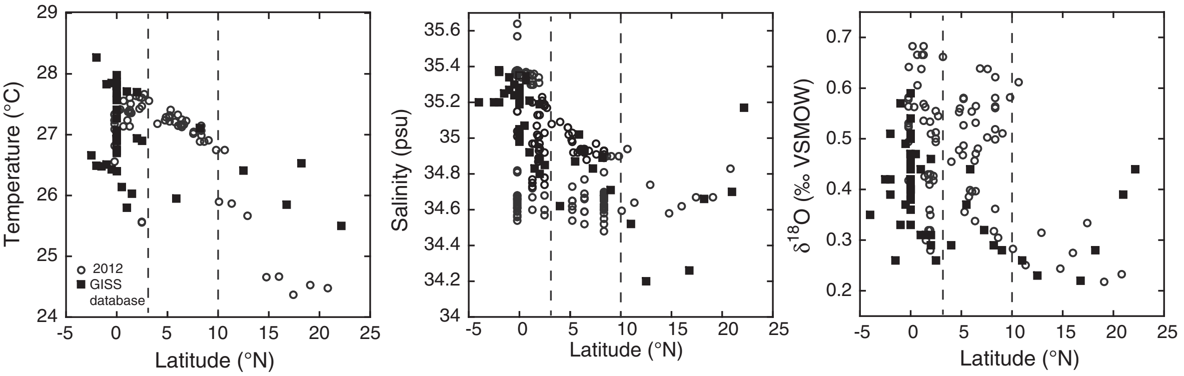

Fig. 1. Seawater temperature (left), salinity (middle), and $\delta^{18}O_{sw}$ values (right) versus latitude for the May 2012 central tropical Pacific dataset (open circles) and previous data from region archived in GISS database (squares). Dashed lines, from south to north indicate SEC, NECC, and NEC regions.