Oxygen isotope–salinity relationships of discrete oceanic regions from India to Antarctica vis-à-vis surface hydrological processes

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Abstract

Coupled measurements of the oxygen isotope and salinity of surface waters at every degree latitude along a transect from India to Antarctica during summer 2010 were carried out to gain insight into the surface hydrological processes active in the Indian and Southern Oceans. It is possible to identify discrete water masses from the Indian and Southern Oceans based on oxygen isotope and salinity. We determine the relationship between oxygen isotope and sea surface salinity ($\delta^{18}O$–SSS) pertaining to those distinct water masses by combining our data with those available at the NASA-GISS data center. These relationships are predominantly governed by evaporation/precipitation except in the Antarctic Zone (beyond Polar Front) where sea ice melting/freezing plays a dominant role. We obtain more representative, long-term mean values of the slopes and intercepts of the salinity–oxygen isotope relation that will help to determine paleosalinity from carbonate fossils from sediments more accurately. The Subtropical and Polar Fronts were identified at 44° S and 54° S, respectively. These new data will also be useful to fill the gap in the existing global gridded $\delta^{18}O$ data sets obtained by interpolating the observed values.

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1. Introduction

Polar regions of the world are experiencing rapid climate change, and the Southern Ocean is no exception (e.g., IPCC, 2007). Consequently, the freshwater budget of the Southern Ocean is significantly affected (Meredith et al., 2008); this needs to be documented to better understand its consequences. Freshwater variability affects the salinity and the stable oxygen isotope ratio ($\delta^{18}O$) of surface seawater significantly (Bigg and Rohling, 2000; Clark and Fritz, 1997). Oxygen isotope–sea surface salinity ($\delta^{18}O$–SSS) relationship is an important information for several hydrological processes such as the balance between meteorological input i.e., evaporation/precipitation (E–P) and glacial melt water, sea ice melting/formation, river run-off, and upwelling or advection and also provides an important tool to delineate different water masses (Bigg and Rohling, 2000; Meredith et al., 1999; Srivastava et al., 2007). Furthermore, recent interest in the Southern Ocean regarding its role in carbon sequestration has led to several paleoclimatic studies in that region (Mayewski et al., 2009 and references therein). The $\delta^{18}O$–SSS relationship is widely used in paleoclimatic studies as well to estimate the salinity variability in the past that is relatable to changing climate, which further strengthens the need to understand the temporal variability of this relationship. In view of this, a few studies have been carried out in the western Indian Ocean sector of the Southern Ocean (e.g., Srivastava et al., 2007), but recent studies in the northern Indian Ocean have shown that this relationship can change significantly over the years (e.g., Singh et al., 2010); so it becomes important to assess this variability over a sufficiently long period (Rohling and Bigg, 1998). The global gridded data set prepared by LeGrande and Schmidt (2006) has also raised the issue of the sparseness of observations for certain oceanic regions that include the southern Indian and the Southern Oceans. They further stress that the $\delta^{18}O$–SSS relationship may alter over time scales ranging from seasonal, annual, and interannual. The Indian sector of the Southern Ocean has received much less attention compared to others. Therefore a systematic and persistent data collection is required for this sector to reduce the uncertainties.

Here we present new data on the oxygen isotope ratio of surface seawater collected at every degree latitude from a transect starting from Goa, India (14.04° N, 73.11° E) to the Antarctic coast (66.72° S, 58.83° E). This study, spanning more than a quarter of the globe, would help identify distinct surface water-masses with separate $\delta^{18}O$–SSS relationship important for paleosalinity determination and distinct regions dominated by particular surface hydrological processes such as excess of evaporation over precipitation (E–P), sea ice melting/freezing, water mass advection, continental snowmelt affect and so on. Furthermore, this new data set would complement and add to the existing global gridded $\delta^{18}O$ data that is obtained by interpolating the observed $\delta^{18}O$ values.

2. Materials and methods

Surface water samples were collected at every degree latitude during the 4th Indian Expedition to the Southern Ocean in the austral summer (January–February) of the year 2010 along the track shown...
in Fig. 1, spanning the Arabian Sea, tropical Indian Ocean, southern Indian Ocean, and the Southern Ocean. Fig. 1 also depicts the surface circulation features of the Indian and Southern Oceans (Barker and Thomas, 2004; Schott and McCreary, 2001), and the position of the Intertropical Convergence Zone (ITCZ) (Webster, 1987). The seawater samples from the surface were collected using a clean bucket, which was then transferred to 60 ml dry HDPE plastic bottles having a very low permeability to water vapor (Illig, 2001). These were filled up to the brim without letting any bubble and capped tightly. Thereafter, another round of Teflon tape was tightly wrapped on the cap to seal it from the ambient environment to prevent any evaporation that may alter the isotopic content. Salinity was calculated using its conductivity, measured by a thermosalinograph (Sea-Bird Electronics Inc.; model name: SBE 45) installed on-board that uses the 1978 Practical Salinity Scale (PSS-78) equations with a precision of ±0.003 mS/cm. The resulting precision for salinity is ±0.005. The sea surface temperature (SST) was measured on-board using a bucket thermometer to a precision of ±0.5 °C. The oxygen isotope values were measured in the Marine Stable Isotope Lab (MASTIL) at the National Centre for Antarctic & Ocean Research, Goa, India, using an “isotope dual inlet-stable isotope ratio mass spectrometer” using the well established CO2 equilibration method (Epstein and Mayeda, 1953; Gonfiantini, 1981). The water samples were stored at around 22 °C for about four months before measurement, which was completed within 3 days. The isotopic values are reported with respect to the international standard V-SMOW (Vienna-Standard Mean Ocean Water). The reproducibility of the δ18O measurement is better than ±0.1‰ (1σ standard deviation) as determined by repeated measurements (n = 25) of the lab standard, which is seawater from 52° 02’ S and 57° 32’ E with δ18O value of −0.18 ±0.05 with respect to V-SMOW.

The δ18O–SSS relationship has been obtained by ‘linear regression’ using the ‘least squares’ method (Topping, 1962). The confidence limits of the correlation coefficient values presented here have been determined using ‘Student’s t-test’. The uncertainties on the slope (m) and intercept (c) have been calculated according to Topping (1962) as follows: when y = mx + c, ‘n’ is the number of data points, and the ‘residual’ i.e., d = y − yobserved, then error on the slope is σ = \(\sqrt{\frac{n}{(n-2)(\sum d^2(n-2)-(\sum y)^2)^2})}\) while that on the intercept is \(\sigma_c = \sigma_m(n\sum x^2/n)^{1/2}\). Here ‘y’ is the δ18O value while ‘x’ is the sea surface salinity.

3. Results and discussion

3.1. Oxygen isotope, salinity, and SST vs. latitude

Fig. 2 shows the salinity, temperature (SST), and δ18O value of surface seawater vs. latitude (also see Supplementary Table 1) southwards from Goa (from ~14° N). The first sampling point, which is very near the coast, shows considerably less salinity (35) than the subsequent locations (salinity ~36), farther away from the coast, as near the Goa coast, several small streams, namely Mandovi, Zuari, Terekhol, Chapora, Baga, and Sal debouch into the sea. Subsequently from 6° N to 2° N, there is a narrow zone of declining salinity (by 2 units; from 36 to 34) while δ18O value decreases by 0.4‰ (from 0.8‰ to 0.4‰). This coupled decline in δ18O values and salinity indicates freshening of the seawater due to the Northeast monsoon induced precipitation and oceanic currents. Although the core of the ITCZ during Northeast monsoon lies farther south, yet precipitation of 40 mm/month is recorded in this region (http://iri.ldeo.columbia.edu), which reduces salinity/δ18O (Dansgaard, 1964; IAEA/WMO, 2006). Additionally, the Northeast monsoon current brings lower salinity/δ18O waters of the Bay of Bengal (Fig. 1: Antonov...
would result in a decline in salinity and a slight increase in ice reaches a minimum (Deacon, 1984). The extensive sea ice melting period of the sample collection from beyond the Polar Front when sea salinity can be as low as 7 (Meredith et al., 2008). Mid-February was the 2.9 coast. Sea ice is enriched in the heavier oxygen isotope by about 2.6 to 3.2. Long-term oxygen isotope tracer can be either in the form of surface runoff or melt water from ice melting process. The southernmost point of this study at 66.7° S appears to be affected by the continental snow/glacial melt water having very low salinity/δ18O values due to its proximity to Antarctica. Continental ice is made up of evaporated water (and subsequent meteoric precipitation) that is highly depleted in the heavier isotope of oxygen (δ18O values of ice can be as low as −20‰; Potter and Paren, 1985), so when it melts, it reduces the salinity as well as the δ18O values of the ambient seawater (Archambeau et al., 1998). This input of freshwater can be either in the form of surface runoff or melt water from ice shelf directly in contact with seawater, which is seen in the case of the southernmost point.

3.2. Long-term oxygen isotope–salinity relationship of discrete water-masses: implications to paleoclimatic interpretations

δ18O–SSS slope is widely used in paleoclimatology/paleoceanography to delineate the effect of salinity from the oxygen isotopic composition of carbonate shells of marine microfossils such as foraminifera. Singh et al. (2010) have shown that the δ18O–SSS relationship in a fresh water dominated area, such as the Bay of Bengal, is variable on different time scales. Presently, the slopes (m) of this relationship being used are mostly based on measurement of samples collected during a single cruise representing a specific season (e.g., Duplessy, 1970; Duplessy et al., 1981; Srivastava et al., 2007). In contrast, this study attempts to obtain a long-term value for the δ18O–SSS relationship by adding data stored at NASA-GISS (Schmidt et al., 1999) from previous isolated studies carried over past few decades (Craig and Gordon, 1965; Delaygue et al., 2001; Duplessy, 1970; Duplessy et al., 1981; Frew et al., 1995; Kallel, 1985; Østlund et al., 1987; Singh et al., 2010; Srivastava et al., 2007) including data from the large programs such as SWINDEX and CDOHC (Schmidt et al., 1999) to the present study. The data points selected are from depths of up to 100 m and in between 40°E to 80°E except for latitude 14°N to 7°N where the data represent the eastern Arabian Sea. This provides us an opportunity to determine the δ18O–SSS slope for some of the least studied regions of the world's oceans. Additionally, we have improved on the earlier studies that club together huge areas (e.g., whole of the Indian Ocean or Southern Ocean) by identifying distinct regions in the Indian Ocean and Southern Ocean (Clusters 1 to 5 in Fig. 3). This should yield a relationship that is more representative of the area under consideration (Fig. 4c to g pertaining to Clusters 1 to 5 of Fig. 3).

The x, y and z axis in Fig. 3 represent salinity, δ18O values and latitude respectively. Cluster-1 pertaining to tropical samples (14°N to 7°N) from the northern hemisphere has higher δ18O values coupled with higher salinity. The 2nd distinct cluster shows samples from the northern equatorial and southern tropical Indian Ocean (7°N to 17°S) representing a large spatial extent. Cluster-3 depicts samples from the subtropical region of the southern hemisphere (24°S to 44°S) where we note higher salinities and δ18O values. A clear distinction is evident as we cross 44°S and moves into the Southern Ocean (Clusters 4 and 5). Such a distinction was also visible in SST, δ18O values and salinity plots (Fig. 2; shown by dashed line). In the Southern Ocean, unambiguous distinction is visible between the Subantarctic/Polar Frontal Zone (Cluster-4; 44°S to 54°S) and the Antarctic Zone (Cluster-5; 54°S to 68°S) with progressively lower oxygen isotope and salinity values as we move southwards due to the effect of sea ice and glacial melt water.

The oxygen isotope–salinity (δ18O–SSS) relationship observed in the present study in the case of the whole of the Indian Ocean (Fig. 4a) shows a positive relationship (slope of 0.15 ± 0.05; n = 52) i.e. both δ18O values and salinity covary implying the role of evaporation/precipitation in this region. In the region south of 44°S (Southern Ocean), we observe a slope of 0.03 ± 0.06 (n = 24) and a correlation of determination (r2) = 0.03, which is not only nonexistent but is also not significant at the 99% or 95% level (p = 0.01 or 0.05) determined using Student's t-test. In Fig. 4b, we add data from the previous studies to the present study (shown by differently colored and shaped symbols) and again divide them in the Indian and Southern Oceans similar to Fig. 4a. We note that the slope becomes steeper both for the Indian Ocean (m = 0.39 ±
and the Southern Ocean ($m = 0.24 \pm 0.04$) but the errors are quite large, especially in the case of the Indian Ocean, which may be due to the large spatial area covered. This stresses the need of dividing such large areas into discrete regions, which we do here onwards based on the clusters identified in Fig. 3. Fig. 4c shows the $\delta^{18}O$–SSS relationship from the northern tropical Indian Ocean (14° N to 7° N; Cluster-1 in Fig. 3) with $\delta^{18}O$–SSS slope of 0.41 ± 0.24; $r^2 = 0.12$; $n = 26$; significant at $p = 0.95$. In this case, the low value of $r^2$ may result because the samples are from regions affected by processes causing widely fluctuating salinities and $\delta^{18}O$ values. For example, samples near the Indian coast.
will be affected by surface runoff and lower salinity waters from the NMC while those away from it will be affected by the E-P balance. In the equatorial Indian Ocean and southern tropical Indian Ocean (7° N to 17° S; 40° E to 80° E), the δ18O–SSS slope changes to 0.08 ± 0.05; r² = 0.04; n = 87; significant at p = 0.95 as determined using Student’s t-test (Fig. 4d). The weak correlation may result because of wide spatial and temporal scales covered in this case. Interestingly, in the Fig. 4d, comparison of the results of the present study (red colored closed circles) with those of previous studies yields a much steeper slope. Addition of freshwater increases the slope and decreases the intercept (Delafague et al., 2001; Singh et al., 2010). During the sample collection period (January) the ITTCZ was over the southern tropical Indian Ocean that appears to play a major role in controlling the slope via precipitation. This observation further strengthens the case of using a temporally averaged slope value instead of relying on a single study during a specific season. In the subtropical region of the southern Indian Ocean (24° S to 44° S; Cluster-3; Fig. 4e), we observe a δ18O–SSS slope of 0.44 ± 0.03; r² = 0.69; n = 115; significant at p = 0.99. We find a steep slope and a strong correlation of high significance indicating a dominance of evaporation/preparation in controlling the surface δ18O–SSS relation in this. In the Subantarctic/Polar Frontal Zone (Cluster-4; 44° S to 54° S; Fig. 4f), the δ18O–SSS relationship is δ18O=(0.51 ± 0.06) SSS-(17.45 ± 2.18); r² = 0.44; n = 111; significant at p = 0.099. The slope is steeper here with a significant coefficient indicating dominance of evaporation/preparation. This is a cycloic region characterized by strong winds and therefore experiences high evaporation/preparation, which was also observed by Srivastava et al., 2007. The data from the Antarctic Zone (Cluster-5; 54° S to 68° S; Fig. 4g) exhibits a δ18O–SSS slope of 0.11 ± 0.05; r² = 0.09; n = 51; significant at p = 0.95, which implies an increasingly dominant role played by sea ice melting/freezing. The low slope reflects the fact that sea ice melting/freezing alters the salinity [salinity of sea ice is low (around 7; Meredith et al., 2008) as brines are expelled during sea-ice formation increasing the seawater salinity] but has very little effect on the δ18O because of small isotope fractionation between seawater and ice (Beck and Münich, 1988; Melling and Moore, 1995). In the southern subtropical Indian Ocean, the Subantarctic/Polar Frontal Zone, and the Antarctic Zone, the data of the present study is similar to the data of the earlier studies. A few data points from earlier studies and from the present study (in the case of Antarctic Zone) do exhibit wider spread of salinity, which imply the existence of varying meteorological conditions during different periods of sample collection reiterating the need for accounting the temporal variability. The δ18O–SSS slope values of distinct water masses incorporating long-term variability presented in the Fig. 4 of this study are more representative of their respective regions and would therefore help in the more accurate paleosalinity determination.

4. Conclusion
This new data set elucidates the spatially and temporally varying relationship between δ18O and sea surface salinity from one of the least studied regions of the world viz. Indian sector of the Southern Ocean and the adjoining Indian Ocean. This relationship, in the region north of the 54° S, appears to be governed predominantly by evaporation/preparation (represented as Clusters 1, 2, 3 and 4 in this study). In contrast, in the Antarctic Zone (Cluster 5), sea ice melting/freezing plays a dominant role governing the δ18O–SSS relationship. The fact that the δ18O–SSS slope in the Antarctic Region (beyond Polar Front) is much lower than the region prior to the Polar Front attests to the dominance of sea ice melting beyond it. Based on coupled measurement of isotopes and salinity, we observed the presence of Subtropical Front and Polar front at 44° S and 54° S latitude respectively. The effect of continental ice melt is observed only at the southernmost location at 66.73° S latitude. Importantly, this study presents specific region-wise, long-term values for δ18O–SSS slope that will help to more accurately determine the salinity contribution to oxygen isotopes of carbonates.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jmarsys.2013.01.001.

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