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**Seasonal changes in sea surface temperature and salinity
during the Little Ice Age in the Caribbean Sea
deduced from Mg/Ca and ^{18}O / ^{16}O ratios in corals**

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ABSTRACT

The oxygen isotopic composition ($\delta^{18}\text{O}$) of coral skeletons reflects a combination of sea surface temperature (SST) and the $\delta^{18}\text{O}$ of seawater which is related to sea surface salinity (SSS). In contrast, the magnesium/calcium (Mg/Ca) ratio of a coral skeleton reflects SST independent of salinity. By using the relationships among coral Mg/Ca ratios, coral $\delta^{18}\text{O}$, seawater $\delta^{18}\text{O}$ and SST, it is possible to uniquely determine past SST and SSS. Such determinations were made and calibrated using the Mg/Ca ratio and the $\delta^{18}\text{O}$ of the modern part of a 3 m long coral core (*Montastrea faveolata*), collected from the southwest coast of Puerto Rico in the Caribbean Sea where both SST and SSS changes seasonally and the seawater $\delta^{18}\text{O}$ measured at the coral site. Our results yielded three relationships (coral Mg/Ca-SST, $\delta^{18}\text{O}_{\text{coral}}-\delta^{18}\text{O}_{\text{water}}-\text{SST}$, and $\delta^{18}\text{O}_{\text{water}}-\text{SSS}$). With these calibration equations seasonal changes in SST and SSS during the Little Ice Age (LIA) in the Caribbean Sea were reconstructed. The $\delta^{18}\text{O}$ and Mg/Ca ratio of the coral skeleton between 1699 and 1703 suggests that the SST during the LIA was approximately 2°C cooler than present with the SSS showing greater seasonal changes as well. These results are in good agreement with climate-based reconstruction from corals based on oxygen isotopes, although the possibility of some uncertainty remain in our estimation including long-term decadal scale trends in climate.

Keywords: Little Ice Age, Caribbean, Corals, Trace Elements, Oxygen Isotopes, *Montastrea*

1. Introduction

1-1. Coral as proxies

Coral skeletons provide high-resolution records of climate variability in the tropical oceans during the last several hundred years. Coral skeletal $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_\text{c}$) reflects a combination of sea surface temperature (SST) and the $\delta^{18}\text{O}$ of ambient seawater ($\delta^{18}\text{O}_\text{w}$) which is related to the sea surface salinity (SSS). Coral $\delta^{18}\text{O}$ records can provide ambient SST variations in regions with constant hydrologic balance (e.g. Leder et al., 1996; Wellington et al., 1996) alternatively they can provide records of hydrologic balance in regions where temperature is constant (e.g. Cole and Fairbank, 1990).

The Caribbean is a semi-enclosed sea where SST and SSS vary seasonally. In such regions, it is necessary to remove SST effects from the coral $\delta^{18}\text{O}$ by an independent method in order to track SSS changes. Trace element ratios (e.g. Mg/Ca, Sr/Ca, U/Ca) in biogenic carbonates can provide such salinity-independent paleothermometric constraints (e.g. Chave, 1954; Oomori et al., 1982; Beck et al., 1992; Nürberg et al., 1996; Klein et al., 1996; Mitsuguchi et al., 1996). Using both trace elements and the $\delta^{18}\text{O}$ from corals it is possible to reconstruct past changes in the $\delta^{18}\text{O}$ of seawater, as long as the signal to noise ratio is low. In our study, we adopted Mg/Ca ratios as our primary paleothermometer because of the narrow range of SST in our research area at La Paraguera (4°C) and the relatively large dependence of the Mg/Ca ratio in corals on temperature (3-4% °C⁻¹: Mitsuguchi et al., 1996; Sinclair et al., 1998; Fallon et al., 1999), compared to that of Sr/Ca (0.6-0.8%/°C: e.g. Beck et al., 1992; Villiers et al., 1994; Shen et al., 1996; Alibert and McCulloch, 1997; Gagan et al., 1998).

In our investigation, we first evaluated the fidelity of coral records as proxies of both SST and SSS based on the combination of $\delta^{18}\text{O}$ and Mg/Ca ratios of the part of a coral core for which measured SST and SSS were known. Using the modern section as a calibration, we then determined the seasonality in SST and SSS of the Caribbean Sea during the climatically important LIA, partly because of the lack of direct information in the Caribbean on this time period and the role the Caribbean may play in helping to decipher the mechanisms responsible for the LIA.

1-2. The Little Ice Age

The Little Ice Age (LIA), a cold climatic interval from the middle of the 15th century to the late 19th century, was spatially and temporally complex (Jones and Bradley, 1992; Mann et al., 1998). Most reconstructions of air temperature during the LIA come primarily from high latitude regions with data sets that include ice cores, tree rings, mountain glacier movement, lake levels, and historical documents. The longest instrumental record those from middle England showed that the air temperature during the 18th century was 2°C cooler than present (Manley, 1974). These cooler temperatures are also reflected in tree ring data (Jacoby and D'Arrigo, 1989; Jacoby et al., 1996) and from ice cores (Dansgaard et al., 1975). In particular, the period from mid 17th to early 18th century between 1609 and 1703 is interesting because during this time solar activity was anomalously low and Sunspots disappeared (Wallance and Hobbs, 1977). Wigley and Kelly (1990) and Lean et al. (1995) have reconstructed the radiation change for the last 350 years and their results suggest that solar irradiance was at a minimum from 1645-1715 and that the reconstructed solar irradiance and Northern Hemisphere surface air temperature were positively correlated ($r = 0.86$). Seawater temperature records from marine biogenic carbonate including coral and foraminifera all indicate that tropical ocean temperature were lower by anywhere from 0.5° - 5° C during the LIA (Druffel, 1982; Glynn et al., 1983; Danbar et al., 1994; Linsley et al., 1994; Keigwin, 1996; Winter et al., in press) with the vast majority of studies indicating a 1-2°C change.

Seasonal movements of the Inter Tropical Convergence Zone (ITCZ) affect precipitation and cloudiness in topical regions. However, there are few reports on salinity and its related variable, precipitation, in the tropical region during the LIA. Verschuren et al. (2000) reported that it was wetter than present in east Africa from the 16th to 18th century, based on lake-levels and the species components of fossil diatom and midge assemblages. Similarly, a series of large-amplitude $\delta^{18}\text{O}$ oscillations in corals from the Gulf of Chiriqui, Panama, during the latter part of the LIA have been interpreted as evidence for past changes in the amount of Caribbean tropical precipitation related to ITCZ activity (Linsley et al., 1994).

3. Materials and Methods

3.1. Site and samples

On June 2, 1994 SCUBA divers using a hydraulic drilling apparatus extracted a 3 m long, 5 cm-diameter core from the coral *Montastrea faveolata* at 7 m depth off La

Parguera, Puerto Rico (Fig. 1). The core was slabbbed parallel to the axis of maximum growth and X-rayed to observe density banding. Each slab was cut to a thickness of 4 mm by a double diamond-cutting saw. The middle slab chosen for this work had 329 high-low density band couplets. Assuming that each band couplet represents one year of coral growth (Knutson et al., 1972) these were used to date the coral from 1665 and 1994 (Fig. 2).

Contact prints of the X-radiographs were scanned and the images were analyzed using NIH-Image software. This program assigns a value for the optical density (OD) of each pixel of the scanned images, ranging from 0 (white) to 255 (black).

3.2. Freezing microtome sampling technique

Samples were collected from the coral slab along growth axis in two intervals, a six-year interval between 1984 and 1989 and a five year-interval between 1700 to 1704. The coral slab was sampled for Mg/Ca ratios and $\delta^{18}\text{O}$ analyses using the freezing microtome technique (Watanabe and Oba, 1999) in which a microtome in a cold room (-20°C) is used to peel off samples at 300 μm intervals (corresponding to weekly resolution) from a frozen plug of the coral's theca-wall, eliminating possible contamination arising from other skeletal elements (e.g. Pätzold, 1992; Bernes and Lough, 1993; Lough et al., 1997;). Each sample was immediately freeze-dried to remove water from the peeled sample.

3.3. Isotopic analysis

Powdered samples (0.1 mg) were reacted with 100% phosphoric acid at 70.0°C with an automated individual-carbonate reaction device (Kiel device) and the $\delta^{18}\text{O}$ of the extracted CO_2 was determined by a coupled Finnigan MAT 251. Isotopic values were expressed relative to the isotopic ratio of the carbon dioxide gas derived from the Pee Dee Belemnite (PDB) in conventional delta notation through NBS-20 standard. The oxygen isotopic values have been expressed in per mil (‰).

The analytical error (2σ) was estimated by multiple analysis of a homogenizing powder of crushed coral. The analytical errors for the standard deviation (2σ ; 95% confidence) of fifteen replicate measurements are 0.08 ‰ and 0.05 ‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, respectively. For oxygen isotopic analysis of seawater, 2 ml of sample was equilibrated with carbon dioxide (4 ml) of known $\delta^{18}\text{O}$, by shaking between seven to twenty-four

hours at $25.0 \pm 0.1^\circ\text{C}$ (Yoshida and Mizutani, 1986). Then the equilibrated CO_2 gas was injected into the vacuum line for CO_2 extraction. The purified CO_2 was measured by a Finigan MAT 251. The $\delta^{18}\text{O}$ of seawater is expressed relative to the V-SMOW standard.

3.4. Elemental analysis

Magnesium and calcium were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) at Hokkaido University. Approximately 1.5 mg of cleaned powder samples were dissolved into 4 ml of 0.5 M nitric acid and introduced into a Leaman Labs - JICP-PS. An internal reference standard solution derived from the coral skeleton and milli-Q water, was measured after every three analyses in order to correct for low-frequency drift due to change in room temperature, plasma, and electronics. A correction factor for each sample was calculated using the average value of the reference measurements, similar to the method of Schrag (1999). The analytical error for fifteen replicate measurements of homogeneous coral powder was $0.1 \text{ mmol mol}^{-1}$ (2σ ; 95% confidence).

The purification process for the sample preparation was carried out with the greatest possible care for our ICP-AES analysis, because trace elements are highly susceptible to pre-existing surface contamination (detritus and organic) and to contamination introduced during sample recovery and preparation (Bernes and Lough, 1993). We compared several cleaning procedures for Mg analysis of coral *Montastrea faveolata* described in previous papers (Hasting et al., 1998; Shen and Boyle, 1988) and determined that the best process for the removal of organic matter and for minimizing sample loss was to use a 50-50 mixture of 30 % H_2O_2 and 0.1 M NaOH in a 60°C water bath for 15 min.

3.5. Environmental data

Seawater samples were collected for isotopic analysis from 5 m water depths, just above the top of the corals used in this study. Such samples have been taken sporadically since 1991 and systematically about every three to four weeks between November 1996 and January 1998. Each sample bottle was overflowed with seawater and 0.5 mg of mercuric chloride was added to prevent any biological activity. The caps was then sealed with aluminum package tape to avoid air contamination. Each seawater

sample was kept in a refrigerator (below 5°C), until analyzed.

SSTs during 1989-1993 were measured at the field station of the University of Puerto Rico, La Parguera, situated 3 km from the corals in the study area. A plastic bucket was lowered at the dock to a depth of 5 m, where it remained for five minutes. Upon retrieval, water temperature was measured immediately in the shade with a mercury thermometer. Daily precipitation records were also obtained from the field station at La Parguera.

3.6. *Age model*

For our coral age model, conversion of the x-axis from distance units to time scale units was done in three steps using the Analyseries program (Paillard et al., 1996), which uses tie-points to constrain the age of a record, and assumes constant coral growth rate within tie-points. Our previous work has shown that high-density (HD) bands of *M. faveolata* corals, growing at La Parguera, are precipitated once each year (Knutson et al., 1972; Quinn et al., 1996; Swart et al., 1996; Quinn et al., 1998; Swart et al., 1999) in Spring (Winter et al., 1991; Oba et al., 1998; Watanabe, 1998). Therefore our first task was to assign a calendar year to each density-band couplet (HD/LD) by counting downward from the colony surface, deposited at a known date. Then, highest Mg/Ca values from the coral skeleton, for each year, were tied to the highest values of SST (occurring August-September) and the lowest Mg/Ca values tied to the lowest values of SST (February-March). This is in accord with laboratory and field experiments that show that temperature is the primary control on Mg/Ca in corals (Mitsuguchi et al., 1996; Sinclair et al., 1998; Fallon et al., 1999). Lastly we added eight additional time markers (tie points) by tying the lowest coral $\delta^{13}\text{C}$ values for each calendar year with the time of year which had the lowest cloudiness values (winter) and highest coral $\delta^{13}\text{C}$ with the period of highest cloudiness for each year (October). Values for cloudiness were taken from the COADS data set. Previous studies in the study area (Winter et al., 1991; Oba et al., 1998; Watanabe, 1998) found a high negative correlation between cloudiness and coral $\delta^{13}\text{C}$ ($r = -0.79$) because coral $\delta^{13}\text{C}$ is primarily controlled by the activity of symbiotic algae which are affected by insolation.

4. Modern calibration

4.1. $\delta^{18}\text{O}$ and Mg/Ca ratios of modern coral skeletons

The range in the $\delta^{18}\text{O}$ of coral skeleton between 1989 and 1993 is 1.43 ‰ (-4.73 to -3.30 ‰; average -4.16 ‰; $n = 140$, Fig. 3). The range of the Mg/Ca ratio of coral skeleton during the same period was 2.11, the ratio varying between 3.46 and 5.56 mmol mol^{-1} ; average 4.47 mmol mol^{-1} ($n = 147$) (Fig. 3). A seasonal cycle is observable in both $\delta^{18}\text{O}$ and Mg/Ca (Fig 3).

4.2. Calibration of Mg/Ca ratio to temperature

The relationship between measured Mg/Ca ratios in the coral skeleton and the known SST, using the tie points and mean values for each year our (Fig. 4-a. solid circles), yields the following regression line with 95% confidence limits for the slope and intercept:

$$\text{Mg/Ca (mmol mol}^{-1}\text{)} = 0.28 (\pm 0.04) \times \text{SST (}^{\circ}\text{C)} - 3.24 (\pm 1.15), r = 0.92 (1)$$

When all other Mg/Ca ratios from our study (open circles) are included in this equation, the correlation coefficient of the regression line is 0.74 (Fig. 4-a). The uncertainty in calibration for calculated SST is $\sim 1.03^{\circ}\text{C}$, based on the standard deviation of the residuals of the regression (i.e., subtracting the calculated SST from the observed SST) (Fig. 4-b). The average difference between the calculated and the observed SST are respectively 0.48, 0.90, and 0.55°C for annual maximum, minimum, and mean values for each year.

Previously reported calibrations between coral Mg/Ca and temperature for coral *Porites* (Mitsuguchi et al., 1996; Sinclair et al., 1998; Fallon et al., 1999; Mitsuguti et al., 1998), foraminifera (Nürnberg et al., 1996), and bivalves (Klein et al., 1996) are plotted in Figure 4 for comparison with our calibration line. As can be seen in this figure, there is clear divergence among previous calibration lines, even among the same coral genus, (i.e. *Porites*). Our calibration line is different from that of *Porites* coral. The discrepancy of calibration lines for *Porites* and *Montastrea* corals suggests that Mg/Ca thermometry may be affected by inter-species differences. On the other hand, it is similar to that of Nürnberg et al., (1996) and the slope (0.28) is close to that of Klein et al., (1996) (0.30).

Figure 5 compares the monthly instrumental SST time series measurements at La Parguera with the calculated SST time series based on our Mg/Ca relationship (Eq 2).

The maximum and minimum SSTs in the La Parguera instrumental time series were 31.1°C and 24.7°C, with an average of 28.0°C. The calculated maximum and minimum SST for the same period were 30.9°C and 24.6°C, with an average of 27.6°C, well within 1.03°C uncertainty of the calculation. Note that both the measured and calculated curves are particularly well matched for the summer temperatures of 1988, 1989, and 1991 and for the winter temperature of 1990, 1991, and 1993. Slight differences between the calculated and measured SST can be attributed to inconstant annual growth rates (Barnes et al., 1995) that can cause some distortions of environmental signals in coral skeletal material. Thus, it appears that coral Mg/Ca can be a good proxy of annual temperature variations.

It is well known that factors other than temperature such as salinity and water chemistry (Klein et al., 1996; Mitsuguti et al., 1996; Nürberg et al., 1996) have little influence on skeletal Mg/Ca ratios. However, presently there is some debate that skeletal growth rate may (Swart, 1998) depend on (Lorens and Bender, 1980; Oomori et al., 1982; Nürberg et al., 1996) kinetic factors that influence skeletal Mg/Ca ratios. In our study, we compared the annual growth rate to the skeletal Mg/Ca ratio for the periods 1987-1993 and 1699-1703 (Fig. 6). No relationship between skeletal growth rate and Mg/Ca ratio could be found even though the corals had different growth rates during these two intervals (from 4 to 9 mm year⁻¹).

4.3. The $\delta^{18}\text{O}$ of seawater

On the basis of analytical determinations of sea water samples, the relationship between the $\delta^{18}\text{O}$ of seawater and SSS at La Parguera between 1991 and 1998 (Fig. 7-a) can be expressed as ($r = 0.93$; 95% confidence limits on the slope and intercept):

$$\delta^{18}\text{O}_w = 0.204 (\pm 0.03) \times \text{SSS} - 6.54 (\pm 0.68), (2)$$

We used 20 samples that measured both the isotopic values and salinity for this calculation. This strong positive correlation shown in Figure 7-a indicates that the $\delta^{18}\text{O}$ of seawater is mostly governed by SSS changes. As can be seen in this figure, the $\delta^{18}\text{O}$ of seawater has a seasonal trend which follows the annual pattern in precipitation ranging from 0.25‰ in November to 1‰ in May-July (Fig. 7-b). The slope of eqn. 2 (i.e. 0.204) is expected from tropical, semi-enclosed seas (Craig and Gordon, 1965;

Rostek et al., 1993; Schmidt, 1999). It should be noted that the $\delta^{18}\text{O}$ /salinity relationship in Figure 7 may be affected by discharge from the Orinoco River. The seasonal outflow pattern from the Orinoco River is not well known, but the maximum plume usually occurs in November (Müller-Karger et al., 1989) coinciding with the precipitation maximum. To determine more precisely the role of the Orinoco River as an environmental factor influencing oxygen isotopes, long-term salinity profiles in the Caribbean are needed. To this end, our calibration may also be useful for estimating paleosalinity from $\delta^{18}\text{O}$ proxies across the Caribbean Sea.

4.4. Comparison between precipitation and the calculated $\delta^{18}\text{O}$ of seawater

Using the age model described in section 4-2. and assuming seasonal changes in the $\delta^{18}\text{O}$ of seawater that are described in section 4-4. are representative, the relationship between SST and the isotopic difference between coral skeletons and seawater ($\delta_c - \delta_w$) is given by the following (Watanabe, 1998):

$$(\delta_c - \delta_w) = -0.19 (\pm 0.04) \times \text{SST } (^\circ\text{C}) + 0.75 (\pm 0.61), r = 0.93 \quad (3)$$

where δ_c is the $\delta^{18}\text{O}$ of the coral skeleton (vs. V-PDB) and δ_w is the $\delta^{18}\text{O}$ of the seawater (vs. V-SMOW) adding a -0.27 ‰ correction between PDB and SMOW scales (Hut, 1987, discussed by Bemis, 1998).

The slope of eqn (3) is $0.20\text{‰ } ^\circ\text{C}^{-1}$ which is very similar to that derived from inorganic calcite ($0.23\text{‰ } ^\circ\text{C}^{-1}$; O'Neil et al., 1969), molluscan aragonite ($0.21\text{‰ } ^\circ\text{C}^{-1}$; e.g. Grossman and Ku, 1986), and coral skeleton ($0.21\text{‰ } ^\circ\text{C}^{-1}$ for *Porites*; e.g. McConnaughey, 1989, $0.22\text{‰ } ^\circ\text{C}^{-1}$ for *Montastrea*, e.g. Leder et al., 1996).

Using eqn (3), therefore, it is possible to calculate the $\delta^{18}\text{O}$ of seawater and SSS (from Eq 2), because both skeletal $\delta^{18}\text{O}$ and SST were measured in our study. Making such a calculation we are able to derive SSS from the known relationship between the $\delta^{18}\text{O}$ of seawater and SSS at La Parguera. Although the continuous record of salinity is not available in La Parguera, our calculated SSS was well within the measured salinity range. Comparing our calculated salinity with the precipitation data from La Parguera (Fig. 8), it can be seen that the lowest values of calculated SSS correspond to peaks in precipitation. The correlation coefficient (r) between spikes of precipitation and the calculated $\delta^{18}\text{O}$ is 0.86 ($n = 5$). However, there are some discrepancy and uncertainty in

the relationship, especially the end of 1998. Differences are probably due to the fact that the salinity in La Parguera area is also affected to some extent by the outflow from the Orinoco River (Müller-Karger et al., 1989).

5. Paleoenvironments of the Little Ice Age in the Caribbean Sea

5.1. SST reconstruction of the Caribbean Sea during the LIA: Comparison of the Mg/Ca ratio between the two periods (1699-1703 and 1987-1993)

The range of Mg/Ca ratios in our coral skeletal material during the LIA period (1699-1703) is $1.43 \text{ mmol mol}^{-1}$ ranging from 3.18 to $4.61 \text{ mmol mol}^{-1}$, (average $3.83 \text{ mmol mol}^{-1}$; $n = 131$). Comparison of Mg/Ca ratio of our coral skeleton between the LIA and the present is shown in Fig. 9-a. A seasonal cycle can be observed for Mg/Ca ratios during both periods. Equation 1 was used to convert the coral Mg/Ca ratios (left axis) to SSTs (right axis). The calculated SST during the LIA period (1699-1703) yields an average SST of 25.8°C , a maximum of 28.9°C , and a minimum of 23.8°C . Comparison of derived SST between the LIA (1699-1703) and the present (1987-1993) suggests that the mean SST was about 2°C cooler in the LIA with the summer SST being $\sim 2^{\circ}\text{C}$ cooler and the winter being $\sim 1^{\circ}\text{C}$ cooler. These results are in good agreement with climate-based reconstruction from corals based on oxygen isotopes (Danbar et al., 1994; Druffel, 1982; Glynn et al., 1983; Linsley et al., 1994; Winter et al., in press). However we need the future paleoenvironmental study based on fully measurements through long coral cores in order to eliminate the possibility of some uncertainty including longer-term decadal scale trends in climate.

5-2. Reconstruction of SSS in the Caribbean Sea during the LIA: Comparison between the residual $\delta^{18}\text{O}$ signal during the two periods (1699-1703 and 1987-1993)

The maximum and minimum values recorded for $\delta^{18}\text{O}$ in the LIA section (1699-1703) is -3.31 and -4.65‰ respectively (range = 1.34‰) with an average of -3.87‰ ($n = 131$; Fig. 9-b). Our coral $\delta^{18}\text{O}$ shows a strong seasonal cycles, with the differences in skeletal $\delta^{18}\text{O}$ values between the 1700's and 1990's reflecting the influence of both SST and seawater $\delta^{18}\text{O}$ changes. Combining coral $\delta^{18}\text{O}$ and Mg/Ca provides an opportunity to calculate past SSS changes. Such changes can be evaluated

from the Mg/Ca ratio of coral skeleton using the relationship Eqn. 1. The past $\delta^{18}\text{O}$ of seawater can then be calculated by removing the temperature component from the $\delta^{18}\text{O}$ of coral skeleton, using Eqn. 3. Finally, the calculated $\delta^{18}\text{O}$ can be converted to the SSS using the equations Eqn. 2. Completing this series of calculation, the calculated SSS between the two periods (1699-1703 and 1987-1993) are shown in Figure 10. From this figure, the calculated SSS during 1699-1703 shows more distinctive variability than that during 1987-1993, especially in early summer when the $\delta^{18}\text{O}$ of seawater is more than -0.5‰ which corresponds to a salinity of 30 ppt.

Comparison of the LIA and Recent salinity records (Fig. 10) suggests that seasonal variability was stronger during the LIA than today and that LIA wet and dry seasons were more pronounced. Because water temperatures at La Parguera are representative of changes occurring in the wider Caribbean, at least over the last 100 years (Winter et al., 1991), it seems reasonable to assume that La Parguera proxy records should be representative of large-scale environmental changes back beyond the historical record and at least, down through the LIA.

6. Conclusion

Our study, calibration equations for SST and SSS were established by combining the Mg/Ca ratio and $\delta^{18}\text{O}$ values in modern coral skeletons with meteorological data. Our results yielded three relationships:

$$(1) \text{Mg/Ca (mmol/mol)} = 0.28 (\pm 0.04) \times \text{SST (}^{\circ}\text{C)} - 3.24 (\pm 1.15), r = 0.92$$

$$(2) (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) = -0.19 (\pm 0.04) \times \text{SST (}^{\circ}\text{C)} + 0.75 (\pm 0.61), r = 0.93$$

$$(3) \delta^{18}\text{O}_w = 0.204 (\pm 0.03) \times \text{SSS} - 6.54 (\pm 0.68), r = 0.93.$$

Using these calibrations, the seasonal variability in SST and SSS in the Caribbean Sea during the Little Ice Age were reconstructed. The techniques and equations provided in this paper provide the basis for quantitative reconstruction of past salinity within seasonal resolution using coral skeletal material. This approach is particularly well suited for paleoenvironmental reconstructions made from corals of long-term decadal scale trends in climate. Key conclusions we are able to draw from our data are that:

(1). Mg/Ca ratios in corals correlate well with the SST record at La Parguera.

- (2). the residual coral $\delta^{18}\text{O}$ signal representing the $\delta^{18}\text{O}$ of seawater, can be used to calculate past SSS.
- (3). comparison of the Mg/Ca ratio between the two periods (1699-1703 and 1987-1993) suggests that SST during the Little Ice Age (LIA) were about 2°C cooler today: and
- (4). comparison between the residual $\delta^{18}\text{O}$ signal during the two periods (1699-1703 and 1987-1993) suggests that the SSS in the LIA had stronger seasonality than it does today.

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Figure Captions

Fig. 1 Location of the study area with regard to the Puerto Rican coast (right inset) and the sampling location (dot) of coral and seawater (main diagram; large solid dot). Seasonal shifts of the Inter tropical Convergence Zone (ITCZ) in the Caribbean are shown in the inset (dashed line).

Fig. 2 X-radiograph of coral core *Montastrea faveolata* showing 360-years of banding. Collected from La Parguera, Puerto Rico, Caribbean Sea. The periods 1989-1993 and 1699-1703 are used to represent modern condition and reconstruct the LIA condition, respectively. Each age was determined by assigning a calendar year to each density-band couplet (HD/LD) by counting downward from the colony surface, deposited at a known date.

Fig. 3 Records of coral Mg/Ca, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, optical density (OD) from image-analysis, and SST for the period 1987-1993. Striped vertical lines represent the high density bands of the coral skeleton.

Fig. 4-a Relationship between the skeletal Mg/Ca ratio and the monthly mean SST. Solid circles represent tie-points that were used to constrain the age of the record. All other points are represented by open circles. The regression line (solid line) for this study was calculated using the tie points (solid circles): $\text{Mg/Ca (mmol/mol)} = 0.28 (\pm 0.04) \times \text{SST (}^{\circ}\text{C)} - 3.24 (\pm 1.15)$, ($r = 0.92$). Also shown are published calibration lines for the coral *Porites* (hair lines: Mitsuguchi et al., 1996; Sinclair et al., 1998; Fallon et al., 1999; Mitsuguti et al., 1998), foraminifera (solid dashed line: Nürberg et al., 1996), and bivalves (dashed line: Klein et al., 1996).

Fig. 4-b Residual SST obtained by subtracting the estimated SST from the measured SST. Dashed lines denote the standard deviation (2σ) of the residuals.

Fig. 5 Measured SST (grey line) and calculated SST (black line) from the skeletal Mg/Ca ratio. The monthly SST was recorded at the meteorological station at La Parguera, Puerto Rico, located about 3 km from the corals the study area.

Fig. 6 Coral Mg/Ca ratio vs. growth rates. Respectively, solid diamonds and cross symbols indicate the annual average and the annual data the periods 1987-1993. Open diamonds and cross symbols indicate those data from the periods of 1700-1703. Growth rates are defined as the distance between each high-density band.

Fig. 7-a Linear relation between the $\delta^{18}\text{O}$ of seawater ($\delta^{18}\text{O}_w$) and SSS (S) at the coring

site.

Fig. 7-b The $\delta^{18}\text{O}$ of seawater at our coral site from 1991-1998. Dashed line represents the overall collective monthly averages.

Fig. 8 Comparison between the calculated $\delta^{18}\text{O}$ of seawater and precipitation at La Parguera. The $\delta^{18}\text{O}$ of seawater is calculated from the measured $\delta^{18}\text{O}$ (δ_c) and temperature (T) using eqn 2, $(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) = 0.19 (\pm 0.04) \times \text{SST } (^\circ\text{C}) + 0.75 (\pm 0.61)$. The SSS is estimated from the calculated $\delta^{18}\text{O}$ of seawater using eqn 1: $\delta^{18}\text{O} = 0.204 \times \text{SSS} - 6.54$.

Fig. 9-a Comparison of the skeletal Mg/Ca ratio between the two periods (1699-1703 and 1987-1993). The Mg/Ca ratio is used to calculate SST using the equation, $\text{Mg/Ca (mmol/mol)} = 0.28 (\pm 0.04) \times \text{SST } (^\circ\text{C}) - 3.24 (\pm 1.15)$. Dashed lines represent the overall average value for the interval shown.

Fig. 9-b Comparison of the skeletal $\delta^{18}\text{O}$ values between the two periods (1699-1703 and 1987-1993). Dashed lines represent the average value for the interval shown.

Fig. 10 Comparison between the calculated $\delta^{18}\text{O}$ during the two periods of 1699-1703 (black lines) and 1987-1993 (grey lines). The $\delta^{18}\text{O}$ of seawater (δ_w) is calculated from the measured $\delta^{18}\text{O}$ (δ_c) and Mg/Ca ratio of coral skeleton using the eqn 1 $(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) = -0.19 (\pm 0.04) \times \text{SST } (^\circ\text{C}) + 0.75 (\pm 0.61)$ and $\text{Mg/Ca (mmol mol}^{-1}\text{)} = 0.28 (\pm 0.04) \times \text{SST } (^\circ\text{C}) - 3.24 (\pm 1.15)$. Also the SSS is estimated from the calculated $\delta^{18}\text{O}$ of seawater using the equation, $\delta^{18}\text{O} = 0.204 \times \text{SSS} - 6.54$.

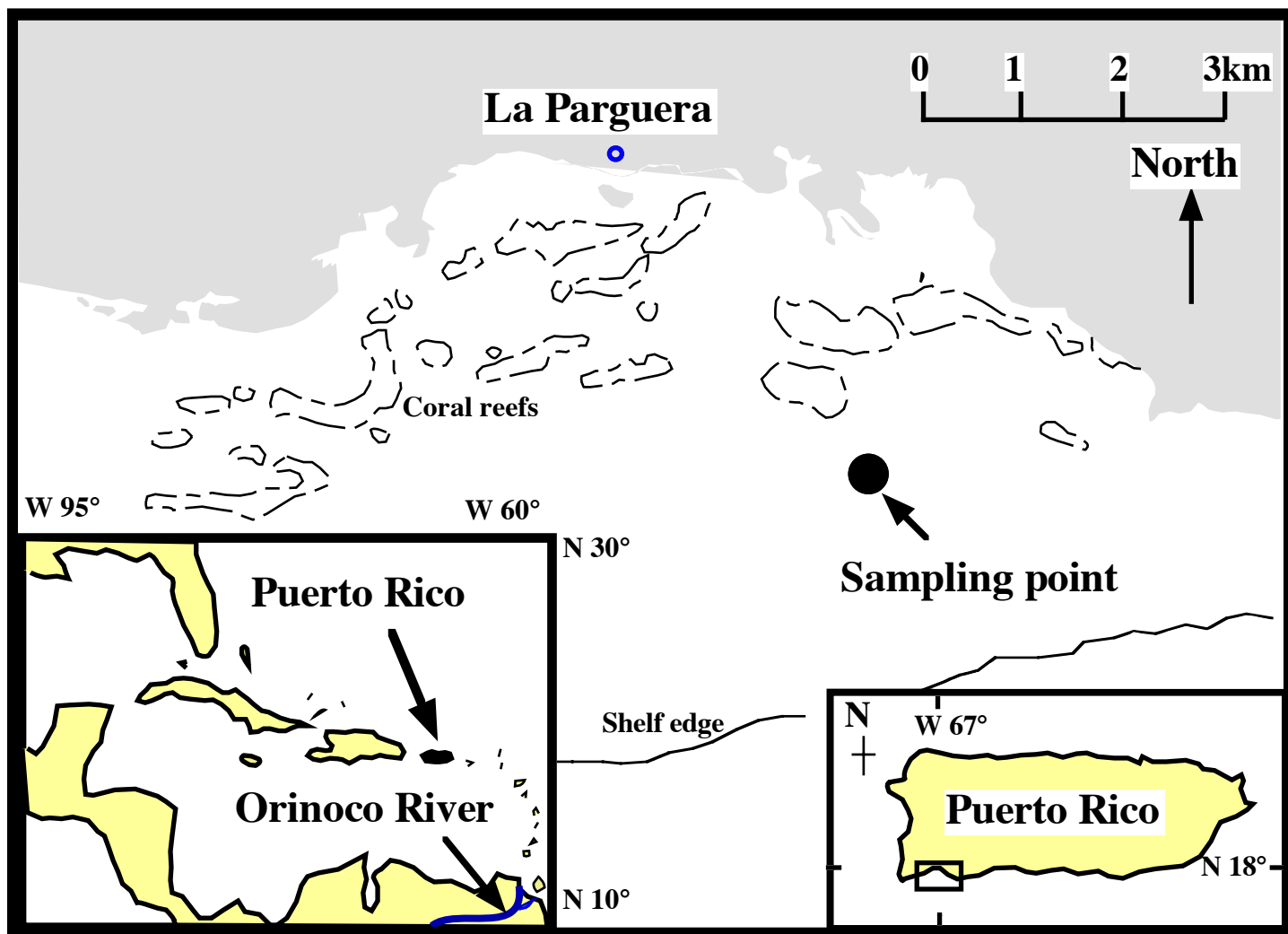


Figure 1

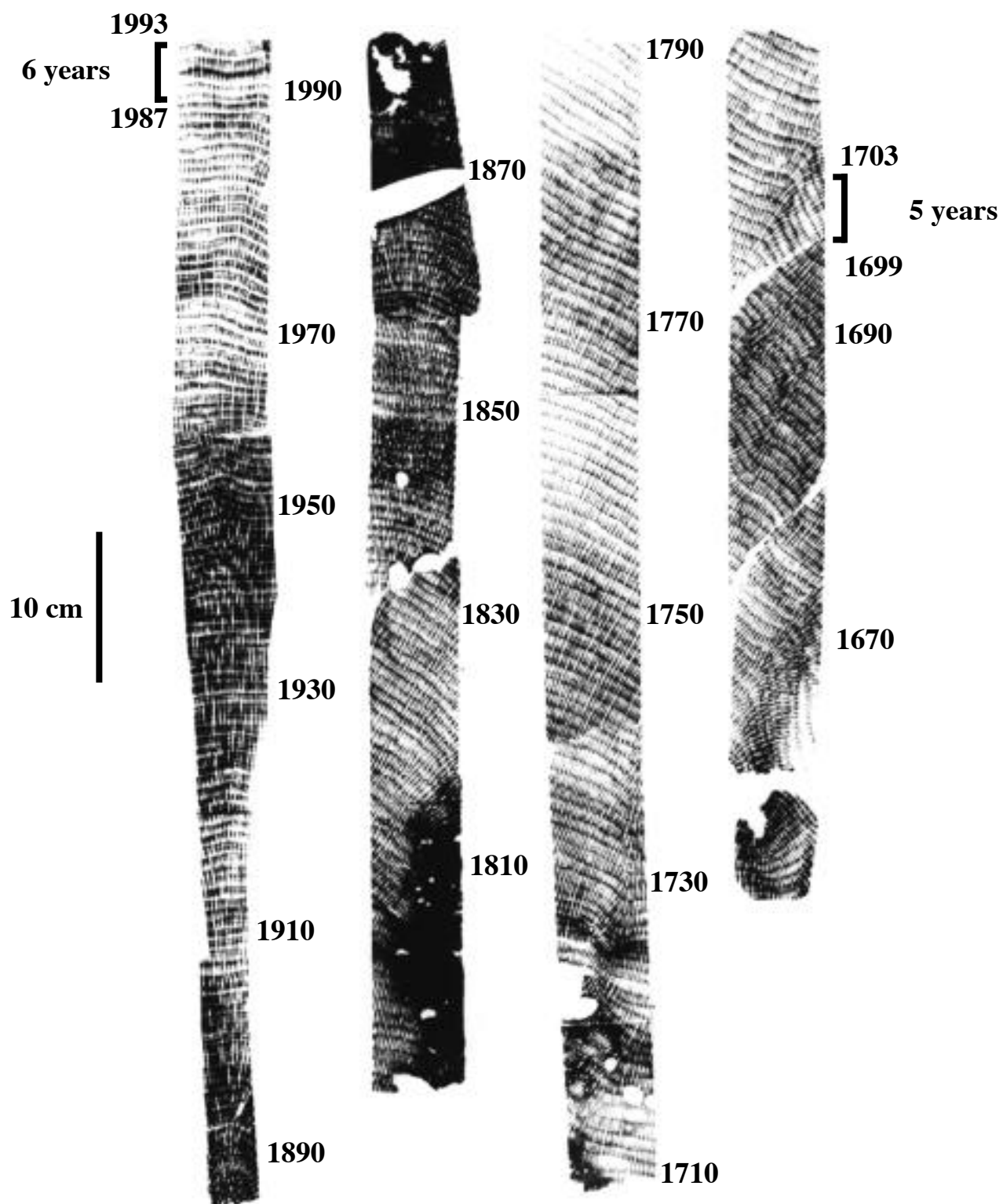


Figure 2

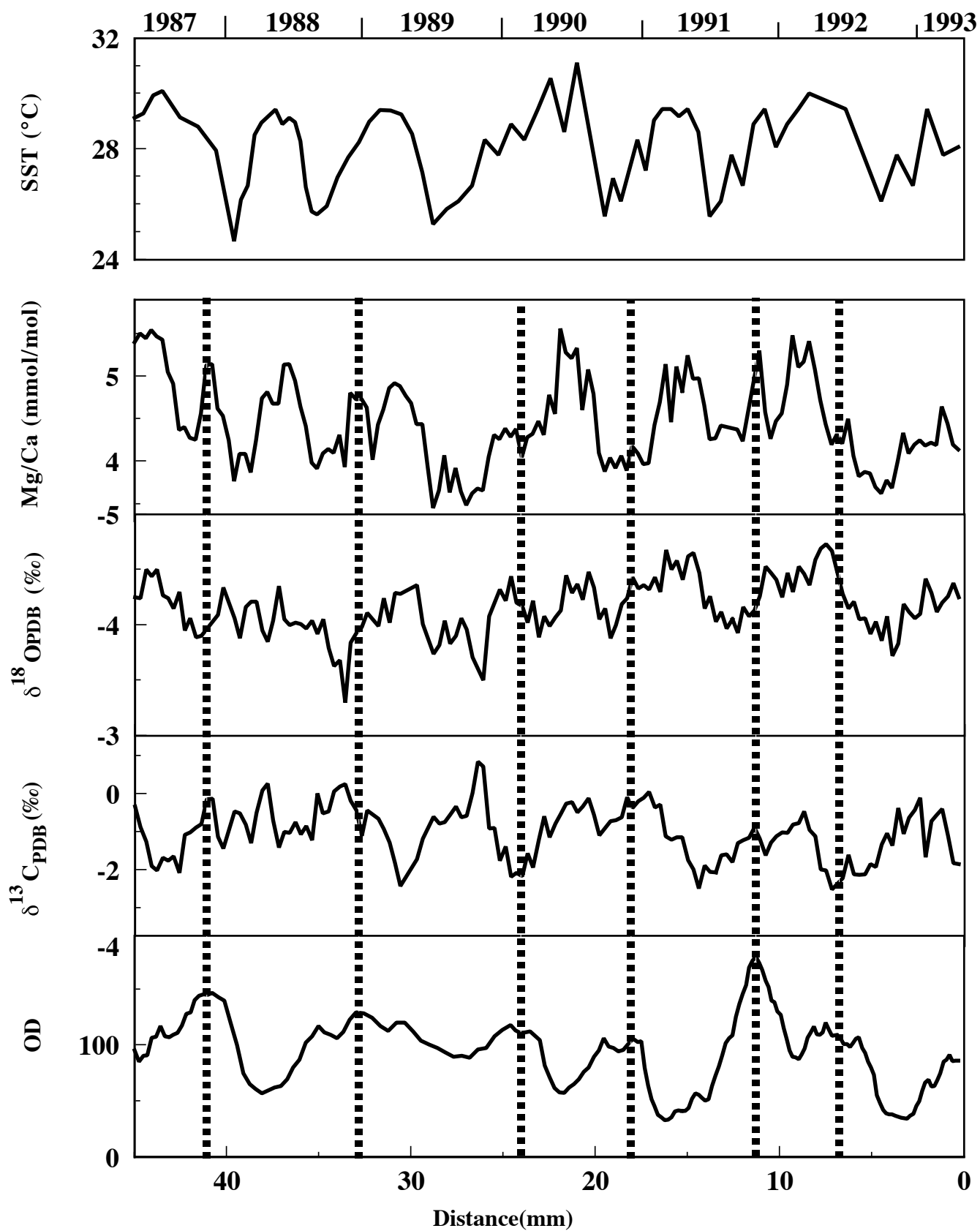


Figure 3

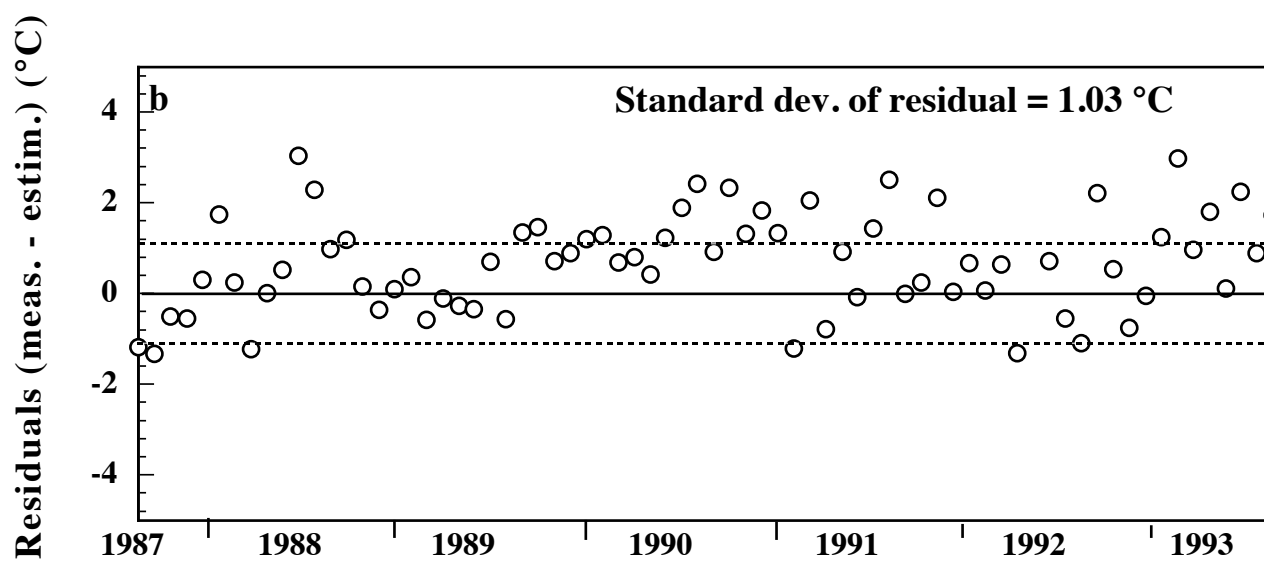
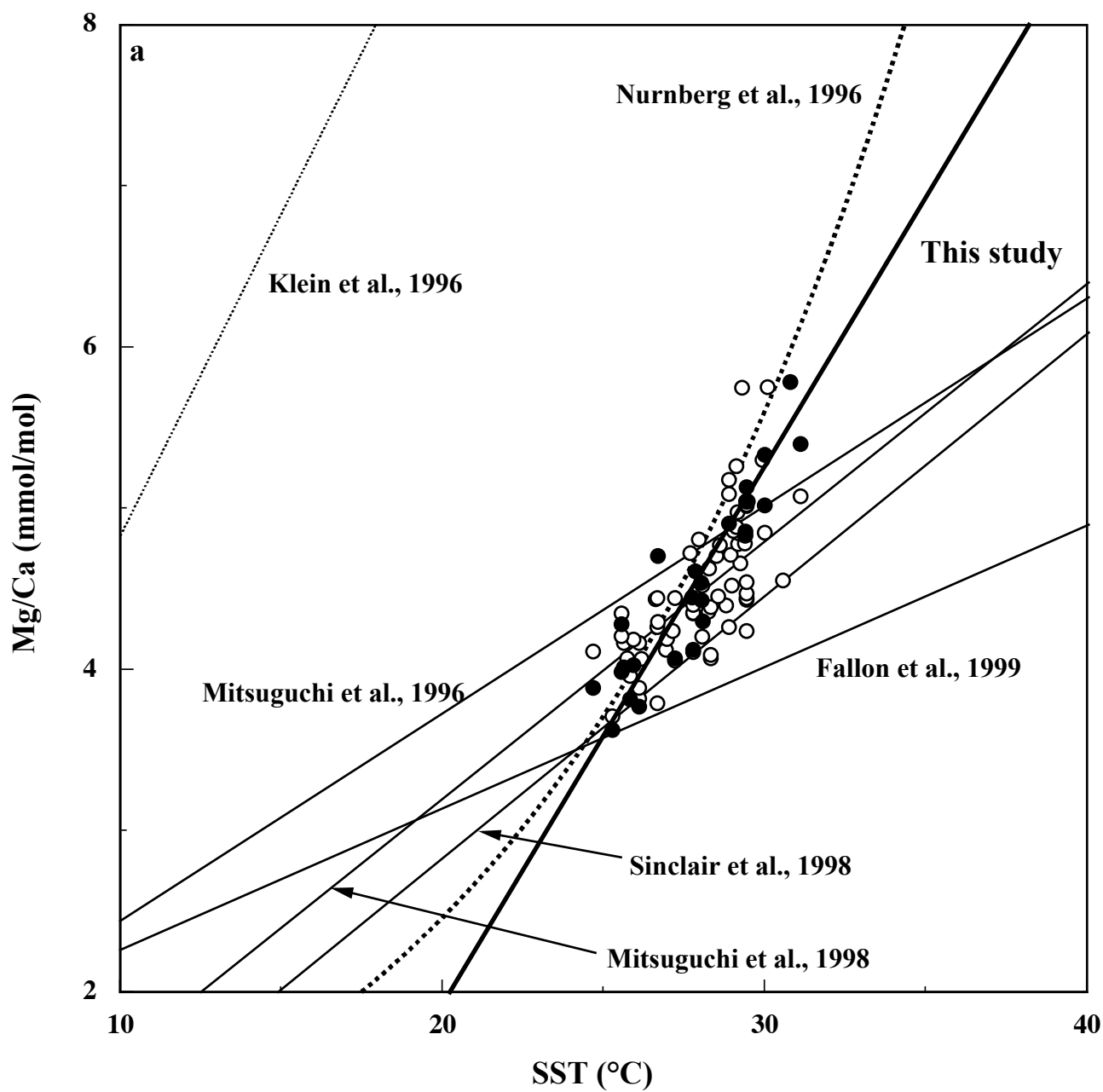


Figure 4

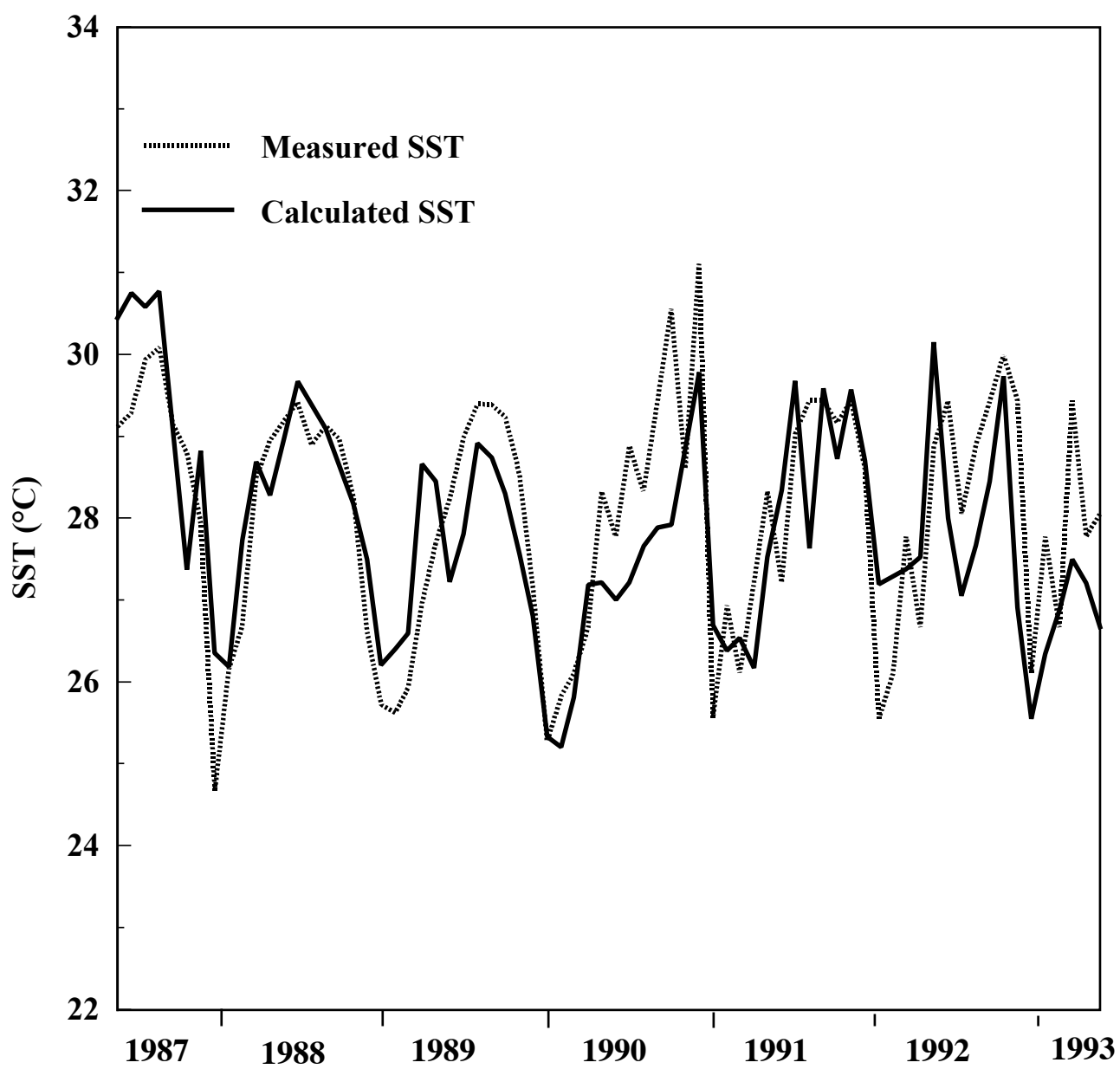


Figure 5

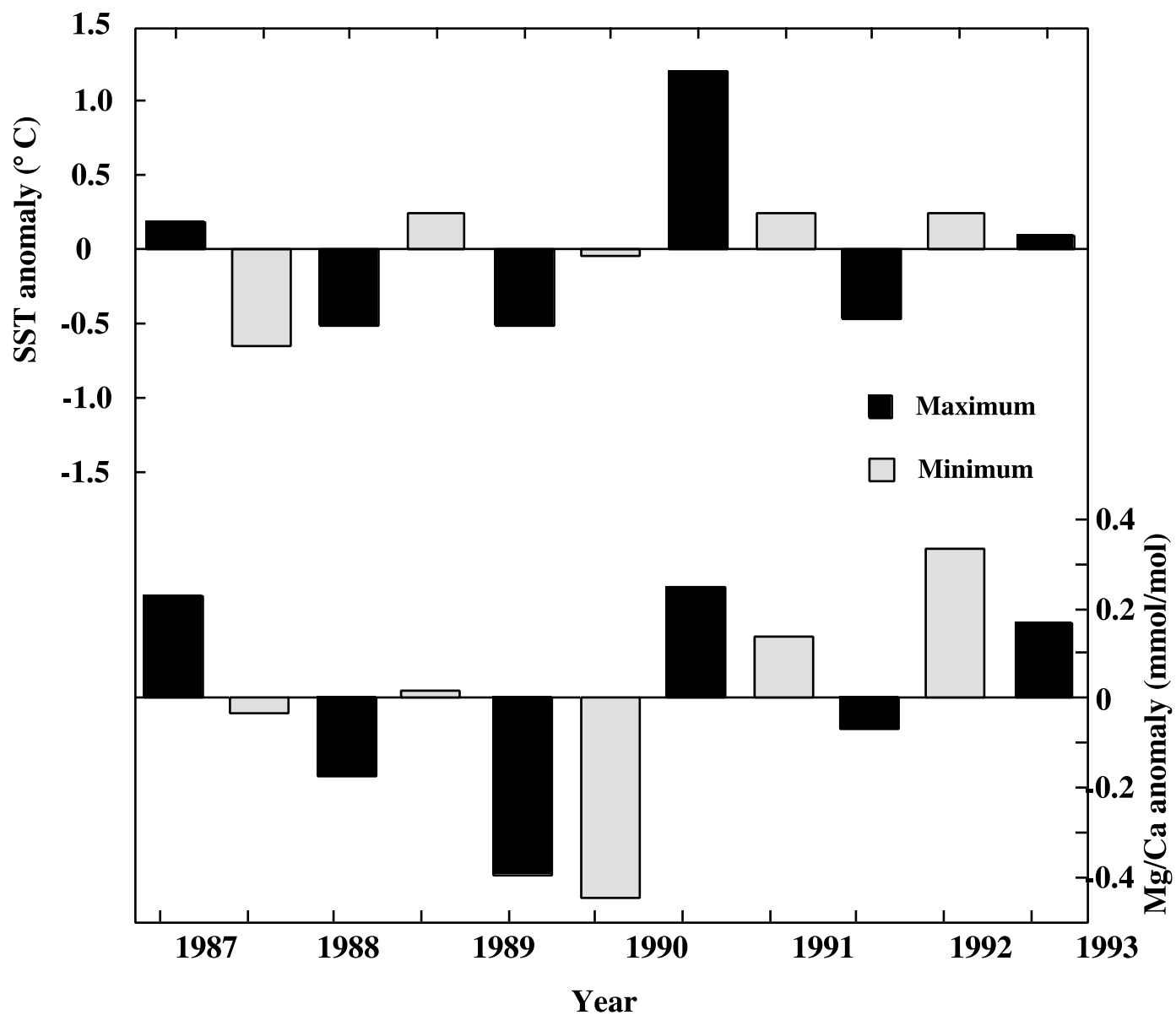


Figure 6

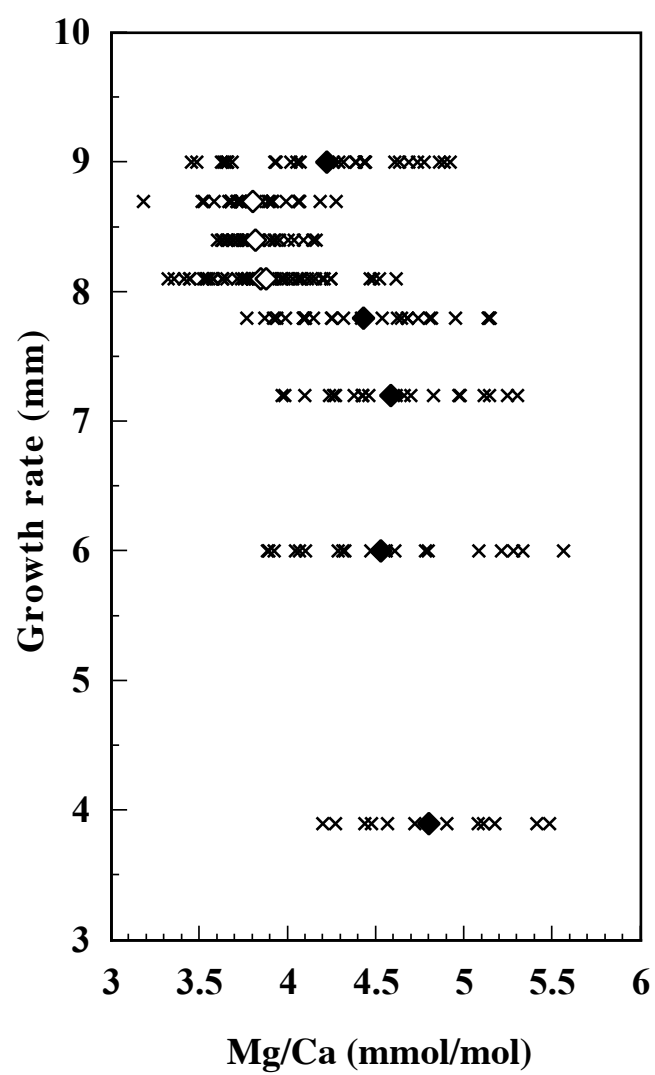


Figure 7

$$\delta^{18}\text{O} (\text{‰})_{\text{SMOW}} = 0.204 (\pm 0.03) \times \text{SSS} - 6.54 (\pm 0.68), r = 0.93.$$

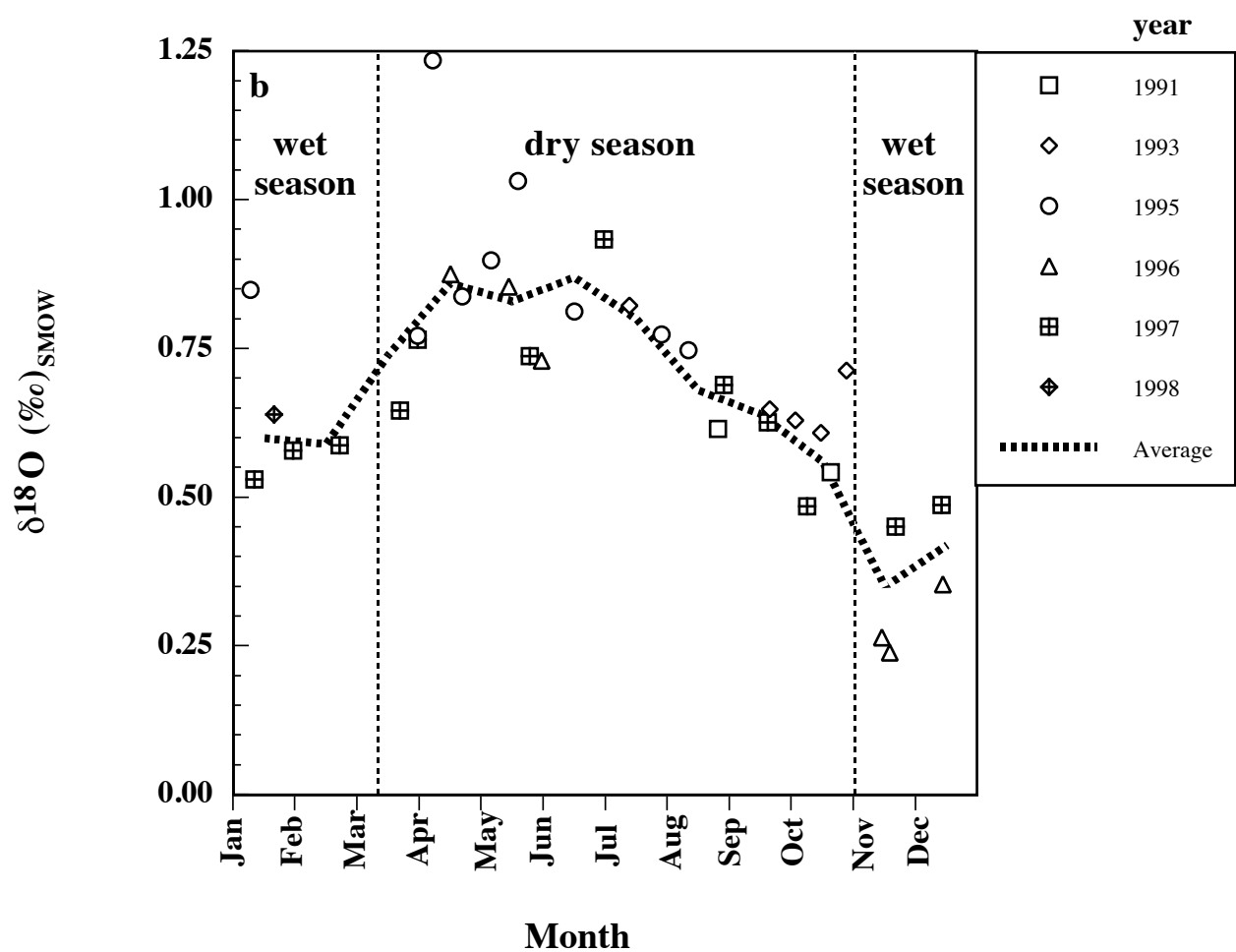
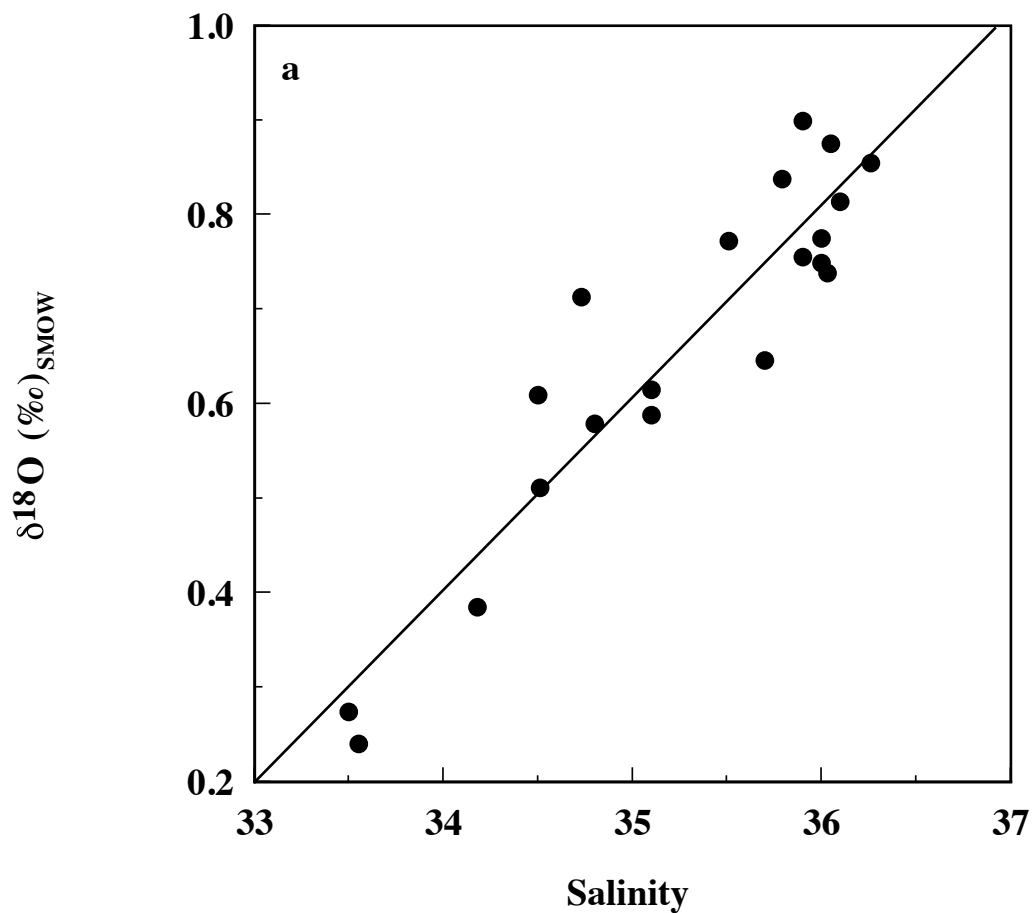


Figure 8

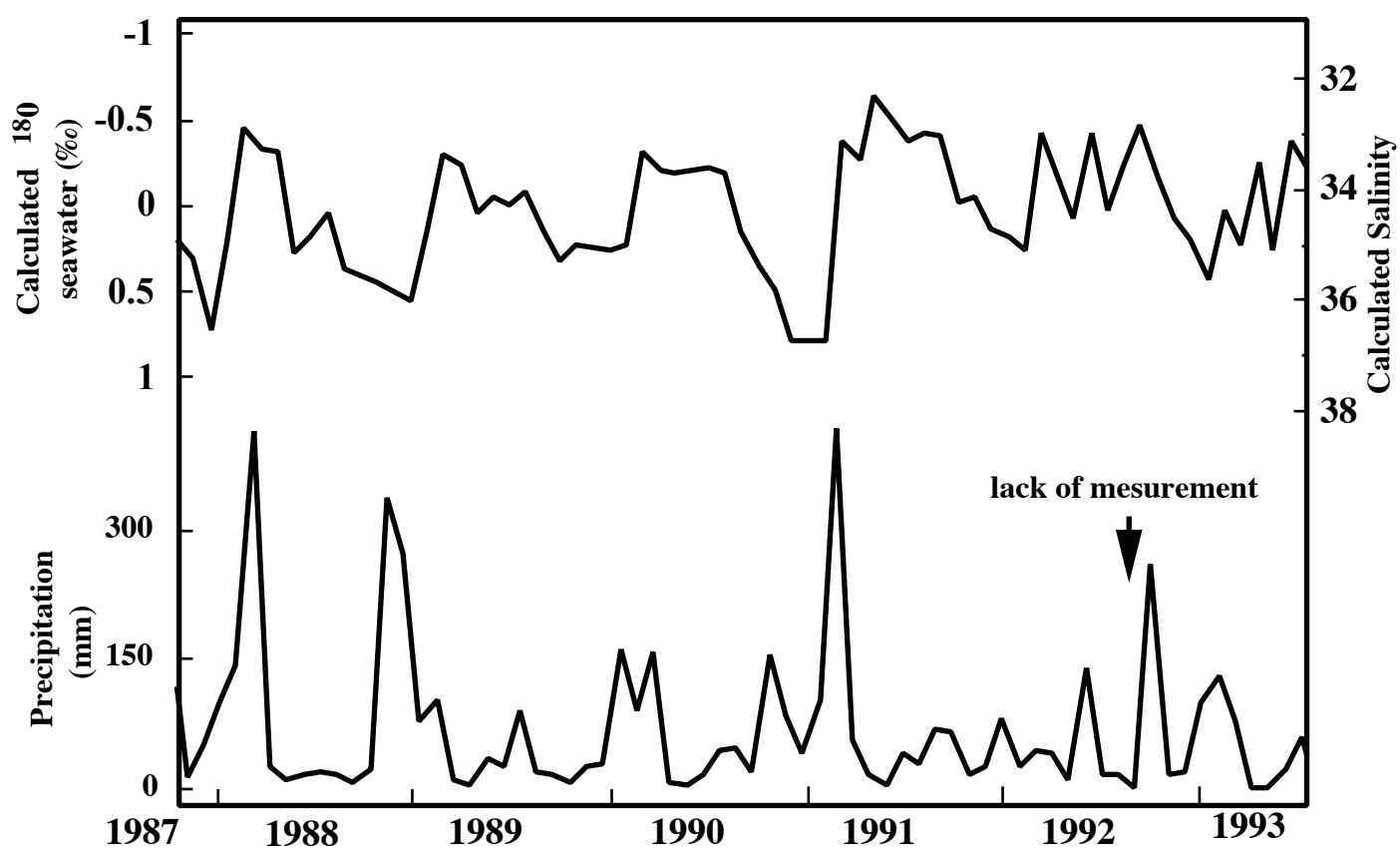


Figure 9

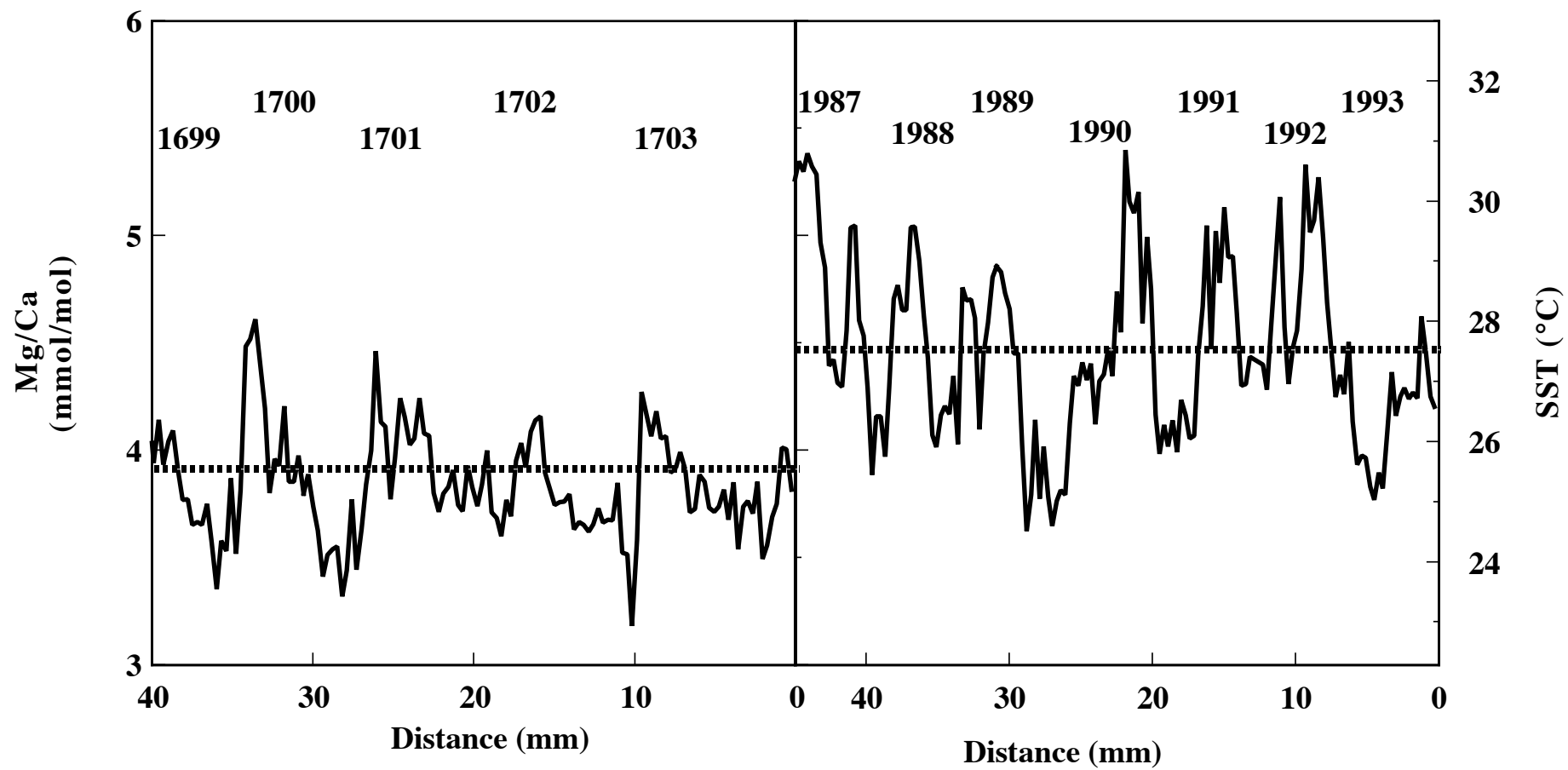


Figure 10

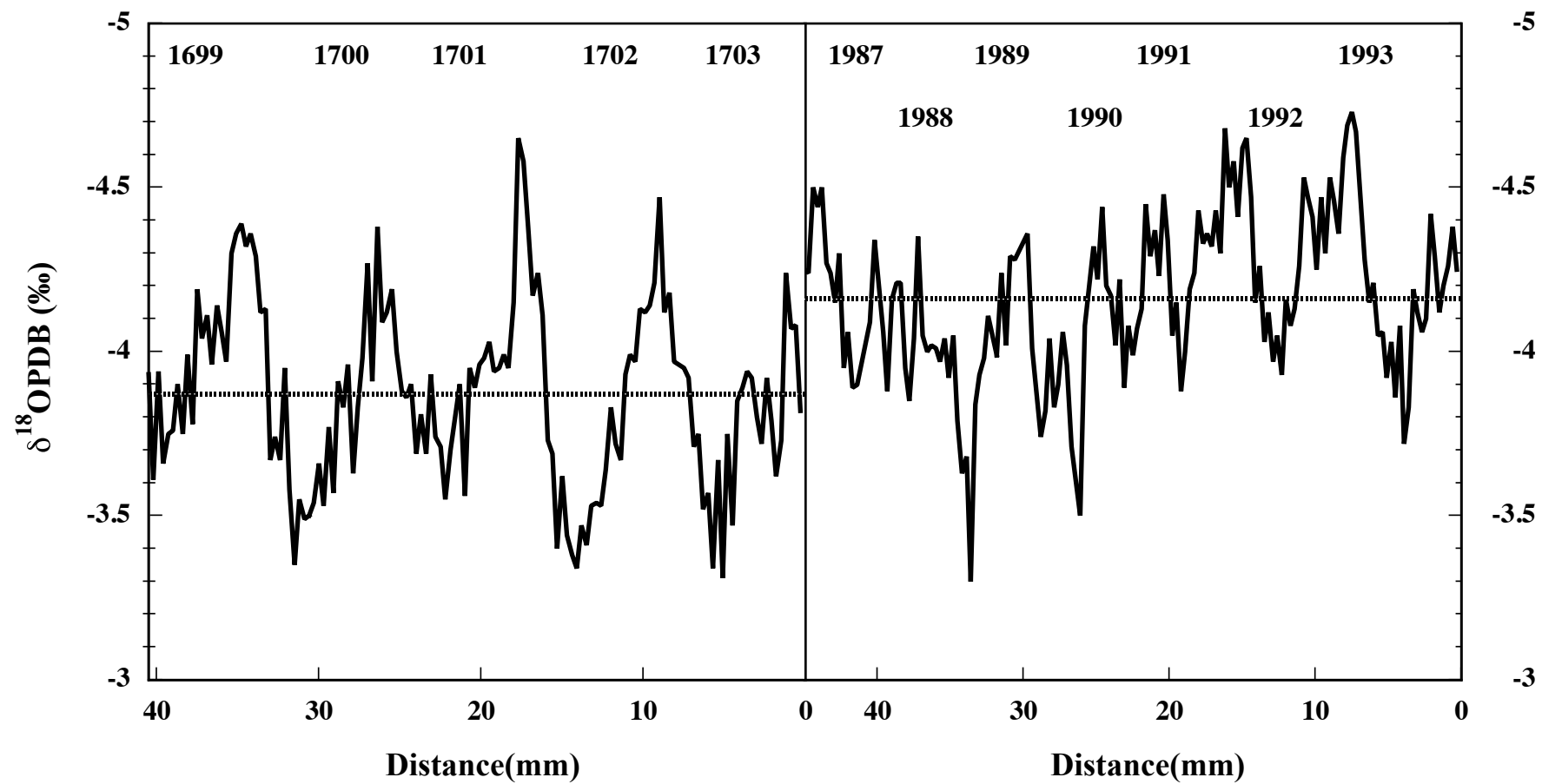


Figure 11

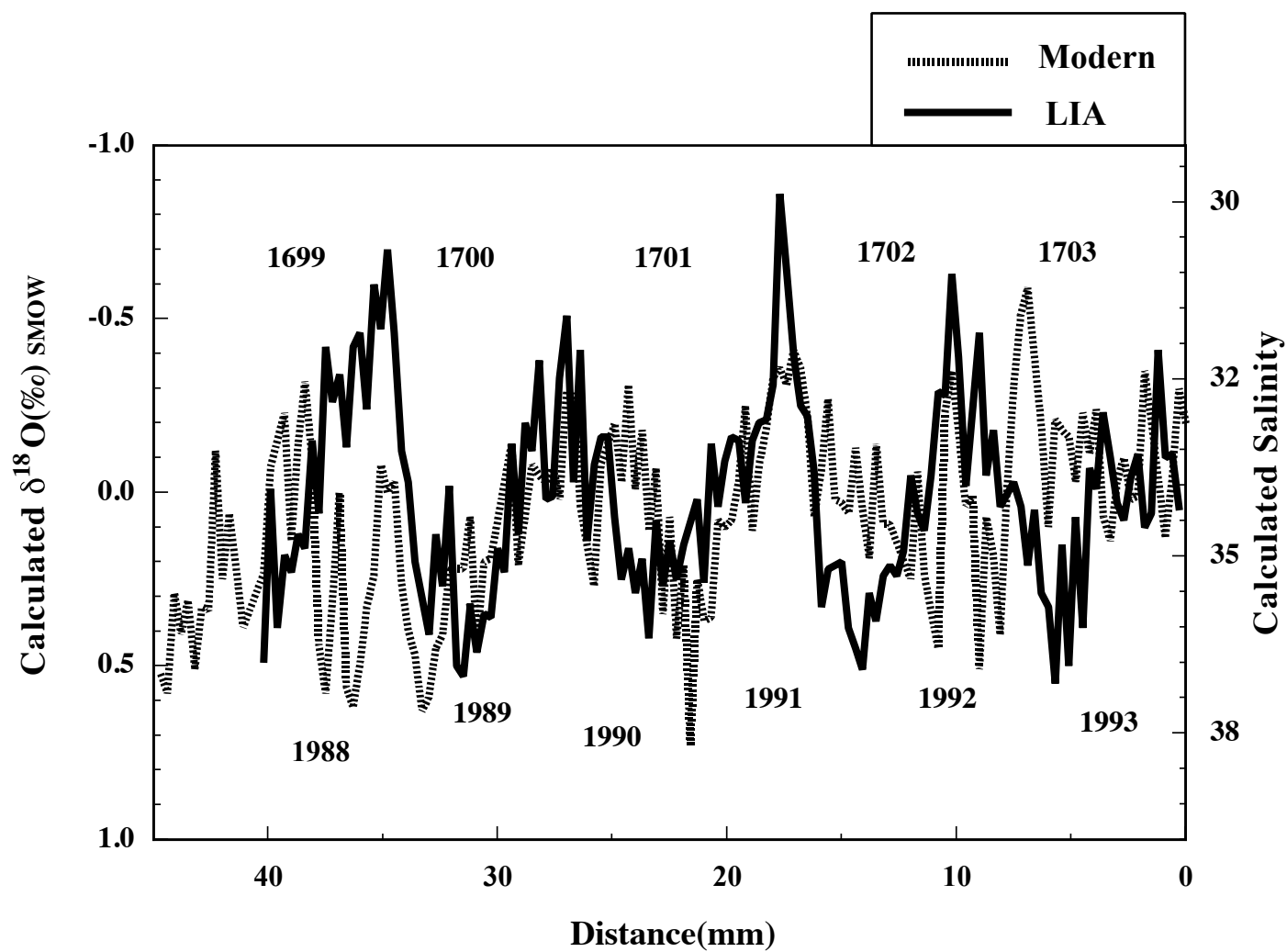


Figure 12