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Validation of coral temperature calibrations

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Abstract. Geochemical analyses of coral skeletons are increasingly used to estimate past sea surface temperatures (SSTs). In this paper we suggest that the standard method of calibrating geochemical time series against a (usually short) local time series requires modification. In order to draw large-scale inferences about climate from coral proxy data it is also necessary to (1) calibrate against larger fields such as the local gridded data sets and (2) validate results against an independent data set (e.g., early 20th century). This approach has been applied in a pilot study to a coral record from New Caledonia. Despite a high δ^{18} O correlation (r = -0.88) with the in situ and gridded SST data sets, estimated early 20th-century temperatures are more than 1.5°C colder than observed if the standard seasonal calibration is used. Regression against mean annual temperatures, which has a different slope relation, yields better estimates of early 20th-century SSTs. However, testing of a Sr/Ca record from New Caledonia yields better agreement with early 20th century SSTs. Routine validation exercises for other coral sites are necessary to clarify the robustness of geochemical coral proxies as estimators of past environmental change.

1. Introduction

In the past few years there has been a great deal of interest in the use of corals as paleoenvironmental indicators. Much of this interest has stemmed from the potential to retrieve information on fluctuations in tropical oceans prior to development of the instrumental network. Some corals have also been used to estimate sea surface temperature (SST) in the tropics for the Pleistocene [Beck et al., 1992, 1997; Guilderson et al., 1994; McCullough et al., 1999], with results suggesting SSTs \sim 5°-6°C cooler than present, significantly colder than those estimated by Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP Members) [1981]. These results, if verified, have substantial implications for the estimation of climate sensitivity [Crowley, 1994].

To estimate paleotemperatures, most recent studies have calibrated monthly geochemical data against the seasonal cycle of temperatures, usually at a nearby station or in situ thermometer. Such correlations are often quite impressive [e.g., *Beck et al.*, 1992; *Dunbar et al.*, 1994; *Quinn et al.*, 1996]. However, these time series are often short. We maintain that there are two important additional steps that must be taken to validate coral calibrations: (1) in order to draw large-scale inferences about a coral site, it is necessary to demonstrate that the coral correlates well against larger-scale SST fields such as the local gridded SST data set. Such comparisons also

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Paper number 1999PA900032. 0883-8305/99/1999PA900032\$12.00 have the advantage of a longer time series for calibrating coral observations against temperature or precipitation; (2) the gridded calibrations must be validated against an independent data set, usually from the earlier part of this century. This procedure is routinely followed in tree ring studies [e.g., *Fritts et al.*, 1979; *Cook et al.*, 1996]. Failure to test proxy coral calibrations against an independent data set could conceivably lead to erroneous conclusions about the nature and magnitude of past climate change.

In this paper we demonstrate that scaling a coral δ^{18} O record up to a local grid box and validating it against an independent data set can lead to some surprising results, namely, that a record that has a very good seasonal calibration yields incorrect estimates of early 20th century SSTs. A different δ^{18} O calibration at mean annual timescales yields a better estimate of SSTs. Although we focus on a coral record from New Caledonia [*Quinn et al.*, 1998] as the target for our investigation, we have tested our result against two other coral records, with similar conclusions. We also examine Sr/Ca calibrations from the New Caledonia coral to determine whether results are sensitive to the particular geochemical proxy employed. We close with some preliminary discussion of possible factors responsible for the observed trends and the potential significance of results to prior coral-based estimates of SSTs.

2. Methods

A large coral head (*Porites lutea*) was drilled in 3 m of water near Amedee Lighthouse, New Caledonia $(22^{\circ}S, 166^{\circ}E)$ in June 1992 and has been extensively described elsewhere



Plate 1. Comparison of 20th-century GISST2 observations [*Parker et al.*, 1995] with New Caledonia coral temperatures using (a) seasonal temperature calibration as determined from Figure 1b, (b) mean annual temperature calibration as predicted from regression in Figure 2b. Use of a mean annual calibration provides the better estimate for the early 20th century. See text for discussion of uncertainties; the prominent disagreement between the coral and the SST estimates for 1946-1947 could reflect correction errors resulting from the transition from bucket to ship intake SSTs [cf. *Quinn et al.*, 1998].

[Quinn et al., 1996, 1998]. On the basis of the occurrence of distinctive volcanic cooling events, the chronology of the coral record appears to be accurate to within 1 year back to at least to 1800 [Crowley et al., 1997]. The core was sampled at 12/yr. over a calibration interval from 1951 to 1991 and over the validation interval of 1899 to 1910 and at 4/yr. from 1951 to 1657. The mean δ^{18} O values for 12/yr. sampling for the 1899-1910 interval agree to within 0.04‰ with the previously sampled 4/yr. record [Quinn et al., 1998]. This result provides additional support for the conclusion of Quinn et al. [1996] as to the reliability of moderately low frequency sampling of coral records for climate studies.

We also test our δ^{18} O conclusions with Sr/Ca measurements. Coral Sr/Ca determinations were made using a highresolution, inductively coupled plasma mass spectrometer (HR-ICP-MS) at the University of California at Santa Cruz using a technique developed by T. M. Quinn and D. S. Sampson (Rapid and precise generation of multic-proxy, coral-based records of climate change by high-resolution inductively coupled plasma mass spectometry (HR-ICP-MS), submitted to Geochemica et Cosmochomica Acta, 1999, hereinafter referred to as Quinn and Sampson, submitted manuscript, 1999). Sr/Ca ratios can be determined with high precision (<0.3% and 2 σ) and at a rapid rate (>12 samples per hour) using HR-ICP-MS [cf. Schrag, 1999]. A monthly-resolved record of Sr/Ca variations, determined from the same Porites coral head that has previously been used for stable isotope studies from New Caledonia [Quinn et al., 1996, 1998], extending from 1992 to 1968, was produced by Quinn and Sampson [submitted manuscript 1999]. The Sr/Ca-SST relationship (Sr/Ca)*1000=10.383-0.0614*SST and r = -0.92) is quite similar to previously developed equations [cf. Sinclair et al., 19981.

The calibration between the instrument and proxy records was evaluated using standard ordinary least squares regression (OLS) and reduced major axis regression (RMA). The attributes of both of these techniques were discussed by *Quinn et al.* [1998], who justify in more detail use of the OLS method. Another reason to choose SST as the dependent variable is because that is the approach utilized before for both the original calibration of aragonite and molluscan δ^{18} O variations [*Epstein et al.*, 1953; *Grossman and Ku*, 1986] and for foraminifera [*Erez and Luz*, 1983], and one purpose of this paper is to compare our SST predictions with previous approaches using the same methodology.

3. Results

3.1. New Caledonia 818O Record

Monthly measurements of coral δ^{18} O and monthly averages of daily SST measurements over the interval 1967–1989, obtained by the French Institut Français de Recherché Scientifique_pour_le_développement_en_Coopération -(ORSTOM) group at New Caledonia, are highly correlated (r = -0.86 and p<0.01), as are coral measurements (r = -0.88, p<0.01) with monthly SSTs (Figure 1) from the appropriate 1° x 1° grid box from the GISST2 dataset [*Parker et al.*, 1995]. The mean SST value of the ORSTOM data set is 1.34°C cooler than that calculated from the GISST2 dataset (23.32°C versus 24.66°C) be-



Figure 1. Comparison of monthly δ^{18} variations from the New Caledonia coral record with sea surface temperature (SST) observations from 1967-1989 for (a) local monthly average of daily SST measurements from Amedee Lighthouse, and (b) gridded 1° x 1° record from *Parker et al.* [1995]. Although there is a slight offset in intercept (because of the grid box's embracing areas of warmer SST than the point measurement), the overall correlations are not significantly affected.

cause of the location of ORSTOM in the southern part of the grid.

Despite the impressive seasonal correlation, application of the OLS-based monthly New Caledonia $\delta^{18}O/SST$ relationship to the earlier part of the century results in an estimated decadal mean cooling of 2.25°C (Plate 1a). ~4 times larger than the temperature change (0.54°C) estimated from the GISST2 data set. Similar results (not shown) were obtained using the Kaplan et al. [1998] SST data set. The $\delta^{18}O$ -based standard deviations are also 25% greater (0.44°C) for the early 20th century, as opposed to only 0.01°C for the GISST2 reconstruction. The decadal mean difference between the $\delta^{18}O$ -



Figure 2. Comparison of δ^{18} O and SST for (a) monthly gridded 1° x 1° observations [*Parker et al.*, 1995] from 1952-1991, (b) mean annual data taken from (Figure 2a), (c) mean annual time series extended from 1903-1991, (d) entire time series from 1903-1991 after three-point smoothing.

based and GISST2 estimates are unlikely to be due to errors in the SST reconstructions for the early 20th century (unlisted for the GISST2 data set but 0.19°C for the Kaplan et al. [1998] SST data set). The cooling is substantially greater than tropical air temperature trends in the 20th century [Nicholls et al., 1996] and even the Northern Hemisphere temperature estimates during the Little Ice Age [Mann et al., 1998]. The predicted magnitude of the decadal-scale oscillation at the end of the 19th century (3°C) in the New Caledonia coral is also an order of magnitude larger than the SST anomalies associated with the more recent, and better documented, decadal oscillation in 1976-1977 [cf. Graham, 1995]. It is more difficult to assess the reliability of the GISST2 standard deviations because the interpolation schemes used to construct these indices could conceivably suppress real changes in interannual variability.

In the course of investigating this problem we regressed $\delta^{18}O$ and SST observations against mean annual values. Results (Figure 2b) of the 1952-1991 comparison indicate a difference in slope ratio of 2.9 for the earlier period and a reduction in the correlation coefficient to 0.53. This change occurred even though the exact same data were used to calculate the regressions for seasonal and mean annual temperatures. Although the slope differences are significant at the 95% level, the clustering of points in the mean annual 1952-1991 regression (Figure 2b) could still potentially lead to an inaccurate estimate of the slope. Extension of the comparisons of the mean annual correlations to 1898 (Figure 2c) continues to

indicate a significant difference in slope for mean annual temperatures. Three-point smoothing of the time series (Figure 2d) suppresses some of the higher-frequency variability, yielding a third estimate of the mean annual slope. Regardless of how the data sets are sampled, significant differences in the slopes for mean annual values and seasonal data always occur.

Prior work from Quinn et al. [1998] provides some possible explanations for this reduction in correlation to annual averages (see also discussion section). Cross-spectral analysis of the δ^{18} O and SST time series indicates high coherence only during periods of strong interannual (El Nino) variability, with low coherence during times when forcing is weak. These intervals of low coherence could in turn be related to underestimation (Plate 2b) of high frequency (~1 year) variability by the coral record [*Taylor et al.*, 1995]. Regardless of source of error, the net effect would be a lower probability of accurate predictability for a particular year but reasonable predictability for longer-period fluctuations, which in some respects should be the principal target of coral paleoclimate investigations.

As a test of the mean annual 1952-1991 correlation, we applied it to the mean annual δ^{18} O record from New Caledonia for the interval 1850-1991 (Plate 1b) and validated the results against the observed SST field from GISST2. The mean annual regression yields early 20th century temperature estimates that are in line with observations; the 20th-century trend in mean annual temperatures now agrees with the observed trend to within 0.01°C (this level of closeness is probably a chance



Plate 2. Observed versus predicted SSTs for the early and late 20th century at New Caledonia. Predicted SSTs are derived from (a) and (b) coral δ^{18} o and (c) and (d) coral Sr/Ca. Observed SST data are from appropriate 1° x 1° grid box from the GISST2.3 gridded SST data set [*Parker et al.*, 1995].

occurrence). We interpret these results as indicating that although prediction of mean annual temperatures for individual years may have some degree of uncertainty, the mean annual approach retrieves good estimates for longer term changes in mean annual temperature.

3.2. Results From Two Other Coral δ^{18} O Records

Are the results discussed above some artifact of the particular site or coral analyzed? With respect to the former we consider the possibility unlikely, for the site was carefully chosen to be well mixed with open marine water. Furthermore, there is some evidence for slope changes in other coral $\delta^{18}O$ records from Galapagos [Dunbar et al., 1994] and from the Seychelles Islands in the western Indian Ocean [Charles et al., 1997]. In the Galapagos study [Dunbar et al., 1994], near-monthly and mean annual coral $\delta^{18}O$ records (Porites gigantea) from Urvina Bay, Isabela Island were correlated with local SST data. An approximate factor of 2 (1.85) decrease in the slope for the mean annual record was observed and attributed to attenuation of the isotopic signal in response to skeletogenesis [Dunbar et al., 1994]. However, the near monthly coral δ^{18} O-local SST and the mean annual coral δ^{18} O-local SST both have impressively high correlation coefficients of -0.95 and -0.90, respectively, over the calibration interval of 1965-1982 [Dunbar et al., 1994]. Despite these correlations, differences of the order of ~1.5°C between predicted and observed mean annual SSTs occur during the pre-1965 portion of the 20th century (Figure 3b). The correlation coefficient between the predicted and observed mean annual SST records in the validation interval is only 0.36.

The δ^{18} O variations in a *P. lutea* coral, collected offshore of Mahre Island in the Seychelles (equatorial Indian Ocean), are reported [Charles et al., 1997, p. 925] to be a "relatively simple proxy for SST" over the 150 year long record. A correlation coefficient of 0.72 exists between coral δ^{18} O and gridded SST records [Charles et al., 1997]. However, the long-term trend in the coral δ^{18} O data implies a warming of SST by 0.8°C, a value that is substantially larger than the one indicated by the instrumental record. Applying the same calibration/ validation scheme to the Seychelles coral record as we did for the New Caledonia record reveals offsets of 0.5°C between estimated and observed mean annual SSTs for the early part of the 20th century (Figures 3c and 3d), with a correlation coefficient between predicted and observed SST records of 0.50. Results from these two corals therefore support the conclusions obtained from analysis of the New Caledonia coral.

3.3. Analysis of Sr/Ca Records

Is the validation problem related to choice of geochemical index? We investigated this problem by examining coral Sr/Ca records. Elemental ratios in coral skeletons are reported to be unbiased paleothermometers [e.g., *Beck et al.*, 1992].



Validation/Calibration Studies of Galapagos/Seychelles Corals

Figure 3. Comparison of 20th-century observations (solid line) [*Parker et al.*, 1995] with (a) Galapagos and (c) Seychelles coral temperature estimates. The differences between predicted and observed mean annual SST variations for (b) Galapagos and (d) Seychelles are also shown. Galapagos coral δ^{18} O were converted to SST values using the mean annual equation given by *Dunbar et al.* [1994], whereas Seychelles coral δ^{18} O were converted to SST values using the calibration of *Gagan et al.* [1994]. Note that the misfit between predicted and observed mean annual values is of the order of 0.5° to 1.5°C.

However, the multidecadal Sr/Ca record from a *Porites* coral from the Great Barrier Reef [*Alibert and McCulloch*, 1997] predicts an increase of 1.3°C in SST between 1965 and 1993, whereas Southern Hemisphere land and marine temperature records indicate a warming of only ~0.4°C [*Alibert and McCulloch*, 1997].

The above result suggests that there may also be some problems with the Sr/Ca paleothermometer. To further evaluate this issue, we determined Sr/Ca ratios on samples from our New Caledonia coral for two 10-year segments from the early and late 20th century. We employed the technique and the Sr/Ca-SST calibration developed by Quinn and Sampson (submitted manuscript, 1999) for metal analyses (see section 2). Results (Plate 2) suggest that the Sr/Ca-SST proxy temperature changes are 0.58°C cooler for the 10 year segment of the early 20th century, consistent with the GISST2 estimate of 0.52 but slightly larger than the Kaplan et al. [1998] estimate of 0.37°C. Estimates of the uncertainty associated with early 20th-century SST reconstructions are unavailable for the GISST2 data set but are calculated to be 0.19°C in the Kaplan et al. [1998] data set for this time interval. The analytical uncertainty determined by Quinn and Sampson (submitted manuscript, 1999) is 0.4°C if cast in terms of temperature. Given these uncertainties, the differences between estimated and observed temperature anomalies are not considered significant at the 95% level, especially since the cited errors are for individual measurements, and the mean error for pooled estimates decreases according to

$$\sigma_{\rm tot} = (\sigma_{\rm ss}^2/N)^{1/2}$$

where σ_{tot} is the total uncertainty, σ_{ss} is the single-sample uncertainty, and N is the number of independent samples (in this case the total number of analyses in a decadal interval (120)

divided by the autocorrelation (3)). The pooled decadal mean uncertainties (1 σ) for SST estimates are therefore ~0.06°C for Sr/Ca and 0.03°C for Kaplan et al. [1998]. If the unknown GISST2 errors are comparable to Kaplan et al. [1998], there is no significant difference between the decadal mean Sr/Ca SST estimate and the GISST2 decadal mean. There is a very slight difference (0.03°C) at the 2 σ level between the Sr/Ca early 20th-century SST estimate and the Kaplan et al. [1998] estimate that is probably not worth emphasizing.

Overall, our results support the application of the Sr/Ca paleothermometer for decadal mean estimates of SST at New Caledonia. However, inspection of Plate 2c indicates that the Sr/Ca and SST correspondences for individual years are sometimes quite low, for example, 1901, 1904, and 1908 (the differences for the latter 2 years are also manifested in the δ^{18} O record (Plate 2a)). These disagreements lead to a substantially lower Sr/SST correlation for the early 20th century as opposed to the late 20th-century calibration interval (-0.66 versus -0.92). It is not clear whether these differences reflect a problem in the geochemical proxies or whether band counting in this interval has somehow missed 2 years. Although prior work [Crowley et al., 1997] suggests that the coral chronology may be accurate to within a year, we cannot dismiss the possibility of a chronology problem contributing to these discrepancies. Obviously, more work would have to be done to determine the reliability of the Sr/Ca proxy and to understand the discrepancies between the Alibert and McCullough [1997] results and those reported here.

4. Discussion and Conclusions

The above results raise several questions: (1) are proxy estimates affected by growth rate changes at the New Caledonia site?; (2) how can the δ^{18} O results be reconciled with the original mean annual calibrations of *Weber and Woodhead* [1972]?; and (3) what causes the change between seasonal and mean annual slopes for the δ^{18} O-SST relationship? In this section we attempt a start at answering some of these questions. However, we cannot provide definitive answers; the problems require more work. This lack of a full explanation does not undermine the observation that the seasonal calibration for δ^{18} O simply does not work for New Caledonia, nor the assertion that it is essential to calibrate coral measurements against gridded data sets and validate against an independent data set.

4.1. Growth Rate Assessment

The estimated seasonal and mean annual temperatures are unlikely to be strongly influenced by growth rate changes in the coral [Quinn et al., 1998] because: (1) there is a low correlation between δ^{18} O and growth rate (0.37), suggesting that only 14% of the variance in the former can be explained by growth rate changes; (2) a recent study [Leder et al., 1996] suggests that growth rate changes may be less important than originally proposed [McConnaughey, 1989]; (3) any effect of growth rate should influence both the seasonal and mean annual slopes, still leading to differences between the slopes; and (4) significant estimated SST changes in the late 19th century occur during times of small growth rate changes [Quinn et al., 1998].

4.2. Conflict with Weber-Woodhead Calibration

Another question involves the difference between our results and those of Weber and Woodhead [1972], who also developed a regression for mean annual temperatures. In their now classic paper, Weber and Woodhead [1972] defined the coral δ^{18} O-SST relationship for 44 coral genera, generating genera-specific SST equations in the form $T(^{\circ}C)=A+B^{*}(\delta^{18}O)$. The slope values B in their equations vary from a high of -2.79‰ °C to a low of -8.33‰ C°; the slope value for Porites is -3.31‰ C°. Application of the *Porites* δ^{18} O-SST equation of Weber and Woodhead [1972] to our mean annual coral δ^{18} O data also results in a misfit between observed and predicted SST (Figure 4a). A similar misfit (Figure 4b) between observed and predicted SST occurs when coral $\delta^{18}O$ from Abraham Reef, Great Barrier Reef, Australia [Druffel and Griffin, 1993], are cast in terms of SST using the Porites equation of Weber and Woodhead [1972]. This misfit exists despite the fact that $\delta^{18}O$ data from 27 Porites corals from New Caledonia and 17 Porites corals from Gannet Reef, Great Barrier Reef, Australia (similar latitude and longitude as Abraham Reef) are part of the Weber and Woodhead [1972] data set.

Application of the Weber and Woodhead [1972] Porites equation to a Porites δ^{18} O record from the Philippines, whose variations have been attributed to SST [Patzold, 1986], again yields estimated SSTs substantially different than observations (Figure 4c). The Weber and Woodhead [1972] equation errs by up to 4°C in estimating absolute temperature for one of the sites. One could, of course, apply a salinity "correction" to any SST estimate determined by the Weber and Woodhead [1972] approach, but in the absence of additional justifying data, such corrections have an ad hoc element that undermines the merit of the method, especially when the correction is applied to older time intervals (e.g., Last Glacial Maximum (LGM)) when the basic state of the climate system is different.

There is a critical difference in methodology between our approach and that of Weber and Woodhead [1972]. They regressed their "core-top" coral data against a spatial array of mean annual data, whereas we regress in time for an observation at one point. Which is more appropriate? One possible consideration is that the critical question in determining the slope of the regression line is not that of seasonal versus annual calibrations, but the range over which the calibration is taken. A number of data points taken across the Pacific Basin form an ensemble in the statistical sense in that a large range of temperatures and isotope ratios are sampled. Twelve months of measurement at a site with a strong seasonal cycle samples roughly the same set of temperatures and ratios. Thus the two calibrations should agree. Calibrations based on annual means at a single point, however, sample a different range and need not be expected to give the same linear fit as samples over larger ranges. It may therefore be reasonable that the annually

averaged fit of *Weber and Woodhead* [1972] could agree with the seasonal calibration but not the annual calibration at one site. We offer this suggestion as a speculation rather than explanation, but our failure to provide a full explanation for the differences does not detract from our observation that the *Weber and Woodhead* [1972] regression does not work well when tested against independent data.



from the Weber and Woodhead [1972] mean annual equation for Porites. The coral δ^{18} o data are from New Caledonia [Quinn et al., 1998], the Great Barrier Reef data are from Druffel and Griffin [1993], and the Cebu, Philippines, data from Patzold [1986].

4.3. Preliminary Assessment of δ^{18} O Slope Changes

An important question to address involves why the slopes of the regression relation are different for seasonal and mean annual δ^{18} O measurements for the same samples. In this regard an implicit assumption in coral studies needs to be highlighted, namely, that despite the clearly cyclical nature of the signal there is an assumption that the relationship between two variables is stationary in time. Even in the presence of obvious cyclicity, it may be appropriate to assume this relationship as a first test of a problem. However, the assumption has to be tested. For the record many statistical climatologists routinely remove the seasonal cycle when compiling statistics concerning the variable in which they are interested.

Why should a relationship not be stationary? One possibility involves salinity changes. Whereas decadal, interannual, and intra-annual changes in salinity at New Caledonia [Ouinn et al., 1996, Figure 2] are comparable (~0.3-0.4‰), the seasonal cycle of SSTs (~4°C) is approximately 4 times larger than the interannual variability and ~10 times larger than the decadal variability. Thus, salinity becomes proportionately more important for mean annual and decadal SST estimates. For example, using the δ^{18} O/salinity relationship discussed by Broecker [1989], a 0.3-0.4‰ decadal salinity shift should cause about a 0.2‰ (~1.0°C) δ^{18} O shift, potentially accounting for much of the overestimated early 20th century δ^{18} O-based SST shift, if the same salinity relationships occurred in the early 20th century as in the 1976-1977 transition (i.e., more saline when cooler). Although we are hardly the first to point out the likelihood of an overprint of salinity on δ^{18} O-based SST estimates, relatively new results from our study indicate that the problem occurs even when high corre-



Figure 5. Effect of noise on regression slopes as determined from theoretical and simulated values of the relationship between the correlation of the annual signals and the relative slopes of the seasonal and annual regressions. Open circles and asterisks are results of numerical simulations in which white noise was added to otherwise perfectly correlated artificial time series with properties characteristic of New Caledonia. The latter numbers vary only slightly from average tropical seasonal and interannual values. The open circles reflect results of an ensemble of simulations in which a trend is mimicked by a quarter wavelength of a 400 year sinusoid; the asterisks refer to ensemble runs for an entire 400 year cycle. The solid line is determined by substituting the temperature coefficients of the above time series into the algebraic formulae for the correlation and line of regression and then solving for the slope ratio as a function of the coefficients [e.g., Newland, 1993]. Note that individual realizations diverge from the theoretical curve because of their finite length.

lations are obtained for a calibration and that there may be a cyclical nature to the overprint that could conceivably be addressed with additional statistical methods (e.g., cyclostationary statistics). *Shen et al.* [1996] indicate that there may also be some influence of salinity changes on Sr/Ca.

Another truism that is necessary to recall is that the isotopic and elemental partitioning between coral aragonite and seawater is biologically mediated and that this partitioning is different from aragonite that is inorganically precipitated from seawater. Mean δ^{18} O values for corals are often 4.0% different (about 12°C according to the standard calibration) than the expected value for aragonite inorganically precipitated from seawater. Strontium concentrations in scleractinian corals are about a factor of 8 greater than in aragonite inorganically precipitated from seawater, and some of the Sr in corals is in the form of strontianite [Greegor et al., 1997]. The cause(s) of such geochemical differences between biotic and abiotic aragonite is poorly understood, has long been folded under the rubric "biological fractionation," and has been accompanied by the usually unstated assumption that this offset does not vary with time. In fact, we have no a priori guarantee that the "biological blackbox" will function the same way as present under altered boundary conditions. This might be particularly true for ice age proxy estimates (see below).

Although we may not fully understand how physical (and perhaps biotic) factors affect the incorporation of tracers into coral skeletons, the fact that they do (or could) introduce noise into the relationship between a measured geochemical variable and an observed SST can be explored in a general way by conducting a simple analytic investigation of artificial time series constructed to mimic temperature and proxy variations and how their relationship varies as a function of noise. We assume that both temperature and proxies can be represented by the sum of a seasonal cycle term, a long-term variation (represented by a low-frequency sinusoid for ease of calculation) and a noise term, in such a way that without the noise the two time series are perfectly correlated. Annually averaged time series consist of the same long-term variation plus noise. For example, we mimic the seasonal temperature time series by

$$T_{S} = a_{T} + a \cos(w_{1}t) + b \cos(w_{2}t) + cR_{1}(t),$$

where a_7 , a, b, and c are constants that we can pick to mimic a given temperature record, $w_1 = 2\pi$ is the frequency of the annual cycle, w_2 is some longer period oscillation, and $R_1(t)$ is white noise in the range [-.5, .5]. We mimic the seasonal isotope variations by

$$O_{\rm S} = a_{\rm S} + (a/d)\cos(w_1t) + (b/d)\cos(w_2t) + (c/d)R_2(t),$$

where d is the proportionality constant, and we use the designation R_2 to remind ourselves that this is a different realization of white noise.

Given these time series, one can employ simple formulae [*Newland*, 1993] to determine analytically the ratio of the slopes of the regression lines (seasonal and annual) and the

correlation of the annual temperature with annual isotope ratio. These turn out to be expressible in terms of b and c alone. The analytical solution (Figure 5, solid line) confirms that the regression slopes are different for seasonal and mean annual data, except for the case when there is perfect correlation between the annual time series. In other words, only if there is no measurement error and no physics in the problem that are not perfectly mimicked by a linear relationship will the regression slopes for seasonal and mean annual data be the same [numerical experiments (crosses) with long-period sinusoidal changes agree with our analytical result].

We also examine the case in which the long-term trend is monotonic rather than sinusoidal. The open circles are the results of a number of experiments in which the long-term trend is monotonically increasing. Even in this case, results fit the analytic curve fairly well, which is not surprising, as the seasonal cycle and noise are larger than the interannual trend. These results support the conjecture that even in the absence of systematic (periodic) sources of variability with a different δ^{18} O-SST relationship, stochastic variations can sometimes introduce a different slope relationship into geochemical proxies.

4.4. Implications

If our results are verified by other studies, the implications for estimates of decadal temperature change are substantial. For example, in New Caledonia the factor of 3 reduction of the slope in the δ^{18} O-SST relationship results in a standard deviation of temperatures of 0.23°C for the interval 1657–1900 (prior to the main anthropogenic perturbation), a value that agrees much more closely with a coupled climate model estimate [Voss et al., 1998] from this region (0.28°C) than does the seasonal estimate (0.99°C). Application of our method to validation of coupled climate models is important because correct estimation of unforced variability is essential for detection of climate change [Hegerl et al., 1997]. Mean annual changes for this interval (0.34 ± 0.18°C) are also in line with Northern Hemisphere temperature estimates [Bradley and Jones, 1993; Mann et al., 1998].

The implications of our results for Sr/Ca-based SSTs are more debatable. Although our Sr/Ca calibration is supported by the independent validation of early 20th-century SSTs, it is clear from the Alibert and McCullough [1997] results that the method has not been adequately validated for other records spanning the same time period. The assumption of stationarity is considerably more precarious for times of drastically different boundary conditions, such as the LGM. For example, T. J. Crowley [CLIMAP SSTs re-reassessed, submitted to Climate Dynamics, 1999] has demonstrated that a 5° C tropical SST change would leave 95% of present corals living outside the edge of their optimum tolerance. Stresses might therefore affect the rate in which elements are incorporated into the coral skeleton, thereby violating the usually unstated assumption of stationarity that biological fractionation will be invariant with time.

4.5. Concluding Remarks

Several points can be made from our study: (1) it is necessary to calibrate coral records against regional gridded data sets; (2) it is necessary to validate against an independent data set from the early 20th century; (3) despite a high correlation over the calibration interval the seasonal $\delta^{18}O$ calibration substantially overestimates early 20th-century SST changes; salinity changes may be responsible for this drift even in a record with very high correlations over a calibration interval; (4) early 20th-century Sr/Ca SST estimates are supported for New Caledonia, but evidence from the Great Barrier Reef indicates the need for further testing at other sites; and (5) the assumption of stationarity for Sr/Ca for ice age level applications may not be valid as SSTs 5°-6°C colder than present should result in significant ecological stresses, thereby potentially affecting biological fractionation. Although more testing and analysis of discrepancies are needed before the issues discussed herein can be completely verified and understood, even at its present state, the need for increased validation is evident. The validation strategy can also be applied to other faunal groups. For example, foraminiferal proxies in varved records and mollusc samples from museums could be validated against early 20th century SST observations.

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