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Decadal variations in trace metal concentrations on a coral reef: Evidence from a 159 year record of Mn, Cu, and V in a *Porites* coral from the northern South China Sea

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Key Points:
- Mn, Cu, and V concentrations in a *Porites* coral show interdecadal variations
- Both the PDO and the EASM influence trace metal concentrations in surface waters

Supporting Information:
- Readme
- Table S1

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Abstract Geochemical cycles of trace metals are important influences on the composition and function of the marine ecosystem. Although spatial distributions of most trace metals have now been determined in at least some parts of the oceans, temporal variations have barely been studied on account of data limitations. In this paper, we report on a 159 year record of trace metal concentrations from a *Porites* coral from the northern South China Sea (SCS), and discuss how oceanic and climatic processes control variations in Mn, Cu, and V concentrations in this region. Our results show that trace metal concentrations in the coral skeleton demonstrate decadal to interdecadal fluctuations, and that their variations are controlled by different mechanisms. The input of Mn to reef water is partly controlled by the Pacific Decadal Oscillation (PDO), which controls precipitation and river runoff. Surface water concentrations of the nutrient-like element Cu are controlled by summer upwelling to the east of Hainan Island. The concentrations of V show complex interrelationships, and are linked to riverine input prior to the 1990 and to upwelling after the 1990. Our results imply that in the northern SCS, ocean-atmosphere climate fluctuations, such as the PDO and the East Asian Summer Monsoon (EASM), are important factors that influence long-term variability of Mn, Cu, and V concentrations in seawater, by controlling precipitation-related river runoff and the strength of upwelling systems.

1. Introduction

Trace metals have provided important data for paleoceanographic studies ever since major advances in modern analytical chemistry and instrumentation allowed determination of their concentrations, distributions, and chemical behaviors in seawater [*Bruland and Lohan*, 2003]. Vertical and horizontal concentration profiles of trace elements have revealed that their spatial distributions are controlled by biological, physical, and/or geochemical processes. In turn, the behavior of trace elements in seawater is related to oceanic processes. However, temporal variations in trace metal concentrations in seawater have received little attention, especially over timespans of decades to centuries.

The calcareous skeletons of corals record variations of the environmental conditions in which they live, and have been widely used in paleoclimatic and paleoceanographic research [*Wei et al*., 2009; *McGregor et al*., 2013; *Zinke et al*., 2014]. Trace elements can be incorporated into coral's aragonite lattice in proportion to their concentrations in ambient seawater, slightly modulated by temperature and vital effects [*Shen*, 1986; *Shen and Boyle*, 1988]. Yet, for many trace elements, the modulation by temperature is not significant. Therefore, their concentration variations in coral skeleton mainly indicate their changes in seawater, thus could be important indicators for seasonal, annual, and decadal surface water variability linked to oceanic and climatic processes [*Shen and Boyle*, 1987; *Shen et al*., 1987, 1992; *Lewis et al*., 2007], and marine pollution [*Scott*, 1990; *Guzman and Jimenez*, 1992; *Guzman and Jarvis*, 1996; *Bastidas and Garcia*, 1999; *Esslemont*, 2000; *David*, 2003; *Prouty et al*., 2008; *Carilli et al*., 2009]. Mn, Cu, and V are among these trace elements. Seasonal and interannual variation in Mn concentrations in corals can serve as an indicator of El Niño-Southern Oscillation (ENSO) events and sediment input into coastal waters from rivers [*Shen and Sanford*, 1990; *Fallon et al*., 2002; *Alibert et al*., 2003; *Lewis et al*., 2007]. Transient elevations in Mn concentrations in corals can be

attributed to large phytoplankton blooms [*Abram et al*., 2003], release from seafloor sediments [*Shen et al*., 1992; *Alibert et al*., 2003; *Wyndham et al*., 2004], and volcanic eruptions [*Shen et al*., 1991]. Studies on Cu and V concentrations in corals are usually related to marine pollution, such as the increasing contamination from land use changes, sewage discharges, oil spills, the misuse of agricultural chemicals and fertilizers, and topsoil erosion, which lead to increased trace metal concentrations in waters and hence coral skeletons [*Scott*, 1990; *Guzman and Jimenez*, 1992; *Guzman and Jarvis*, 1996; *Bastidas and Garcia*, 1999; *Esslemont*, 2000; *David*, 2003; *Prouty et al*., 2008; *Carilli et al*., 2009]. With respect to uncontaminated corals, concentrations of Cu in a seventeenth century pristine coral from the Galapagos Islands have shown significant decadal variations, probably reflecting the variability of Cu in surface water [*Linn et al*., 1990]. Meanwhile, the elements of Mn, Cu, and V, are important micronutrient elements in seawater [*Eyster*, 1964; *Morel et al*., 1991; *Raven et al*., 1999], and their variations in coral records more than likely indicate the changes of nutrient levels in seawater on coral reefs, which may be linked to changes in biological activity or marine productivity.

In this study, we show that Mn, Cu, and V concentrations in a coral from the northern South China Sea (SCS) are much lower than those of contaminated corals and reflect interannual to decadal variations. We discuss how these variations may be related to climatic and environmental variables, such as rainfall and oceanic upwelling. These results may provide evidence for the influence of climatic and environmental processes on interannual to decadal variations in the seawater trace element concentrations.

2. Samples and Methods

2.1. The Study Area

Cores from a specimen of *Porites* coral (LW4), growing at a water depth of ~4 m, were collected in April 2011, in Longwan Bay, 2 km off the east coast of Hainan Island, located in the northern SCS (19°17′11.94″N, 110°39′21.06″E) (Figure 1). The climate of Hainan Island is controlled by the East Asian Monsoon, with higher temperatures and larger amounts of precipitation during summer months and lower temperatures and less precipitation during winter months. Moreover, the island is annually struck by tropical cyclones (storms and typhoons) during summer and autumn, which bring large amounts of rainfall [*Mao et al*., 2006], and the occurrence frequency changes little over the past 4–5 decades [*Chan and Shi*, 1996].

Longwan Bay is located ~20 km from the Wanquan River estuary (Figure 1b). Wanquan River, with a length of 163 km, is the third largest river on Hainan Island, with a drainage area of approximately 3.68×10^3 km^2 and a mean annual discharge of 5.2×10^9 m^3 yr^{-1} [*Wang*, 2002; *Huang et al*., 2011]. As Hainan Island is a tourist island, the industrial inputs of trace metals are relatively small. *Fu et al*. [2013] has found that trace metals concentrations in Wanquan River estuary remain at pristine levels. Therefore, corals thriving in Longwan Bay are bathed in uncontaminated waters.

Several studies have indicated that summer upwelling is common on the northern continental shelf of the SCS [*Shaw and Chao*, 1994; *Deng et al*., 1995; *Kuo et al*., 2000]. In particular, along the eastern coast of Hainan Island, summer upwelling has been identified by both continuous field observations and numerical simulations [*Yu*, 1987; *Jing et al*., 2009]. This upwelling system is generally attributed to variations in alongshore wind stress associated with the East Asian Summer Monsoon (EASM) [*Su and Pohlmann*, 2009; *Liu et al*., 2013]. Mean summer sea surface temperature (SST) data for the northern SCS for 1985–2006 [*Jing et al*., 2009] indicate that Longwan Bay is exactly located in the areas affected by the summer upwelling (Figure 1a).

2.2. Chronology and Sampling

The coral cores were cut into 1 cm thick, 5 cm wide slabs along their major growth axis by a high-speed diamond saw. X-ray radiography was used to identify annual growth banding (Figure 2). Each high and low-density band constitutes an annual couplet, generally representing 1 year of growth [*Knutson et al*., 1972]. An annual time series for the LW4 coral core was established by counting annual couplet along the growth axis, with the outermost band representing ongoing growth in 2011. As a consequence, a continuous 159 year growth record, from 1853 to 2011 was identified.

To remove organic matter and surface contaminants from the samples, the coral slabs were immersed in 10% H_2O_2 for 24 h, followed by ultrasonic cleaning in deionized water for 30 min and rinsed three times, and then dried at 40°C prior to sampling [*Wei et al*., 2007]. To avoid contamination from coring, sawing, and handling, preliminary milling along the designated sample track was undertaken to remove the surface

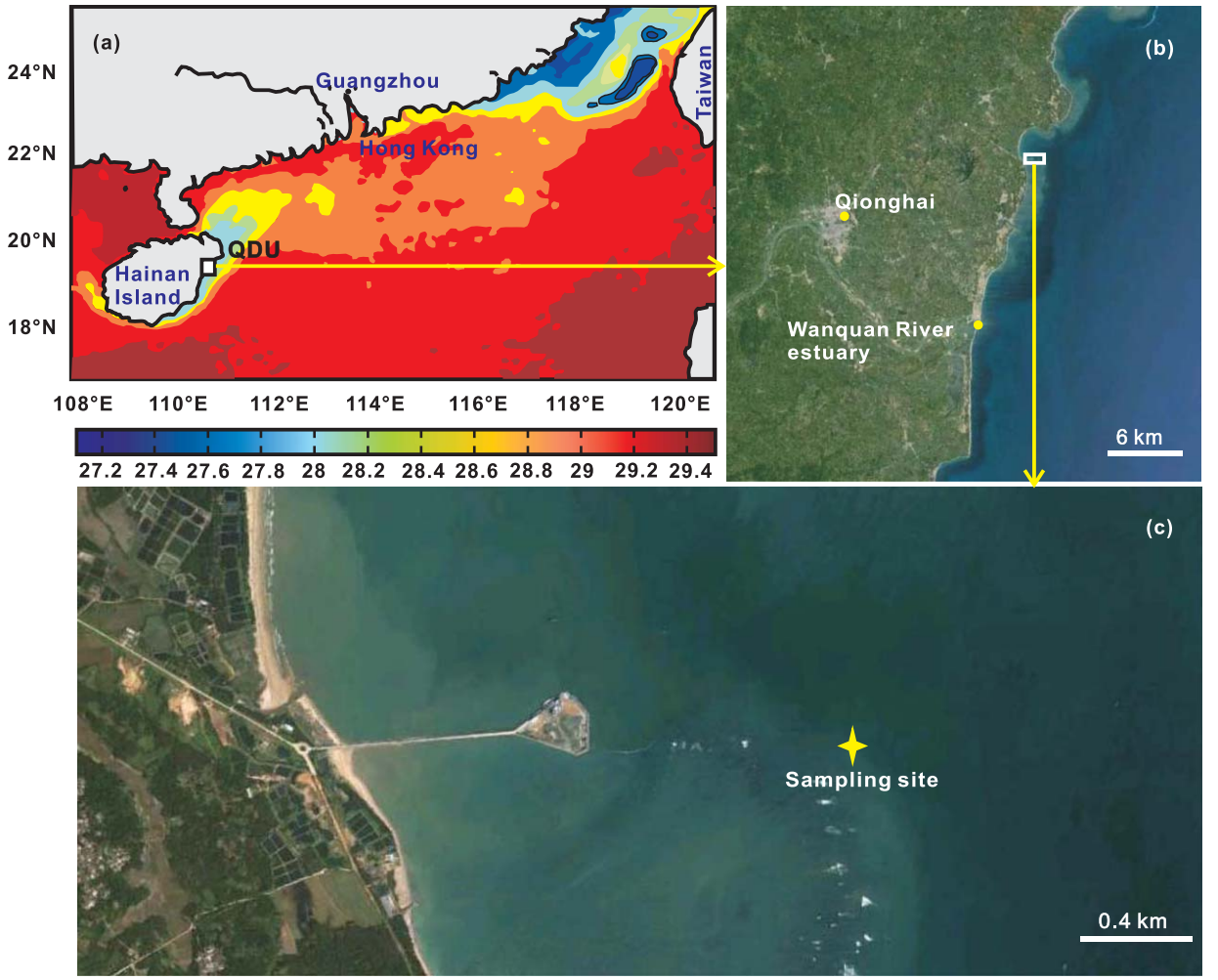

Figure 1. Location maps for the study area. (a) Climatological mean summer SST (°C) distributions in the northern SCS obtained from Advanced Very High Resolution Radiometer for the interval 1985–2006 (modified from *Jing et al*. [2009]), QDU indicates the Qiongdong upwelling system. (b) Satellite image of the Wanquan River estuary. (c) Sampling site. The yellow star indicates the sample location.

1 mm. Annual subsamples were collected continuously along the maximum growth axis using a digitally controlled milling machine. For further details of the sampling method, refer to *Hendy et al*. [2002] and *Wei et al*. [2009], and for the details of the samples, refer to *Deng et al*. [2013a].

2.3. Analytical Methods

Because of the very low concentrations of trace elements in coral aragonite (of the order of ppb), the separation of trace elements (Mn, Cu, V, etc.) from the calcium matrix is essential for good analytical results. The iron-APDC chelate coprecipitation method [*Sun and Sun*, 2007] modified from *Shen and Boyle* [1988] was adopted for trace element separation in this study. The applied reagents are ammonium pyrrolidine dithiocarbamate (APDC, Biochemical grade, Fluka), NaOH (Pure grade), HNO_3 (Electronic industry grade), and a stock solution of 1 mg mL^{-1} Fe in 3% HNO_3 (Perkin Elmer). HNO_3 was purified three times under subboiling with a whole TEFLON device. The 1% APDC solution was filtered prior to use.

A total of 0.5 g of fine coral powder was dissolved by 5 mL of 20% HNO_3 in a 250 mL TEFLON beaker, and dried on a hot plate. Then, 50 mL of Milli-Q water was added to redissolve the sample. After this, 500 μg of Fe was added, and the solution was adjusted to a pH of 4 with dilute HNO_3 and NaOH solutions. Next, 2 mL of 1% APDC was mixed with the sample solution. After standing for 1 h, the precipitate was collected and further washed with Milli-Q water by filtration using a Milli-pore PTFE filter membrane (diameter, 25 mm;

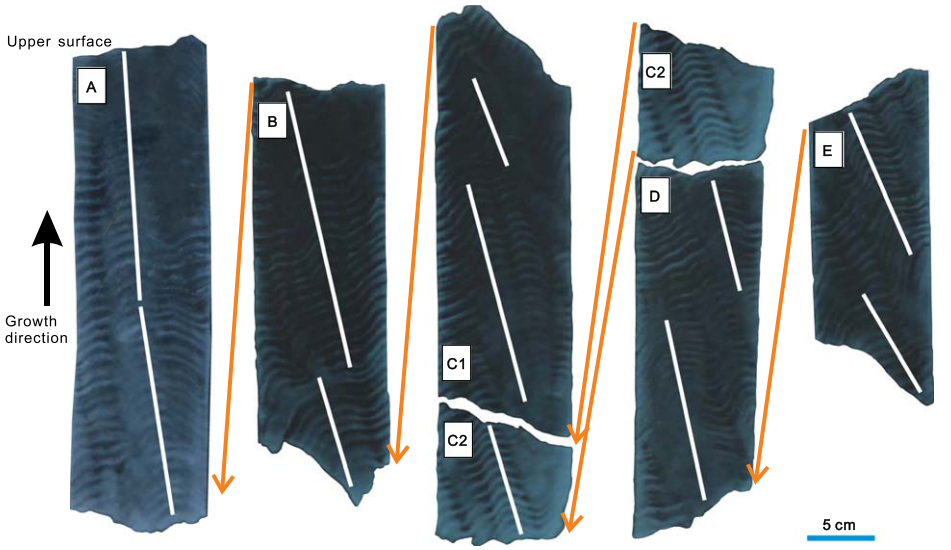

Figure 2. X-ray radiographs (negative prints) of LW4 coral core sections with sampling intervals along the maximum growth axis; annual samples are indicated by white lines. Letters indicate the slice label; slice A is at the living margin of LW4 coral. The orange arrows indicate areas of overlap of X-ray radiographs.

porosity, 0.45 μm). The membrane was returned to the original beaker, and the precipitate was dissolved with 0.5 mL 5% HNO_3 by heating to 100°C on a hot plate. The stock solution, in which 0.2 mL of 10 μg/L Rh was added as an internal standard to correct for instrumental drift during measurement by ICP-MS, was further diluted by Milli-Q water to make a working standard solution. The Mn, V, and Cu concentrations of this solution were determined on a Thermo ICAP Qc ICP-MS in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The precision for these elements was generally better than 5%. For details of the analysis, refer to *Sun and Sun* [2007].

In order to monitor the quality of the measurements, a coral working standard, BH-7 was repeatedly measured along with the samples. The analytical precision (RSD, $n = 20$) for trace metals V, Mn, and Cu is better than 10%.

All the chemical treatments were conducted in ultraclean laboratory. The used TEFLON beakers were boiled in 30% HNO_3 for 30 min, then kept for 48 h under subboiling and finally rinsed with Milli-Q water. The test tubes and pipette tips were soaked in 30% HNO_3 for 1 week and then rinsed with water. This ensured low Cu, Mn, and V blanks with 1.4 ± 0.8, 0.5 ± 0.2, and 0.25 ± 0.05 ng/mL respectively.

3. Results

Variations in Mn concentrations in the LW4 coral core show large peaks (>100 ng/g) in the 1870s and 1900s, and some small peaks in the 1850s and 1950s (50–80 ng/g) (Figure 3b). Background concentrations of Mn are generally in the range of 10–40 ng/g. These values are within the range of the previously reported coral Mn concentrations, 8–30 μg/g [*Shen and Boyle*, 1988; *Fallon et al*., 2002; *Alibert et al*., 2003; *Lewis et al*., 2007], and are similar to those of typical "cleaned" coral aragonite, which are generally less than 1 μg/g, and mostly around 40 ng/g [*Linn et al*., 1990; *Shen and Sanford*, 1990; *Shen et al*., 1991; *Delaney et al*., 1993], and less than those of the corals from contaminated water [*Scott*, 1990; *Guzman and Jarvis*, 1996; *David*, 2003; *Inoue et al*., 2004; *Prouty et al*., 2008].

Concentrations of Cu in the LW4 coral core are in the range of 200–1200 ng/g, with high values generally occurring in the 1860s, 1890s, 1960s, 1980s, and 2000s (Figure 3f). Such large variations in Cu agree with former studies, in which Cu concentrations in corals ranged from ~40 ng/g (Galapagos Islands) to ~3 μg/g (Great Barrier Reef) [*Denton and Burdon-Jones*, 1986; *Linn et al*., 1990].

Concentrations of V in the LW4 coral core are in the range of 20–100 ng/g, with peak values generally occurring in the 1970s and 1990s (Figure 3d). Similar coral V concentrations were reported by *Shen and Boyle* [1988].

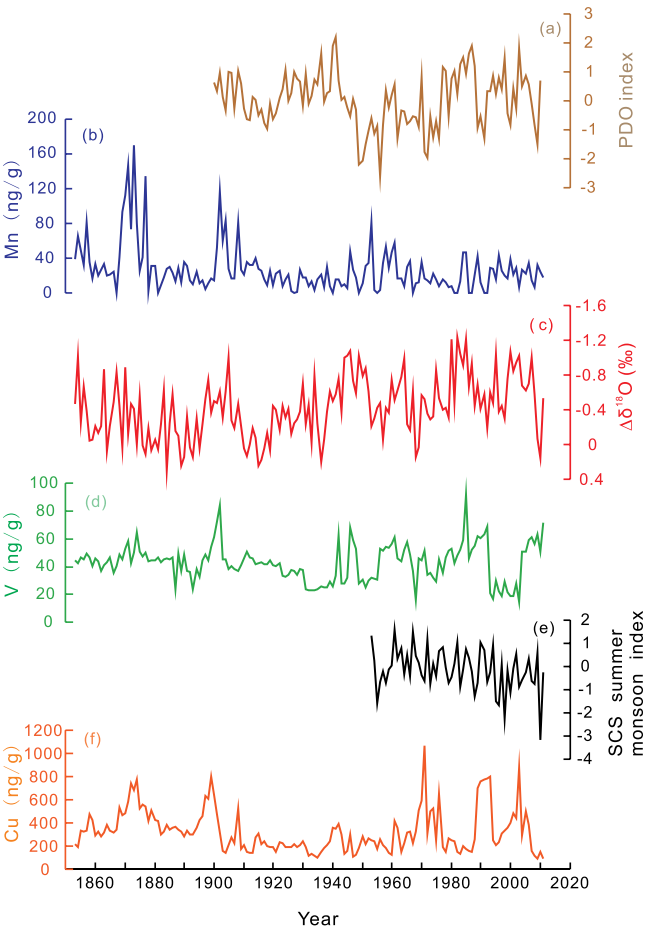

Figure 3. (a) Time series of the Pacific Decadal Oscillation (PDO) index calculated by averaging the monthly January-February-March SST anomalies since 1900 in the North Pacific Ocean poleward of 20°N (data from the University of Washington Joint Institute for the Study of Atmosphere and Oceans, http://jisao.washington.edu/pdo/PDO.latest, *Mantua et al.* [1997]). Time series of the (b) annual-resolution records of LW4 coral Mn concentrations, (c) coral $\Delta\delta^{18}O$ values calculated by subtracting the SST contribution form the coral $\delta^{18}O$ (see text), (d) coral V concentrations, and (f) coral Cu concentrations. (e) Time series of the SCS summer monsoon index defined as a seasonally (June-July-August-September) area-averaged dynamical normalized seasonality (DNS) index at 925 hPa in the SCS monsoon domain (0°N–25°N, 100°E–125°E) [*Li and Zeng*, 2002]. Note that the $\Delta\delta^{18}O$ axis is reversed.

4. Discussion

Trace elements can be incorporated into coral skeletons by several distinct mechanisms: direct substitution for Ca^{2+} in the carbonate lattice, substitution within the interstitial lattice, adsorption onto surfaces, extraneous mineral phases, and in combination with organic matter from coral tissue [*Shen*, 1986]. Only in the first case do trace elements in coral skeletons reflect their variations in ambient seawater and have potential as paleochemical indicators, whereas in other cases, trace elements can be easily and randomly added or removed during coral growth. The substitution of trace elements into the carbonate lattice depends on their chemical similarity to calcium, such as ionic radius, coordination number, charge balance and chemical speciation. The extremely low concentrations of trace elements in coral skeleton hinder the study of inclusion mechanisms of them. Nevertheless, *Pingitore et al.* [2002] has studied the substitution mechanism via X-ray absorption near-edge structure (XANES) and identified that Cu is present in its fully oxidized state in coral aragonite and substitutes for calcium within the carbonate lattice. With regard to Mn and V, their concentrations in coral aragonite are generally consistent with the known dissolved metals distributions in seawater [*Shen and Boyle*, 1988; *Shen et al.*, 1991], partially confirming the lattice uptake of Mn and V by corals. Even though the incorporation pathway is still under dispute, trace metals in coral skeletons are proving to be a valuable tool for reconstructing natural and anthropogenic changes in reef environments [*Scott*, 1990; *Shen et al.*, 1991, 1992; *Bastidas and Garcia*, 1999; *Fallon et al.*, 2002; *McCulloch et al.*, 2003].

Trace metals in corals have been reported to be good indicators of marine pollution, and their concentrations in contaminated corals are extremely high, about an order of magnitude higher than those from pristine reefs [*Scott*, 1990; *Guzman and Jarvis*, 1996; *David*, 2003; *Inoue et al.*, 2004; *Prouty et al.*, 2008]. Owing to the influence of human activities, concentrations of Mn in some corals are high, with extreme values as high as ~30 μg/g [*Guzman and Jimenez*, 1992]. Cu and V values in contaminated corals can be orders of magnitude higher than those in pristine ones, up to ~90 and ~60 μg/g, respectively [*Guzman and Jimenez*, 1992; *Bastidas and Garcia*, 1999]. In this respect, the concentrations of Mn, Cu, and V in the LW4 coral are much lower than those in contaminated corals. Meanwhile, trace metals concentrations in Wanquan river estuary remain at pristine levels [*Fu et al.*, 2013]. This suggests that reef waters around the LW4 coral are unpolluted with respect to trace metals.

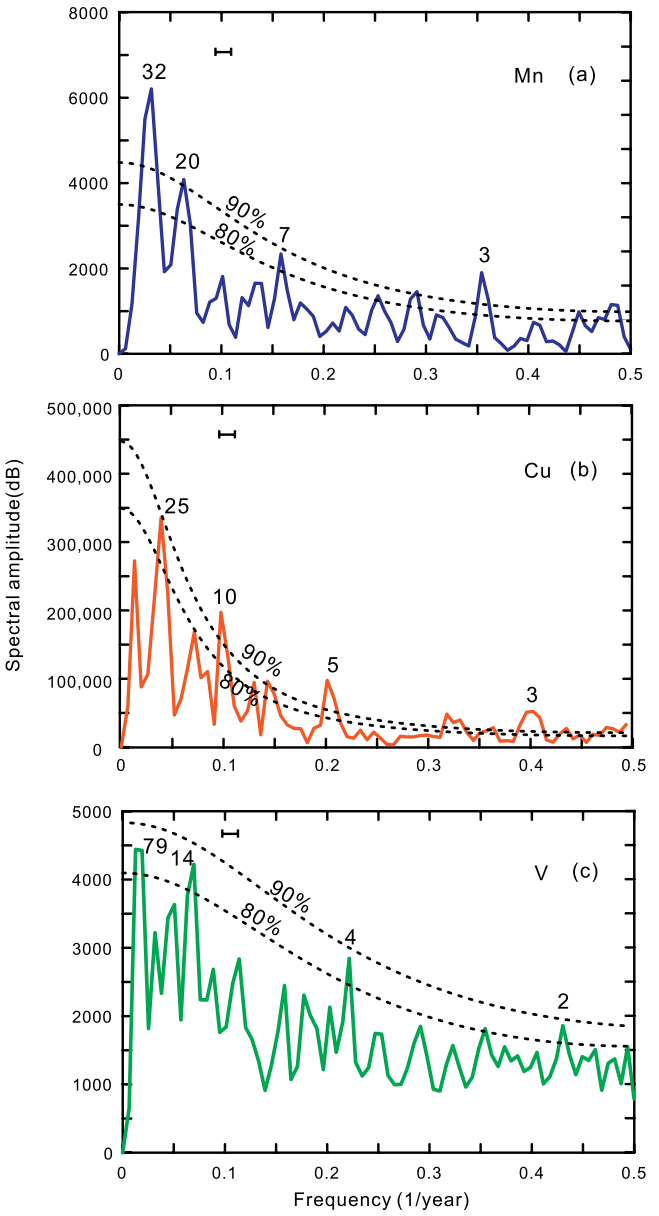

Figure 4. Results of a red-noise spectral analysis of trace metals records for the LW4 coral: (a) Mn, (b) Cu, and (c) V. The 80% and 90% significance levels are indicated. Numbers on the plot indicate the periods (in years) of selected significant peaks. The coral records are the same as those shown in Figure 2.

Figure 3 shows that the Mn, Cu, and V time series all exhibit apparent periodic variations. We performed power spectral analyses (Figure 4) on these time series records to reveal their periodicities, using the software program REDFIT [*Schulz and Mudelsee*, 2002]. Decadal to interdecadal cycles are significant in these trace metal time series. The Mn time series exhibits robust 32 and 20 year periodicities, with spectral powers all significant at the 90% confidence level (Figure 4a). Meanwhile, robust 25 and 10 year periodicities with spectral power above the 90% confidence level were identified in the Cu time series data (Figure 4b). The significance of the periodicities in the V time series data is relatively poor, with the spectral power of the 79 and 14 year periodicities just above the 80% confidence level, but beneath the 90% confidence level (Figure 4c). Decadal-interdecadal variability prevails in both tropical and midlatitude Pacific regions [*Mantua et al.*, 1997; *Zhang et al.*, 1997; *Zeng et al.*, 2007; *Xie et al.*, 2009]. The South China Sea is one of the major monsoon-affected areas of East Asia [*An*, 2000], and the Pacific Decadal Oscillation (PDO) also plays a distinct role on the climate of South China [*Chan and Zhou*, 2005; *Mao et al.*, 2011]. It has been shown that the variability of East Asian Monsoon and PDO influence the geochemistry of massive corals from the SCS [*Peng et al.*, 2003; *Sun et al.*, 2005; *Su et al.*, 2006; *Deng et al.*, 2013a]. The PDO demonstrates two general periodicities: one of 15–25 years and the other of 50–70 years [*Mantua and Hare*, 2002]. Furthermore, the EASM also contains significant periodicities of ~80, 40, and 8–10 years [*Xu et al.*, 1997; *Sun et al.*, 2002; *Guo et al.*, 2004]. It is interesting that trace metals in coral skeletons show similar periodicities with PDO and EASM, indicating that ocean-atmosphere processes may govern the variations of trace metals in surface water on decadal-interdecadal time scales.

4.1. Decadal Variations in Manganese

Variability of Mn concentration (or Mn/Ca ratios) in corals from various places demonstrates regional differences in seasonal, interannual and decadal time scales, which is generally linked to upwelling, ENSO events, or heavy rainfall [*Linn et al.*, 1990; *Shen et al.*, 1991, 1992; *Delaney et al.*, 1993; *Fallon et al.*, 2002]. In addition, volcano eruption can contribute to large excursions in trace metal records in corals [*Shen et al.*, 1991].

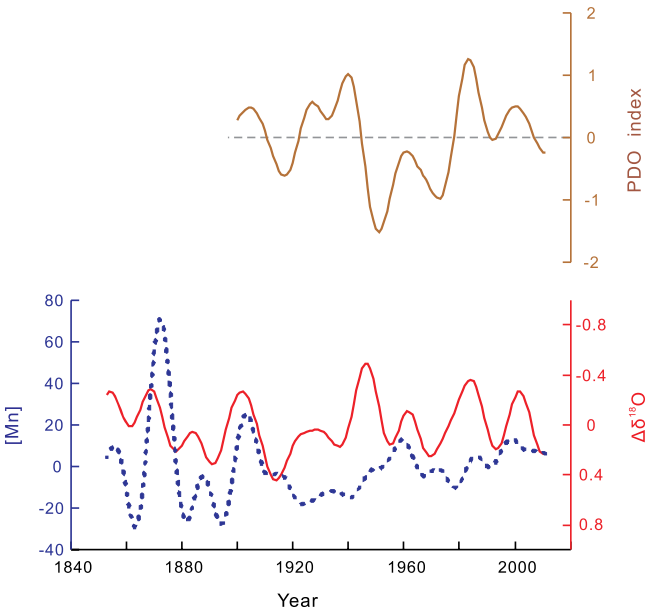

Figure 5. The 13 year cutoff low-pass filtered Mn concentrations (blue dotted line) and $\Delta\delta^{18}O$ from *Deng et al*. [2013a] (red line) records of the LW4 coral in the northern SCS, and the Pacific Decadal Oscillation (PDO) index (brown line). Note that the time series were removed trend before low-pass filtering was performed.

Volcanic eruptions, however, are historically rare nearby Hainan Island, and there is no record of volcano eruption around Hainan Island in the past century. Therefore, the large fluctuations existing in Mn time series in LW4 coral around 1870 and 1900 (Figure 3b) would not be caused by volcano eruption.

In coastal areas, seawater Mn levels are controlled mainly by large fluxes of dissolved and particulate Mn derived from rivers, shelf sediments, and the atmosphere [*Bender et al*., 1977; *Landing and Bruland*, 1980; *Kremling*, 1985], and therefore runoff effects associated with heavy rainfall are important with respect to Mn in coral skeletons [*Fallon et al*., 2002].

The coral residual oxygen isotope ratio ($\Delta\delta^{18}O$) generally represents the changes in the composition of seawater $\delta^{18}O$, and serves as a considerable indicator of rainfall runoff in the northern SCS [*Shen et al*., 2005; *Deng et al*., 2009]. It was calculated by subtracting the temperature contribution in the coral $\delta^{18}O$ [*McCulloch et al*., 1994; *Gagan et al*., 1998], according to

$$\Delta\delta^{18}O = \frac{d\delta^{18}O}{dT} \times \left[T_{\delta^{18}O} - T_{Sr/Ca}\right]$$

where $d\delta^{18}O/dT$ is the slope of the empirical $\delta^{18}O$-SST function shown by *Song et al*. [2006], and $T_{\delta 18O}$ and $T_{Sr/Ca}$ are the apparent SSTs calculated from $\delta^{18}O$ values and Sr/Ca ratios. $\Delta\delta^{18}O$ in LW4 coral has been shown to be influenced by rainfall runoff [*Deng et al*., 2013a], therefore it was employed to indicate the terrestrial inputs and to compare to trace metals.

Mn concentrations in LW4 coral demonstrate evident interannual to interdecadal variations as shown in *Shen et al*. [1991] and *Delaney et al*. [1993]. To extract the decadal to interdecadal variability in Mn concentrations and compare them with terrestrial inputs, we performed low-pass filtering with a 13 year cutoff on both the Mn concentration and the $\Delta\delta^{18}O$ time series data for 1853–2011 [*Deng et al*., 2013a], using the software program PAST [*Hammer et al*., 2001]; the results are shown in Figure 5. Variations in the two low-pass filtered time series (Figure 5) show alternating highs and lows, with higher $\Delta\delta^{18}O$ values generally corresponding to lower Mn concentrations, and vice versa (Figure 5), shown by a moderately negative correlation (Table 1; $r = -0.27$, $N = 159$, $p < 0.0003$). The correlation between two time series might be artificially improved after

Table 1. Correlations Between Trace Metal Concentrations and Coral $\Delta\delta^{18}O$ and The SCS Summer Monsoon Index[a]

Trace Metal Concentrations	$\Delta\delta^{18}O$	SCS Summer Monsoon Index[b]
Mn	$r = -0.27$	$r = -0.34$
	$n = 159$	$n = 59$
	$p < 0.0003$	$p < 0.05$
Cu	$r = 0.06$	$r = 0.55$
	$n = 159$	$n = 59$
	$p > 0.05$	$p < 0.000003$
V[c]	$r = -0.41$	$r = 0.36$
	$n = 137$	$n = 37$
	$p < 0.000001$	$p < 0.05$
V[d]	$r = 0.48$	$r = 0.76$
	$n = 22$	$n = 22$
	$p < 0.02$	$p < 0.00002$

[a]The correlation analysis is based on 13 year cutoff low-pass filtering of data in all of the time series.
[b]The SCS summer monsoon index covers only 59 year data.
[c]V concentrations in coral before the year 1990.
[d]V concentrations in coral after the year 1990.

filtration. In order to evaluate such a risk, we also performed Monte Carlo simulation to estimate the critical correlation coefficient for the filtered time series. The critical correlation coefficient is generally less than 0.1 by testing more than 10 randomly generated time series filtered using the same settings for the LW4 coral time series. The observed correlation coefficient between Mn and $\Delta\delta^{18}$O time series (-0.27) is much larger than the critical value, indicating that such correlation is not an artificial product.

Given that the δ^{18}O value of freshwater is much lower than that of seawater [*Cole and Fairbanks*, 1990], and that river water is enriched in Mn as compared with seawater [*Gaillardet et al*., 2003], enhanced terrestrial inputs of Mn induced by heavy rainfall over adjacent land areas may result in decrease in δ^{18}O and increases in Mn concentrations in seawater over nearby coral reefs. Consequently, the coral may record lower $\Delta\delta^{18}$O values and higher Mn concentrations during this period. Considering the proximity of the LW4 coral collection site to the Wanquan River estuary (Figure 1b), it is reasonable to infer that an increase in precipitation and thereby Wanquan River discharge would deliver greater proportions of freshwater and influxes of terrestrially derived Mn into the fringing reef, and thus decrease δ^{18}O values and increase the Mn concentrations of reef seawater. Therefore, the negative correlation between Mn and $\Delta\delta^{18}$O exhibited in the LW4 coral core implies that variations of the Mn concentrations in coral reef seawater are largely controlled by changes in terrestrial inputs derived from rainfall over Hainan Island. This conclusion agrees with our previous studies that river runoff associated with precipitation on Hainan Island greatly affects coastal water chemistry, and thereby the geochemistry of corals [*Deng et al*., 2009, 2013b]. However, the relationship between Mn and $\Delta\delta^{18}$O on annual time scales is complex (Figure 3). It seems that not all the peaks of Mn concentrations in coralline aragonite can be explained by heavy rainfall as indicated in *Fallon et al*. [2002] and *Shen et al*. [1992]. In addition, the lower levels of significance of the correlation coefficient (-0.27) may indicate that there still exist other factors obscuring the relationship between $\Delta\delta^{18}$O and Mn concentrations. Manganese undergoes a dynamic redox cycle in seawater, and soluble Mn (II) can be readily oxidized to insoluble Mn (III) and Mn (IV) in surface waters [*Sunda and Huntsman*, 1988, 1990]. These transitions strongly dominate the partitioning of Mn between dissolved and particulate phases in natural waters, and thereby regulate the scavenging of Mn from the water column. Taking the redox character of Mn into consideration, we surmise that this chemical behavior of Mn may obscure the relationship between $\Delta\delta^{18}$O and Mn contents, leading to a relatively weak statistical correlation.

Meteorological studies have suggested that interdecadal variations in rainfall over South China are associated with the PDO [*Chan and Zhou*, 2005; *Mao et al*., 2011]. Recently, *Deng et al*. [2013a] have confirmed that the PDO influences the amount of rainfall and river runoff on Hainan Island, using evidence from various geochemical records of corals. During the warm phase of the PDO, it may cause more rainfall and associated runoff, resulting in lower $\Delta\delta^{18}$O values and higher Mn concentrations (Figure 5). The opposite occurs during the cool phase of the PDO. As a consequence, the inverse trends between $\Delta\delta^{18}$O values and Mn time series data in the LW4 coral suggest that decadal variations in Mn concentrations may be a response to variations in terrestrial inputs controlled by rainfall, as influenced by the PDO.

4.2. Decadal Variations in Copper

The distribution of Cu in the water column shows moderate surface depletion [*Bruland*, 1980; *Bruland et al*., 1994; *Bruland and Lohan*, 2003], analogous to that of phosphate in seawater. Thus, Cu is believed to be involved in biogeochemical cycles, being removed from surface waters by phytoplankton and subsequently released in subsurface waters by decomposition of dead phytoplankton or sinking particulate matter.

Given the surface-depleted distribution of Cu and the well-developed Qiongdong upwelling system off east Hainan Island, it seems likely that copper is conveyed by upwelling from deep water to surface water, along with other nutrients. The EASM has been identified as a dominant dynamic factor inducing Qiongdong summer upwelling in the northern SCS [*Guan and Chen*, 1964; *Jing et al*., 2009; *Su and Pohlmann*, 2009]. For this reason, we employed the SCS summer monsoon index, which is defined as a seasonal (June-July-August-September) area-averaged dynamically normalized seasonality index at 925 hPa within the SCS monsoon domain (0°N–25°N, 100°E–125°E; http://ljp.lasg.ac.cn/dct/page/65578) [*Li and Zeng*, 2002] to indicate the activity of Qiongdong summer upwelling, although this index covers only the short period from the 1950s to the present. To identify possible linkages between decadal variations of Cu concentrations in the LW4 coral and upwelling, we performed low-pass filtering on both the SCS summer monsoon index and the Cu concentration time series data with a 13 year cutoff; results are shown in Figure 6. Decadal/

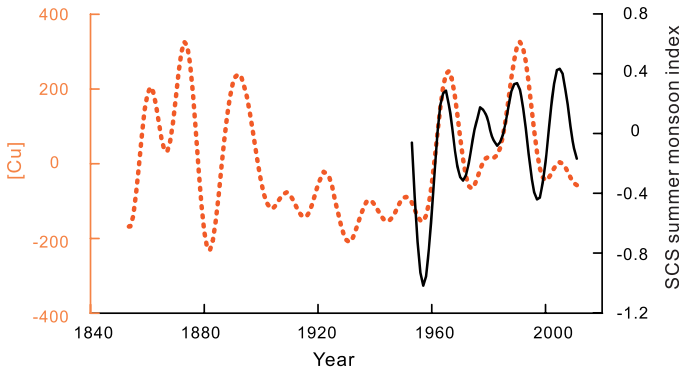

Figure 6. The 13 year cutoff low-pass filtered Cu concentrations (orange dotted line) and the SCS summer monsoon index (black line). Note that the time series were removed trend before low-pass filtering was performed.

interdecadal variations in the coral Cu time series data resemble those of the SCS summer monsoon index from the 1950s to the present, with higher Cu concentrations corresponding to higher values of the SCS summer monsoon index; the positive correlation between these parameters is statistically significant (Table 1; $r = 0.55$, $N = 59$, $p < 0.000003$). Enhanced summer monsoon activity would intensify the upwelling system, bringing an increased flux of nutrient-like elements, such as Cu, to surface waters, and resulting in a strong correlation between the SCS summer monsoon index and coral Cu concentrations. Such a positive correlation may indicate the direct influence of upwelling on Cu inputs to coral reef seawater, and suggest that EASM takes effects on Cu inputs to reef waters on decadal/interdecadal time scales by controlling the intensity of Qiongdong upwelling.

4.3. Decadal Variations in Vanadium

Vanadium, which belongs to a biologically important group of transition elements, is known to play a role in biological metabolism. Its vertical distribution in seawater is similar to that of Cu, showing surface water depletion [*Collier*, 1984], and it has a distribution similar to that of phosphate, especially in estuaries [*Shiller and Boyle*, 1987]. Furthermore, river waters account for the major input of dissolved vanadium into estuaries, with the weathering of silicate rocks being the main source of dissolved vanadium in rivers [*Shiller and Mao*, 2000]. Therefore, both terrestrial runoff and upwelling may contribute V to surface seawater.

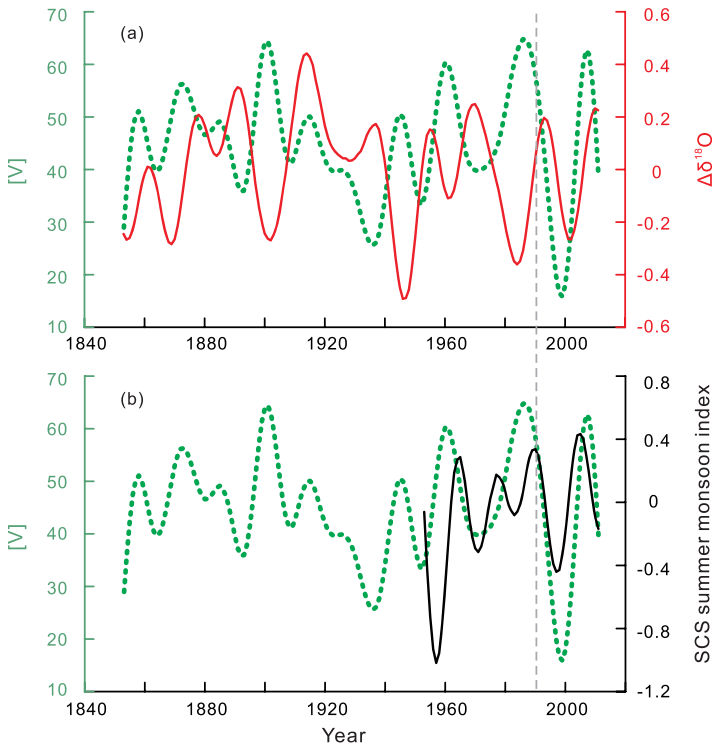

Figure 7. Low-pass filtered vanadium records of coral in the northern SCS: (a) 13 year cutoff low-pass filtered V concentrations (green dotted line) and $\Delta\delta^{18}O$ (red line); (b) 13 year cutoff low-pass filtered V concentrations (green dotted line) and the SCS summer monsoon index. Dashed line indicates the year 1990.

Variations in concentrations of V in the LW4 coral are less regular than those of Mn and Cu, showing lower variability (Figure 3d) with moderate 79 and 14 year periodicities (Figure 4c). Considering the important role of river discharge in supplying V to estuaries, the V concentration time series was filtered using a 13 year cutoff, to compare interdecadal variations in $\Delta\delta^{18}O$. Figure 7a illustrates the relationship between V and $\Delta\delta^{18}O$. As with Mn and $\Delta\delta^{18}O$, filtered V and $\Delta\delta^{18}O$ show a generally inverse relationship, signifying that river runoff is an important source of V. The filtered V and $\Delta\delta^{18}O$ values show a statistically

significant negative correlation during 1853–1989 ($r = -0.41$, $N = 137$, $p < 0.000001$). This may indicate that enhanced river discharge leads to higher concentrations of seawater V. However, this relationship changes after 1990, at which time the sign of the correlation is positive (Table 1; $r = 0.48$, $N = 22$, $p < 0.02$). This positive correlation does not support the control of terrestrial input on V concentrations in coral reef seawater after 1990. We postulate that there may be another factor affecting V concentrations, such as upwelling, that influence the post-1990 input of V to seawater.

As V is depleted in surface water, and as there is an upwelling zone to the east of Hainan Island, it is possible that V variations in the LW4 coral may also record the influence of Qiongdong upwelling, which brings high concentrations of nutrients and bioactive elements (Cd, V, Cu, etc.) to surface waters. A comparison between V concentrations and the SCS summer monsoon index was conducted by low-pass filtering, using a 13 year cutoff (Figure 7b). The correlation between the SCS summer monsoon index and V concentrations in the LW4 coral is more complex than that between the SCS summer monsoon index and Cu concentrations, implying that the effect of upwelling on V inputs may be obscured by effects of river runoff during some periods. Nevertheless, the correlation between the SCS summer monsoon index and V concentrations is still significant after 1990 (Table 1; $r = 0.76$, $N = 22$, $p < 0.00002$). This change corresponds to the end of a negative correlation between $\Delta\delta^{18}O$ and V concentrations, and may suggest that the influence of upwelling somehow altered the relationship between V and runoff.

5. Conclusions

We report records of Mn, Cu, and V in a specimen of *Porites* coral from the northern SCS, spanning the time interval of 1853–2011. The concentrations of Mn, Cu, and V in the coral skeleton show decadal to interdecadal variability. Terrestrial runoff associated with PDO-controlled rainfall partly influences the input of Mn to surface seawater, whereas the supply of Cu is controlled by the Qiongdong upwelling system, driven by the EASM. The situation with regard to V is more complex. Both terrestrial input and upwelling may affect variations in V concentrations in coral reef seawater.

Trace metals are essential micronutrients, and are important in controlling marine productivity. Variations in trace metal concentrations can therefore be used as proxies to indicate changes in nutrient levels in seawater on coral reefs, and may be related to changes in biological activity. In coastal areas, river runoff is often the dominant control on the supply of nutrients to surface seawater; however, in some instances, upwelling also conveys many nutrients from deep waters to the surface. Our results show that both PDO and EASM are important oceanic and climatic processes influencing variations in trace metal concentrations in surface water, through the amount of river runoff and the strength of upwelling systems. Therefore, we propose that PDO and EASM also affect nutrients levels or biological activities in the northern SCS.

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