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REPORT

Evaluation of Mn and Fe in coral skeletons (*Porites* spp.) as proxies for sediment loading and reconstruction of 50 yrs of land use on Ishigaki Island, Japan

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Abstract Manganese (Mn) and iron (Fe) concentrations were measured in coral skeletons (*Porites* spp.) collected from the Todoroki River on Ishigaki Island, Japan, to reconstruct the history of land use in the river catchment area. We prepared (1) five bulk samples to investigate the present spatial distribution and (2) micro-samples from two long cores to study the temporal variability of sediment loading from the Todoroki River. The existing state of the elements Mn and Fe in bulk coral skeleton samples was examined by a chemical cleaning experiment. The results of the experiment suggested that Fe was not incorporated into the crystal lattice of the coral skeleton but that Mn was incorporated, as previously reported. The bulk sample data, with and without chemical cleaning, indicated that the spatial distribution of both elements in corals collected along a sampling line from the river mouth toward the reef crest was complex and most likely reflected salinity changes and the amount of suspended particulate matter. The temporal variation of Mn and Fe, in particular the variation of baseline/background levels, mainly reflected the history of land development on Ishigaki Island. In addition, Mn showed clear seasonal variability that appeared to be controlled by a combination of temperature, primary productivity, and precipitation. The results of the present study suggest that Mn may be a useful proxy for river discharge or biological activity depending on local marine conditions, if the specific behavior of Mn at the coral growth site is known.

Keywords Sediment loading · Manganese · Iron · Coral skeleton · Cleaning experiment

Introduction

The geochemistry of the coral skeleton, in particular that of massive corals such as *Porites* spp. and *Orbicella* (= *Montastraea*) spp. sensu Budd et al. (2012), is a useful proxy of paleoceanographic variability (e.g., Gagan et al. 2000; Watanabe et al. 2001). Comprehensive studies of oxygen isotopes ($\delta^{18}O$) and Sr/Ca ratios of coral skeletons have revealed sea surface temperature (SST) and hydrological variability in many regions around the world ranging from tropical to subtropical. The annual density banding of coral skeletons can be used to reconstruct seasonal variability with monthly resolution. As a result, the presence and activity of El Niño events and differences in the past seasonality of SST and salinity compared with the present have been investigated extensively (Tudhope et al. 2001; Asami et al. 2009; Watanabe et al. 2011; Felis et al. 2012). Whereas the $\delta^{18}O$ and Sr/Ca ratio in corals are used

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to reconstruct climatic variability, trace elements in coral, including heavy metals, have been analyzed to investigate the influence of anthropogenic activities in adjacent coastal and marine areas (Dodge and Gilbert 1984; Inoue et al. 2004a, 2006; Carriquiry and Horta-Puga 2010). Corals in barrier and fringing reefs are often adversely impacted by terrestrial inputs such as nutrients (Tamura et al. 2007), soil/sediments (McCulloch et al. 2003; Lewis et al. 2007), and harmful chemicals (Kawahata et al. 2004). Mn and Fe in corals, among other trace elements, have been used as proxies for sediment loading, which occurs mainly through rivers (Brown et al. 1991; Chen et al. 2010; Moyer et al. 2012). However, reported concentrations of heavy metals, such as Mn and Fe, differ greatly (Inoue et al. 2004b; Chen et al. 2010). Furthermore, different heavy metal concentrations have been recorded even from individual corals growing within a small area (<100 m^2; Prouty et al. 2008). Previous studies have also demonstrated that coral Mn/Ca ratios do not always reflect river discharge (Alibert et al. 2003; Moyer et al. 2012), and Mn concentrations may occasionally be anomalously high, regardless of sediment loading. Therefore, although Mn in corals has been used as proxy for terrestrial sediment input to coastal reef areas, the specific source or controlling factor of the Mn concentration has remained elusive. Meanwhile, studies of Fe in the coral skeletal record have been scarce compared with Ba/Ca and Mn/Ca ratios. As a consequence, the detailed behavior of skeletal Fe is unclear, although a partial mechanism, which involves deposition of iron compounds onto skeletal spines during the tissue retraction, has been proposed by Brown et al. (1991).

The chemistry of Fe and Mn in seawater is indeed complex, and their concentrations vary with changes in salinity (Stolpe and Hassellöv 2007), oxidation state (Sarthou et al. 2011), the amount of suspended particulate matter (SPM; Turner et al. 1992), light intensity (Sunda et al. 1983), and primary production levels (Hunt 1983; Schoemann et al. 1998). The most thermodynamically stable state of Fe in oxic seawater is Fe(III), which rapidly hydrolyzes because of its high insolubility to form various Fe(III) oxyhydroxides (de Baar and de Jong 2001). These species, with $Fe(OH)_3$ dominant in seawater at pH ~8, tend to form colloidal Fe (Kuma et al. 1996), which coagulates to form particulate Fe (Johnson et al. 1997). According to the thermodynamic conditions, Mn is expected to exist in oxic water as insoluble MnO_2 (Ahrland 1975). However, some of the MnO_2 in seawater is reduced by ambient sunlight (Sunda et al. 1983) or photosynthetic activity of phytoplankton (Schoemann et al. 1998) and therefore exists as soluble reduced Mn(II).

Brown et al. (1991) also suggested that under specific stress-inducing conditions, both lattice-bound and non-carbonate metals should be examined independently with appropriate sample processing to extract maximum information from the skeletal record. Therefore, as part of our study, we examined the existing state of Mn and Fe (i.e., lattice bound versus non-incorporated forms) in the coral skeleton with a chemical cleaning experiment. This information was also useful for exploring the existing state or speciation of Mn and Fe in seawater.

The coast of Ishigaki Island is mainly surrounded by fringing reef, and *Porites* cores from the island's reefs have been used in several paleoclimate studies (Mitsuguchi et al. 1996; Mishima et al. 2010; Yamazaki et al. 2011). Although land use changes and the resultant sediment loading into the area of reefs around the mouth of the Todoroki River have been a concern for some time and the spatial distribution of river discharge and characteristics of the currents have been previously studied (Kawahata et al. 2000; Tamura et al. 2007; Blanco et al. 2008), little is known about the temporal variation of terrestrial inputs into coastal waters. In this study, we measured Mn and Fe in multiple coral skeletons (*Porites* spp.) collected around the mouth of the Todoroki River, Ishigaki Island, Japan, to investigate the impact of historical changes of land use on the adjacent coral reefs. Using Mn and Fe from the coral skeletons, we investigated (1) the spatial distribution and (2) the temporal variation of sediment loading. For the spatial distribution, we prepared bulk samples from short cores from the superficial part of the coral skeleton, not including the tissue layer. The resulting coral powder was derived from coral skeletons grown over a 3–4-year period. We used two long cores for temporal reconstruction. On the basis of our examination of the bulk samples and the chemical cleaning experimental results, we discuss the historical variation of the sediment load discharged into the coastal waters from the Todoroki River.

Methods

Coral samples and preparation of subsamples

Ishigaki Island is located in the southwest of the Ryukyu Islands, Japan, with Shiraho Reef situated on the southeastern coast of the island (Fig. 1). The Todoroki River supplies large amounts of sediments and nutrients from the Todoroki watershed into the reefs through 15 km^2 of sugarcane, pasture, and paddy fields distributed within the drainage basin (Nakasone et al. 2001; Paringit and Nadaoka 2003; Hasegawa 2011). The average annual precipitation is approximately 2,000 mm, 60 % of which falls in the rainy season from May to June or is caused by a typhoon in August and September. Soil erosion and potentially excessive discharges of sediments and nutrients onto Shiraho Reef occur during these periods.

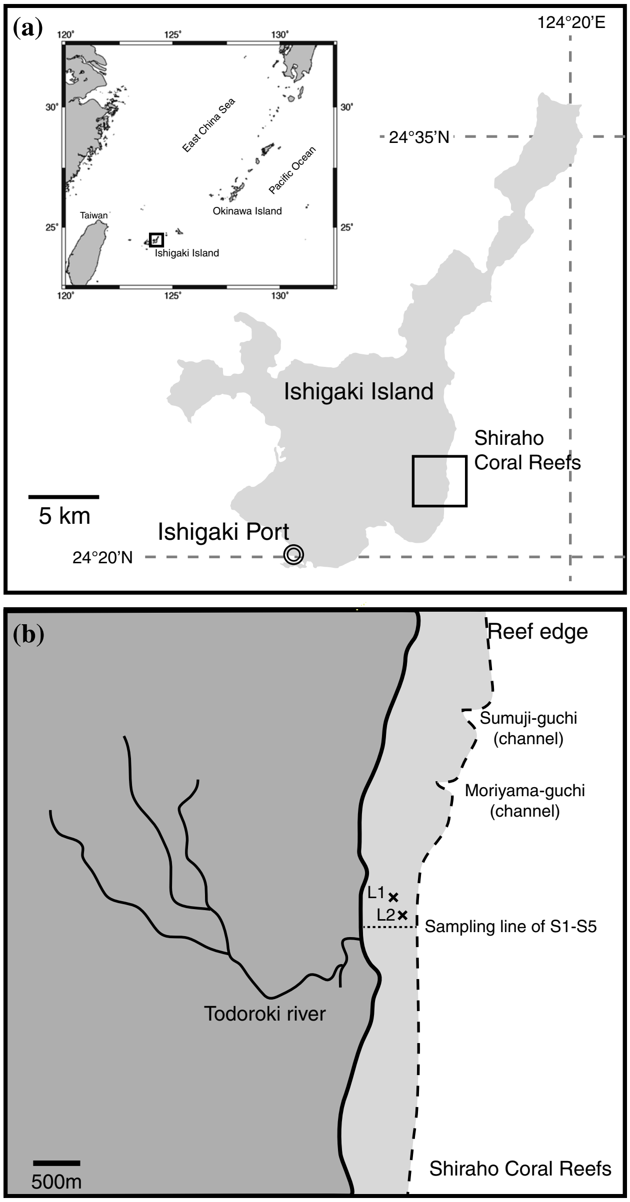

Fig. 1 Locations of coral samples collected from Shiraho Reef, Ishigaki Island, Japan. Samples of S1–S5 are identical with those reported in Yamazaki et al. (2011)

To examine the spatial distribution of sediment loading around the Todoroki River, five short (length ∼30 cm, diameter 2.5 cm) cores were drilled in 2009 vertically down from the top of coral colonies located along a sampling line from the river mouth to the reef crest (Figs. 1, 2). All colonies dwelled at water depth less than 1 m. The short-core samples were labeled S1 (river mouth), S2, S3, S4, and S5 (reef crest), respectively. These sampled coral colonies were from 30 to 70 m apart, and sample S1 was from a colony in the innermost part of the reef, approximately 20 m from the river mouth. In order to remove surface contamination during drilling and handling, all samples were cleaned by ultrasonic washing with Milli-Q water and 0.02 M HNO_3 after an overnight treatment with H_2O_2. For bulk samples, we used X-ray photographs as a guide and selected the part of each short core comprising the coral skeleton that grew between 2005 and 2008, without the tissue layer. Next, we subsampled each bulk sample and then homogenized the subsamples with an agate mortar.

After the general cleaning procedure described above, we performed a cleaning experiment on subsamples of the five bulk samples using methods described by Inoue et al. (2004a). Briefly, the experiment consisted of six chemical cleaning treatments, where each successive treatment added a subsequent cleaning step, in addition to previous steps, as follows: (1) no cleaning (initial condition), (2) Milli-Q wash, (3) 0.02 M HNO_3 wash, (4) cleaning with a 50–50 % mixture of 30 % H_2O_2 and 0.2 M NaOH, (5) a 0.02 M HNO_3 wash, and (6) a 0.02 M HNO_3 wash with ultrasonic agitation with a Milli-Q wash repeated between steps.

To reconstruct the temporal variation of sediment loading, two long coral cores were collected slightly north of the sampling line for the spatial distribution analysis (Figs. 1, 2). Core L1 (length 55 cm) was drilled in 2007 vertically down from the top of a colony, at 1.5-m depth. Core L2 (length 113.5 cm), collected in 2010, was drilled horizontally, as this colony formed a microatoll at 0.8 m depth. For Fe and Mn measurements, the cores were subsampled at 3-mm intervals after cleaning with Milli-Q water using an ultrasonic pulse probe, as described by Gagan et al. (1994). In both cores, the 3-mm subsampling interval corresponds to a time resolution of approximately 2 months.

The age model for both cores was calculated by matching uranium (U) variations since U was measured on the same subsamples as for Fe and Mn measurements and predominantly reflects SST variations (Min et al. 1995). Preliminary data of $\delta^{18}O$ with higher time resolution (1-mm subsampling interval) was also used to assist the age model. The points of maximum U concentration and $\delta^{18}O$ values in each year, indicating lower SST and thus winter conditions, were used as tie-points, and ages between these two peaks were interpolated, because a slight lag exists during the summer between the rainy season and the month with the maximum SST around Ishigaki Island.

Measurements

For the bulk and long-core Mn, Fe, and U measurements, 5 mg of skeletal powder was dissolved with 5 ml of 2 % HNO_3 solution. The Mn and U concentrations in the skeletal samples were measured by using an inductively coupled plasma mass spectrometer (ICP-MS, Hewlett

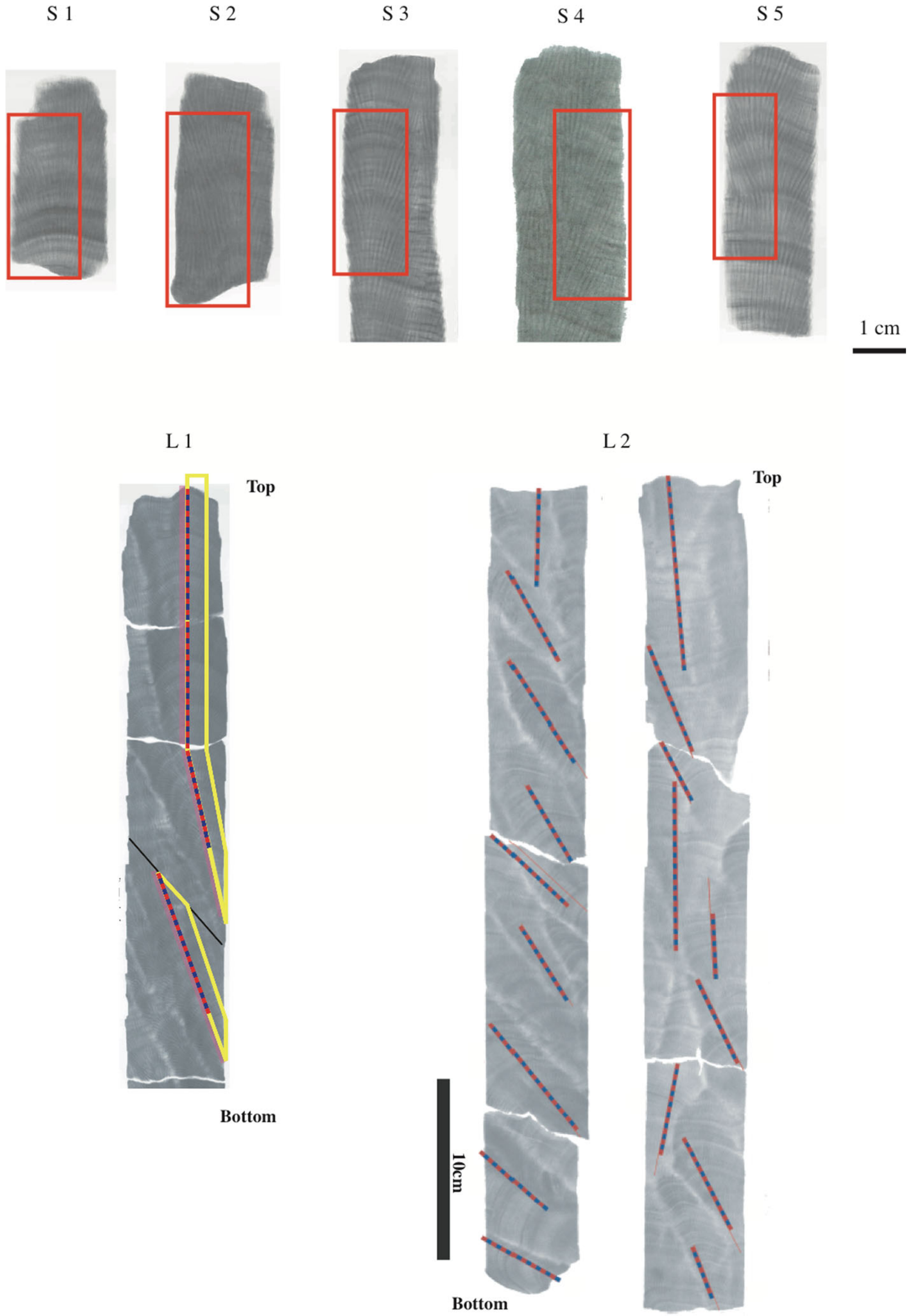

Fig. 2 X-ray photos of coral specimens. S1–S5 were used to investigate the spatial distribution, and L1 and L2 the temporal variation, of sediment loading around the Todoroki River mouth. The *red rectangles* on the S1–S5 samples indicate the skeletal parts used as bulk samples. The *red* and *blue dots* on L1 and L2 indicate subsampling points (3-mm intervals)

Packard HP-4500) following the procedure described by Inoue et al. (2004a, b). A standard solution (1 ppb, SPEX Certiprep) was measured after every fifth sample for data correction. The relative standard deviation (RSD) was 3.4 and 4.5 % for Mn and U, respectively ($n = 25$). The Fe concentrations in the coral skeletons were measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES, Seiko Instruments SPS-7800) using a 248.3-nm wavelength. The same data correction method was applied to Fe by using a 1-ppm standard solution with an RSD of 0.68 % ($n = 21$). The typical detection limit of this method for Fe was approximately 0.1 ppb for the analytical solution, which corresponds to 0.1 $\mu g\ g^{-1}$ for coral samples. Fe concentrations in skeletal samples below 0.1 $\mu g\ g^{-1}$ are therefore represented as 0 $\mu g\ g^{-1}$ in all results. Concentrations of Mn and Fe in all bulk samples, including samples used in the chemical cleaning experiment, were measured in triplicate.

Results

The mean values of Mn and Fe in the skeletal bulk samples before the chemical cleaning (no cleaning step) ranged from 0.37 to 1.21 μg g^{-1} and from 3.15 to 55.08 μg g^{-1}, respectively. The highest values for both elements were found in S4 (Figs. 3, 4a, b). As a result of the chemical cleaning, the concentrations of both elements generally decreased. After the final cleaning step, Fe was below the detection limit in all samples except S4 (0.62 μg g^{-1}), whereas Mn concentrations ranged from 0.03 to 0.99 μg g^{-1}, with the highest values detected in S1 (Figs. 3, 4a). The standard deviations of the triplicate analyses of the bulk samples were higher for the samples that were not treated compared with the chemically cleaned samples. In particular, the standard deviations of Fe in S3 and S4 were high (Fig. 4b), indicating that Fe was incorporated heterogeneously into the coral skeletons.

According to the age determination based on the U and δ^{18}O profile, core L1 spanned 13 yrs, from 1995 to 2007, and L2 covered 54 yrs, from 1957 to 2010. Concentrations of Mn ranged from 0.11 to 3.56 μg g^{-1} in L1 and from 0.06 to 1.97 μg g^{-1} in L2. Concentrations of Fe ranged from 0.08 to 10.26 μg g^{-1} in L1, and they ranged from below the detection limit to 235.91 μg g^{-1} in L2 (Fig. 5). To enable comparison of the concentrations of Fe and Mn in the long-core samples with those in the bulk samples, we calculated average concentrations using data for the period 2005–2006 for L1 and 2005–2008 for L2. The resulting averaged concentrations of Mn and Fe were similar between the two long cores (Mn: 0.23 and 0.26 μg g^{-1} for L1 and L2, respectively; Fe: 2.44 and 2.65 μg g^{-1} for L1 and L2, respectively) and were comparable with the values of the non-cleaned S2 samples (Table 1; Fig. 5).

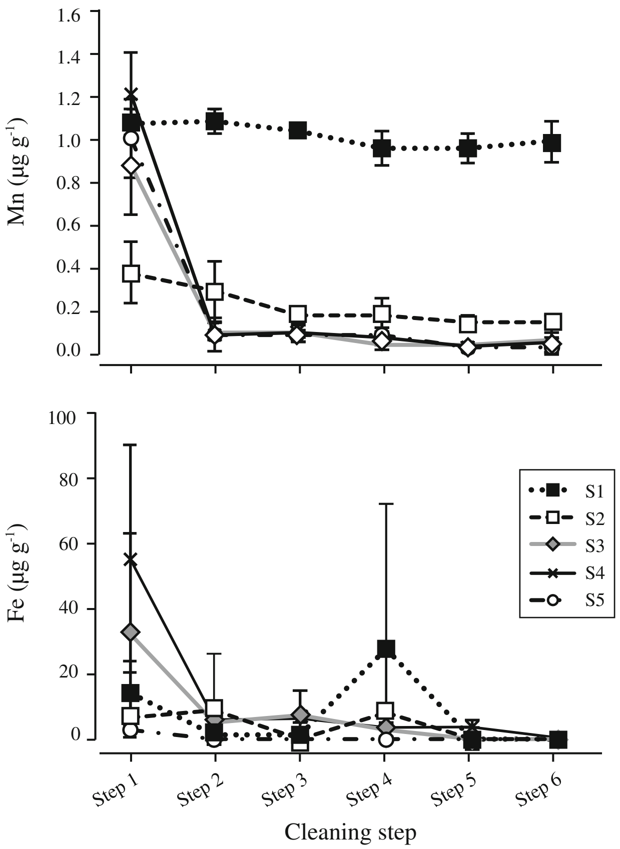

Fig. 3 Results of the six-step chemical cleaning experiment with bulk samples S1–S5: (1) no cleaning (initial condition), (2) Milli-Q wash, (3) 0.02 M HNO_3 wash, (4) cleaning with 50–50 % mixture of 30 % H_2O_2 and 0.2 M NaOH, (5) 0.02 M HNO_3 wash, and (6) 0.02 M HNO_3 wash. Measurements were conducted in triplicate, and the results are presented as means ± 1 SD

Discussion

Chemical cleaning experiment

Coral skeletal samples have been chemically cleaned in previous studies to remove trace elements outside the lattice, that is, elements loosely adhering to the surface or trapped within cavities of the skeletal structure (Shen and Boyle 1988; Shen et al. 1991; Mitsuguchi et al. 2001). Thus, elements removed by chemical cleaning are most likely loosely held on particles on the surface, whereas elements remaining after the cleaning can be regarded as lattice bound within the coral skeleton. Because Fe levels in all bulk samples in this study were below the detection limit following the chemical cleaning, we inferred that Fe, similar to Sn (Inoue et al. 2004a), was not incorporated into the aragonite lattice. In contrast, even after all cleaning steps, Mn was detected at low concentrations in bulk samples S2–S5, and at a relatively high concentration in S1, suggesting that Mn most likely was lattice bound within the coral skeleton, as reported previously (Shen et al. 1991).

It is difficult to evaluate the appropriate interactions of chemical constituents including Mn and Fe of suspended particles with those dissolved in water because of the various physical, chemical, and biological processes that take place in the water column. Therefore, the distribution coefficient (K_D) is used to represent the concentration ratio of chemicals adsorbed onto suspended particles to those dissolved in water:

$$K_D = P/C$$

where P (w/w) and C (w/v) represent the metal concentrations in the particulate and solution phases, respectively (Yan et al. 1991; Turner and Millward 2002). Turner et al. (1992) showed that the K_D of Fe and Mn increased with increases in the SPM concentration in the Weser Estuary, Germany. This result suggests that the suspended particles were relatively enriched in Fe and Mn compared with the surrounding seawater because these elements were

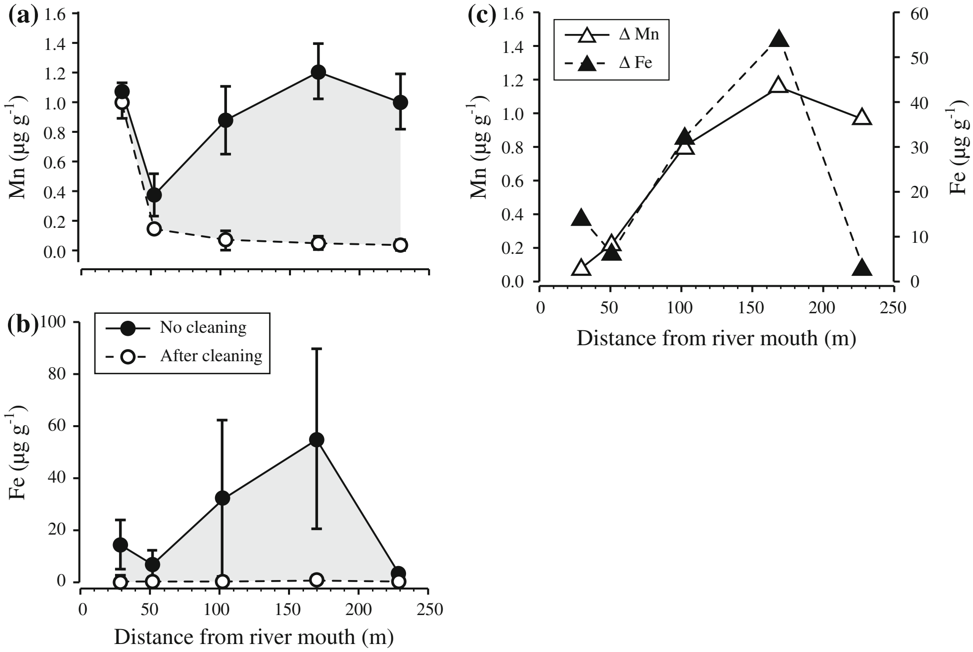

Fig. 4 Spatial distributions of **a** Mn and **b** Fe against distance from the mouth of the Todoroki River after no chemical cleaning (*solid circles*) and after the complete chemical cleaning procedure (*open circles*). Values are means ± 1 SD. *Gray shading* in **a**, **b** indicates the difference in the concentration of Mn or Fe before and after chemical cleaning. **c** Spatial distributions of ΔMn and ΔFe, corresponding to the *gray shaded areas* in **a**, **b**

removed from solution by sorption reactions at the particle surfaces. We suggest that such adsorbed elements correspond to those trapped within skeletal spaces or adhering to skeletal surfaces that were easily removed by gentle cleaning (Fig. 3). Therefore, we inferred that most Fe and Mn detected before the cleaning were not bound to the lattice; rather, they adhered loosely to particulates on the surface and were easily removed, along with the particulate matter, by simple cleaning with Milli-Q water. We therefore regarded the differences in Mn and Fe (ΔMn and ΔFe) between concentrations detected with no chemical cleaning (step 1) and after the final HNO_3 cleaning (step 6) (Fig. 4c) as a proxy for the SPM concentration in the coral reef area near the Todoroki River mouth. When ΔMn and ΔFe are low, Mn and Fe exist in dissolved form in the seawater, although as noted above, Fe, even in its dissolved form, is unlikely to be incorporated into the $CaCO_3$ lattice.

As no chemical cleanings were performed on L1 and L2 core samples, concentrations of both elements in their skeletons apparently represent those in seawater, including SPM form. In this study, we focus on the historical variation of sediment loading from the land. Therefore, reconstruction of Mn and Fe variation in coral skeletons without chemical cleanings would be appropriate because both elements washed out by treatments have information on sediment loading. On the other hand, if an element in dissolved form in seawater is required to reconstruct specific environmental change, chemical cleaning on skeletal samples will be necessary. An appropriate procedure of chemical cleaning would be required according to the purposes of study using trace elements in coral skeletons.

Spatial distribution of skeletal Mn and Fe

The biogeochemical cycles related to suspended particles in estuarine environments are known to be complex, as reviewed by Turner and Millward (2002). Here, we discuss the distribution of SPM in the reef area based on the spatial distribution of bulk skeletal Mn and Fe. Concentrations of both elements displayed similar trends with distance from the river mouth (Fig. 4a, b), with higher concentrations being detected in uncleaned samples from sampling sites S3 and S4 (100–200 m from the river mouth). This trend is more evident in the distribution of ΔMn and ΔFe (Fig. 4c). Higher concentrations of ΔMn and ΔFe at S3 and S4 suggest that the sediments were transported to and accumulated around these sites. In addition, the concentrations may be influenced by resuspended particulate matter. The large standard deviation of Fe in samples without chemical cleaning at these sites is most likely attributable to the variable marine environment, in particular the resuspension of SPM.

In contrast, ΔMn and ΔFe were lower at the sites closest to the river mouth (S1 and S2), which indicates that at those sites, Mn and Fe existed mostly in dissolved form. Dissolved Mn, regarded here as Mn detected after chemical cleaning (Fig. 4a), gradually decreased from inshore to offshore. As discussed above, an increase in dissolved Mn has been reported to be associated with light intensity, SST, primary productivity levels, and salinity. Considering the spatial distribution of the area in this study, the impacts of light intensity and SST can be ignored. Although an effect of spatial differences in primary productivity cannot be

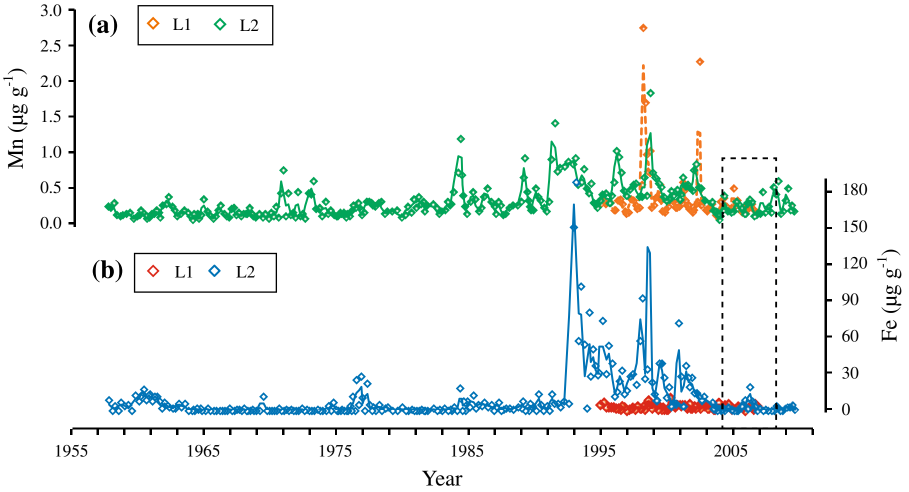

Fig. 5 Temporal variation of **a** Mn and **b** Fe in cores L1 and L2 collected from Ishigaki Island. The *dashed-line rectangle* encloses the data from each core that were averaged and used for comparison with bulk sample data (Table 1)

Table 1 Mean concentrations of Mn and Fe detected from coral skeletons of both bulk and core samples without chemical cleaning

Element (μg g^{-1})	Bulk samples[a]					Core samples	
	S1	S2	S3	S4	S5	L1[b]	L2[c]
Mn	1.07 ± 0.07	0.37 ± 0.14	0.88 ± 0.23	1.21 ± 0.19	1.00 ± 0.19	0.23 ± 0.09	0.26 ± 0.14
Fe	14.17 ± 9.38	6.39 ± 5.97	32.27 ± 30.29	55.08 ± 34.70	3.15 ± 1.40	2.44 ± 1.36	2.65 ± 4.61

Data are shown as mean ± 1 SD

[a] Bulk samples typically represent the period around 2005–2008

[b] L1 represents the period of 2005–2006

[c] L2 represents the period of 2005–2008

ruled out, because salinity changes are likely to be substantial at the river mouth, salinity is probably a major influence on the speciation of Mn in the study area. Studies on the behavior of Mn in estuarine environments have found that Mn desorption from particulate matter is likely to occur in waters with salinity lower than about 20 psu (Knox et al. 1981; Ouddane et al. 1997; Moyer et al. 2012). Kawahata et al. (2000) reported a salinity of 10.93 psu at the Todoroki River mouth, while Blanco et al. (2008) observed a low salinity of approximately 20 psu in the reef near the river mouth after several minor rainfall events. Although water depth may affect salinity as buoyant low-salinity water from river mouth flows at the surface of seawater, all samples in this study were collected from a water depth of less than 1.5 m. Therefore, the distribution of dissolved Mn in this study may simply reflect the surface salinity variation from the river mouth to offshore on Shiraho Reef. These results indicate that, although ΔMn and ΔFe may be useful in general as proxy for SPM, the application of this proxy may be difficult in areas where low-salinity waters mix with seawater, because of the high reactivity and complex chemistry of these trace elements.

Temporal variations of Mn and Fe from 1957 to 2010 in core L2

Comparison of the L2 core results with those from the bulk samples (Table 1) suggests that the present-day environment of the corals at site L2 is similar to those at site S2 (Table 1). We inferred that the majority of the Mn and Fe in the seawater exists in dissolved form, or, alternatively, the concentration of SPM able to adsorb these elements is lower at L2 than at sites S3 and S4. The temporal variations over 54 yrs in core L2 show similar trends for Mn and Fe, with concentrations gradually increasing beginning around 1980, reaching their highest levels in the 1990s, and then decreasing suddenly in 2004 (Fig. 5). Although at present, the amount of river discharge correlates with precipitation (Fig. 6), the temporal trends in Mn and Fe found in this study are not related to a change in a natural parameter such as precipitation or SST.

The trends may, however, be related to land use changes. After Okinawa was returned to mainland Japan in 1972, infrastructure began to be developed and land uses changed, including on Ishigaki Island and especially from the end of

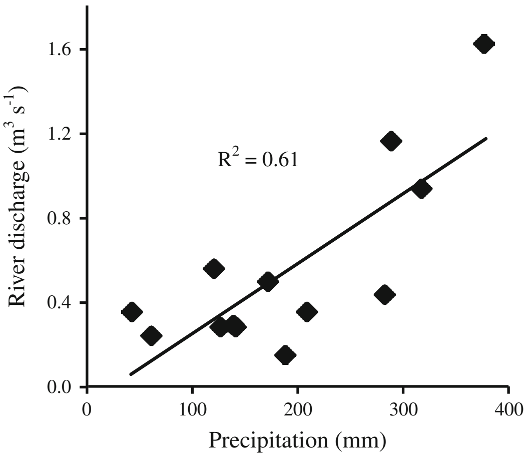

Fig. 6 Relationship between river discharge and precipitation in the Todoroki River catchment. The trend is based on monthly data collected from November 2006 to November 2007

the 1970s. For example, many rice paddies were converted to pineapple fields (Hasegawa 2011). These changes increased the sediment loads reaching coastal waters and thus Mn and Fe in the coral skeleton. In addition, the number of cattle on the island increased at the beginning of the 1990s, which may have contributed to higher Mn and Fe concentrations in the river discharge at this time (Lewis et al. 2007). Spatial modeling of sediment budgets around the Great Barrier Reef (GBR) has shown that catchments with high levels of land clearing, cattle grazing, and cropping show the largest increase in sediment export compared with natural conditions (McKergow et al. 2005). A sharp increase in erosion (sediment loading) was also observed, caused mainly by grazing and cropping, which corresponded to the temporal variation found in Mn and Fe in this study. Land development in the Todoroki River catchment had ended by 2004, which may explain the sudden decrease in both elements in the coral skeleton at this time.

In contrast to the general trends of Mn and Fe, the higher frequency variation in L2 differs between the two elements, in particular the timing of peaks during the 1990s (Fig. 5). As discussed above, the concentrations of Mn and Fe in coral skeletons without chemical cleaning appear to reflect the amount of particulate matter in the ambient seawater. Not only do Mn and Fe have different K_D (Turner et al. 1992), their behaviors in seawater are complex and vary with subtle changes of salinity and the size of colloidal matter (Stolpe and Hassellöv 2007). As a result, changes in the local environment might produce abrupt peaks and cause differences in the behaviors of Mn and Fe. Therefore, it cannot be determined whether a particular peak in the record was caused by a change in sediment loading from the land, or by a change in the seawater environment around the sampled coral.

Although the high-frequency variation cannot be unequivocally tied to sediment loading, Lapworth et al. (2012), who measured over 50 trace elements in 1,569 stream sediment samples and produced a regional geochemical map for southwestern Nigeria, suggested that background (or baseline) data are essential for assessing changes due to anthropogenic activity. In this study, the baseline concentrations of Fe and Mn (minimum concentration in each year) in core L2 increased slightly from the end of the 1970s. Therefore, to focus on the mean variation, which reflects the baseline trend rather than the concentration peaks of both elements, we plotted their average concentrations in each year (Fig. 7). The results show that 1975 was a turning point with regard to the annual variations in the mean concentrations of the two elements. Before 1975, Fe and Mn variability was not correlated, whereas from 1976 to 2004 the yearly variations of the two elements were synchronous (Fig. 7). This result suggests that the variations of both elements probably reflect the same source, namely, increased sediment loading due to land development during 1976–2004. Therefore, we suggest that temporal changes in the baseline skeletal Fe and Mn concentrations, not only the high-frequency peaks, may provide important information for assessing terrestrial inputs into the seawater around the reef due to land use changes.

Seasonal changes of Mn in core L1 and evaluation of controlling factors

As suggested by the Mn and Fe concentrations in core L1, the present environment around the L1 site appears to be similar to that around the L2 and S2 sites (Table 1). However, Mn and Fe variability differed between L1 and L2 during the later half of the 1990s (Fig. 5). Field surveys conducted near the Todoroki River mouth indicate that the river discharge flows northward from the mouth (Kawahata et al. 1998; Tamura et al. 2007). The L1 site is downstream from the L2 site, and most particulate matter carried by the river discharge appears to have been trapped near the L2 site. As a result, SPM concentrations at the L1 site remained comparatively low even when sediment loading was high. This result again shows how subtle differences in the local environment can cause Mn and Fe concentrations, or the form in which they exist in seawater, to differ. Another difference in the pattern of variation between the L1 and L2 sites is that at the L1 site, Mn displayed annual variability (Figs. 8, 9).

Seasonality in Mn (ranging from clear to moderate) has been observed in coral skeletons from the GBR (Alibert et al. 2003; Wyndham et al. 2004), the Galapagos Islands (Shen et al. 1991), and Puerto Rico (Moyer et al. 2012). A dual dependence on temperature and the primary

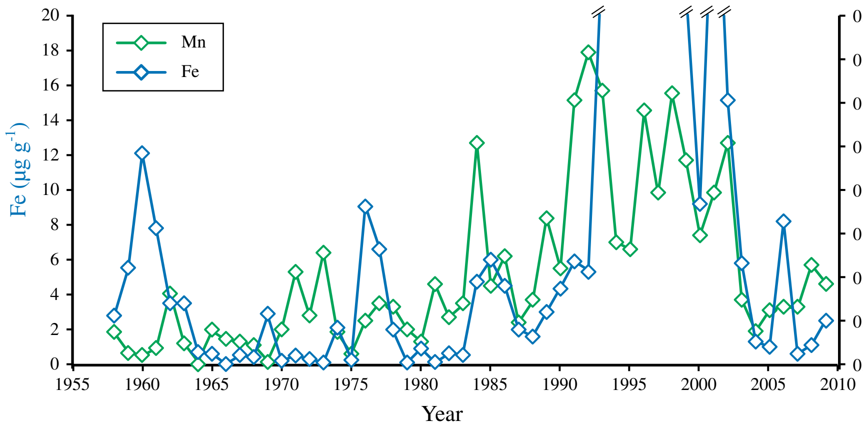

Fig. 7 Temporal variations of annual mean Mn and Fe concentrations calculated using data from core L2

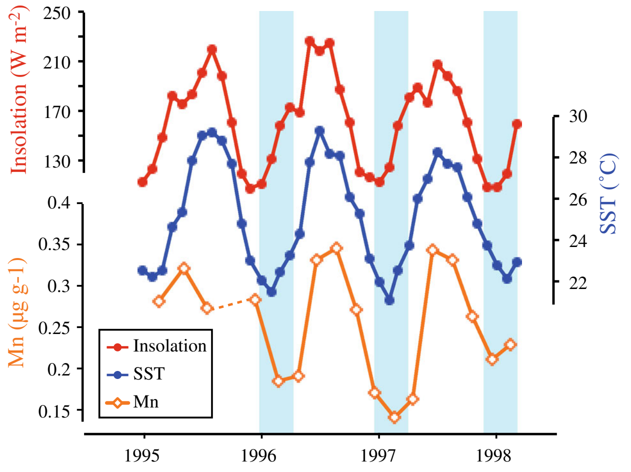

Fig. 8 Seasonality of insolation, SST around core L1, and Mn concentration in core L1 from 1995 to 1998. Monthly mean SST data were provided by the Japan Meteorological Agency recorded at Ishigaki port (24°20′N, 124°8′E) since 1914 and at the observation point (28°32′N, 129°30′E) closest to the coral sampling site from 2003 to 2010. Insolation data were obtained from the CAYAN solar irradiance database (http://iridl.ldeo.columbia.edu/SOURCES/.CAYAN/.Si/) for 25°N, 125°E

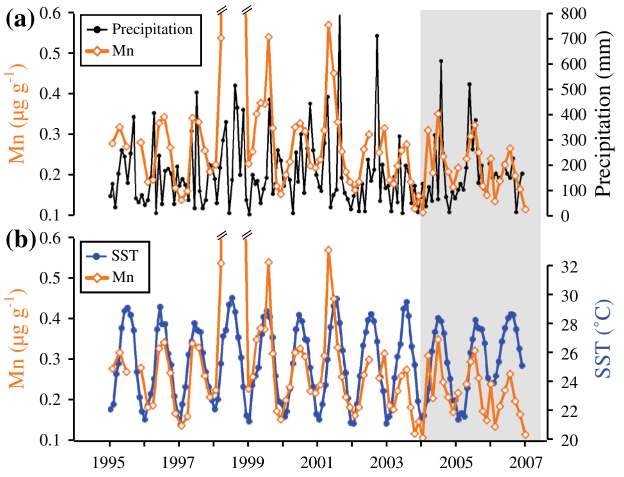

Fig. 9 Relationship between seasonal variation of the Mn concentration in core L1 with **a** precipitation and **b** SST. Precipitation data at the upper course of the Todoroki River were provided by the Japan Meteorological Agency. *Gray shading* indicates the period after the end of land development in 2004

productivity level, rather than on river discharge, has been proposed as a potential cause of Mn variability on annual time scales. Sunda et al. (1983) demonstrated experimentally the photoreduction of manganese oxides by dissolved organic (humic) substances in seawater. Schoemann et al. (1998) reported seasonal increases in dissolved Mn in the water column after peaks in spring diatom blooms generated anoxic conditions. Hunt (1983) also reported that the Mn flux is strongly correlated with the average primary productivity during the month preceding the flux determination, although there is also an exponential relationship between the seasonal magnitude of the Mn^{2+} flux and the temperature. For these reasons, we compared the seasonal trend in Mn in the L1 coral record to trends in insolation and SST for the 3 yrs (1995–1998) for which both insolation and Mn data were available (Fig. 8). Although insolation begins to increase one to two months before SST begins to increase (Suzuki et al. 2003), the trend in Mn most likely reflects SST changes. Therefore, we compared the Mn variation in L1 to precipitation and SST variations from 1995 to 2007 (Fig. 9a, b). We found that the seasonality of Mn in L1 seemed to be controlled by a combination of SST and precipitation. In particular, after 2004, Mn variability reflected changes in precipitation more clearly than it did before 2004 (Fig. 9a). Sediment loading was most likely the main source of Mn in seawater in our study area, and the combined effect of SST and primary production would enhance the production of dissolved Mn. Taking into account the high sediment influx into the study area due to land development before 2004, the Mn changes in L1 likely reflect temperature and/or primary production through the process of generating dissolved Mn from river-discharged Mn. In contrast, following the end of land development in 2004, sediment loading through river discharge, which covaried with precipitation (Fig. 6), was likely the main and direct control of the seasonality of Mn in L1.

The temporal variation of Mn reconstructed over 54 yrs using core L2 data is unlikely to reflect the variation of SST and precipitation because of the local environmental changes discussed above (Fig. 5). In the event of an episodic sediment discharge, including Mn, into the coastal seawater, a coral would take up large amounts of Mn into its skeleton. On this basis, Mn has been used as a proxy for changes in land use (Ramos et al. 2004; Lewis et al. 2007; Carilli et al. 2009; Chen et al. 2010), volcanic eruptions (Shen et al. 1991), and ash fallout from extensive fires (Abram et al. 2003). In the absence of an episodic disturbance, however, skeletal Mn should mainly reflect the variation in dissolved Mn in seawater, which is most likely a function of SST, primary production, and general river discharge (precipitation). In the latter case, it may be difficult, or require special care, to rely solely on skeletal Mn as a proxy for a specific variable. Nevertheless, provided that the characteristics of the behavior of Mn in the water column and the incorporation pattern of Mn into coral skeleton is known, Mn may be regarded as a useful proxy for river discharge or biological activity, depending on the local salinity conditions. Furthermore, by measuring other geochemical tracers, such as δ^{18}O and Sr/Ca, together with Mn, it should be possible to reconstruct river discharge or biological activity more effectively.

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